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Effect of storage time on chemical structure of a single-bottle and a two-bottle experimental ceramic primer and micro-shear bond strength of composite to ceramic

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PURPOSE. This study assessed the effect of storage time on chemical structure of a single-bottle and a two-bottle experimental ceramic primer and micro-shear bond strength (µSBS) of composite to ceramic. **MATERIALS AND METHODS.** This study was conducted on 60 sintered zirconia and 60 feldspathic porcelain blocks. Half of the specimens (n = 30) were subjected to surface treatment with the single-bottle Clearfil ceramic primer (n = 15) and two-bottle experimental primer (n = 15) after 24 hours. The remaining half received the same surface treatments after 6 months storage in distilled water. Composite cylinders were bonded to the ceramics, and they were then subjected to µSBS test. Also, the primers underwent Fourier-transform infrared spectroscopy (FTIR) after 24 hours and 6 months to assess their chemical structure. Data were analyzed with 3-way ANOVA and adjusted Bonferroni test (alpha = 0.05). **RESULTS.** The µSBS of both ceramics significantly decreased at 6 months in one-bottle ceramic primer group ($P = .001$), but it was not significantly different from the two-bottle experimental primer group ($P = .635$). FTIR showed hydrolysis of single-bottle primer, cleavage of silane and 10-MDP bonds, and formation of siloxane bonds after 6 months. **CONCLUSION.** Six months of storage caused significant degradation of single-bottle ceramic primer, and consequently had an adverse effect on µSBS. [J Adv Prosthodont 2024;16:163-73]

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INTRODUCTION

Zirconia restorations are increasingly used due to their optimal esthetics and

mechanical properties, and favorable biocompatibility.[1] Porcelain is also highly popular in contemporary dentistry, and is commonly used for inlays, onlays, laminate veneers, and metal-ceramic and all-ceramic crowns due to excellent esthetics.[2] On the other hand, by the advances in resin-bonded systems and their additional advantages such as better marginal seal, retention, and fracture resistance, their application is also increasing.

Factors such as fatigue, occlusal forces, incorrect design, inadequate preparation, and physical trauma can cause cohesive failure within the ceramic structure. However, due to high cost, time-consuming fabrication process, and difficult retrieval, their repair is often preferred to their replacement.[2]

Application of bonding agents is an important parameter for optimal bonding of composite resin to ceramic surfaces.[2] Primer application on pretreated surfaces of ceramics creates chemical covalent and hydrogen bonds. Ceramic primers often contain silane coupling agent and a weak acid.[1] On the other hand, acidic methacrylates and MDP monomer directly affect the ceramic surface and enable adhesion. The phosphate ester groups of both of the above-mentioned bifunctional monomers are bonded to superficial zirconia oxides and form chemical adhesion. However, the methacrylate groups serve as the monomer matrix and are responsible for polymerization, such that enhanced chemical bonds increase the bond strength provided by MDP-containing ceramic primers to polished zirconia.[3] Nonetheless, due to evaporation and hydrolysis of silane coupling agent, and limited shelf-life of these materials, single-bottle formulations of primers still have shortcomings.[1] The stability of single-bottle primers is still a matter of concern, and they have limited efficacy due to formation of oligomers.[4] It appears that separation of some components of primers that interact with each other, and their packaging in two separate bottles may obviate the existing problems regarding their limited durability and limited bond strength of ceramic primers over time. Thus, this study aimed to assess the effect of storage time on chemical structure of a single-bottle and a two-bottle experimental ceramic primer and micro-shear bond strength (µSBS) of composite to ceramic. The null hypothesis in this study is that pro-

longed storage time has no detrimental effect on single-bottle primers.

MATERIALS AND METHODS

This *in vitro*, experimental study was conducted on 60 zirconia ceramic blocks (MamutDental, Dubai Medical equipment LLC, Dubai, UAE) and 60 feldspathic porcelain blocks (Ceramco II body; Dentsply Ceramco Inc., Burlington, NJ, USA).

The sample size was calculated to be 15 in each group based on alpha = 0.05, Beta = 0.2 (Power = 80%), and effect size = 0.453 from a pilot study, using one-way ANOVA Menu of PASS 21.0.3 software.

Pre-sintered zirconia blocks (Mamut Dental, Dubai Medical Equipment LLC, Dubai, UAE), which are composed of yttria-stabilized zirconia [ZrO_2 (3% Y_2O_3)], were used in this study. Sixty blocks with 1.5 mm thickness, 7 mm length, and 5 mm width were fabricated by a thin sectioning machine (Gillings-Hamco Thin Sectioning Machine. Hamco Machine Co., Rochester, NY, USA). They were sintered at 1500°C for 120 minutes in a furnace (LHT 02/16, Nabertherm; Lilienthal, Germany) to achieve maximum strength as instructed by the manufacturer. Sixty feldspathic porcelain blocks were also fabricated in silicon putty molds with 2 mm height, 7 mm length, and 5 mm width, by mixing the porcelain powder (Ceramco II body A3; Ceramco-Dentsply, Burlington, NJ, USA) with distilled water. This powder contains 50 - 70 WT% amorphous silica, < 20 WT% tin, aluminum, and sodium oxides, and < 5 WT% lithium, magnesium, bromine, and calcium oxides. The specimens were sintered in a porcelain furnace (Elephant Dental B.V, Hoorn, N/A, Netherlands), dried for 5 minutes at 450°C, and baked at 930°C for 1 minute under vacuum. The specimens were then gradually cooled for 17 minutes at a speed of 55°C/minute. The volume of specimens decreased by 20 - 25% after sintering. To obtain a smooth surface and prevent any micromechanical interlocking in the bonding process, the zirconia and porcelain specimens were polished with 180, 200, 240, 400, 600, and 800-grit silicon carbide abrasive papers under running water. They were then immersed in alcohol, and cleaned in an ultrasonic bath (Cristofoli Dental, Ultron I, Ningbo, China) containing distilled water for 6 minutes.

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Sixty blocks in each ceramic group were randomly divided into 4 groups (n = 15) for assessment at 24 hours and 6 months with the application of two ceramic primers.

Clearfil single-bottle ceramic primer (Clearfil Ceramic Primer, Kuraray Noritake Dental Inc., Tokyo, Japan) was applied on the surface of each ceramic control group (both porcelain and zirconia) at baseline with a microbrush, agitated for 60 seconds as instructed by the manufacturer, and air-dried for 15 seconds (n = 15 for each porcelain and zirconia group). The preparation of the ceramic surfaces of the other control group in the second stage of the test, 6 months after opening the bottle, was also done in the same way.

Two-bottle experimental ceramic primer was prepared by mixing equal amounts of 20% WT of 10-MDP (Kuraray Noritake Dental Inc., Tokyo, Japan)[5] and 4% WT silane (Alfa Aesar Inc., Ward Hill, MA, USA).[6,7] The 1% WT MDP solution was obtained freshly from Kuraray, Japan, and the required concentration was prepared by evaporation of solvent under controlled conditions in an oven (EYELA, NDO 400w, Tokyo, Japan) at 48°C, and continuous weighing of the liquid by a digital scale (AL-104; Acculab, Mountville, PA, USA) with 0.001 g accuracy. Also, 99% silane was diluted with ethyl alcohol to obtain the desired concentration of 4% WT. One drop of silane and one drop of 10-MDP were mixed in a plate, and allowed 2 minutes for silane activation.[8] It was then applied on the surface of ceramic specimens in the first intervention group (n = 15 for each porcelain and zirconia group) by a microbrush for 60 seconds.[9] Next, the ceramic surfaces were air-dried for 15 seconds.[9] The same was performed for the second intervention group for assessment after 6 months (Fig. 1). Both primers were kept refrigerated during the study period.

Immediately after preparation of ceramic substrates at both time points, composite cylinders (Valux Plus; 3M ESPE, St. Paul, MN, USA) with 1 mm height and 0.7 mm diameter were bonded to ceramic surfaces in Tygon tubes (Norton Performance Plastic Co., Cleveland, OH, USA). Each composite cylinder was cured for 40 seconds with a quartz halogen bulb (750 mW/cm^2) light curing unit (Optilux 501, Demetron/Kerr,
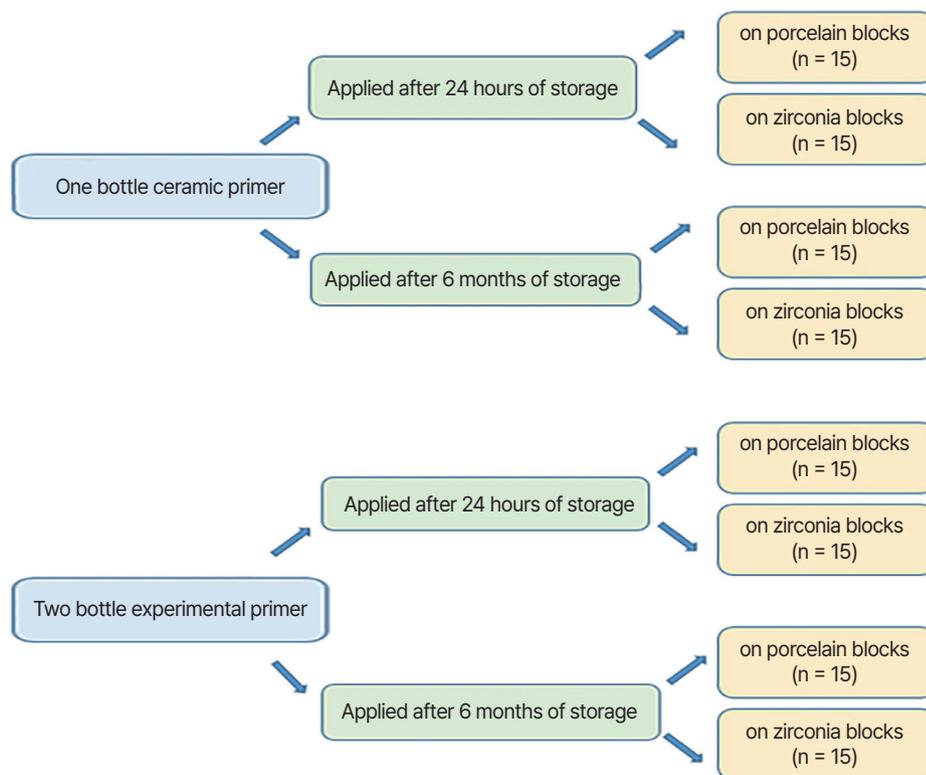

Fig. 1. Schematic illustration of sample preparation.

Orange, CA, USA). Table 1 presents the characteristics of the materials used in this study.

In both time stages of the experiment, the specimens were then incubated at 37°C in distilled water for 24 hours. Next, the Tygon tubes were removed, and the samples underwent μSBS test in a microtensile tester (Bisco, Schaumburg, IL, USA). Micro-shear jigs were used to apply micro-shear force. For this purpose, each ceramic block was adhered to the device with cyanoacrylate glue, and a steel wire with 0.2 mm diameter was connected to the load cell from one side and was tied around the composite cylinder from the other side such that it encircled half of the periphery of the cylinder and was in contact with the ceramic substrate. Load was applied with a crosshead speed of 0.5 mm/minute until failure. The μSBS was recorded in megapascals (MPa) by dividing the applied load at failure in Newtons by the bonded surface area in square millimeters.

Next, all specimens were inspected under a stereomicroscope (SZX9, OLYMPUS, Tokyo, Japan) at ×50 magnification to determine the mode of failure, which was categorized as follows:[5]

- Adhesive failure between the ceramic substrate and composite resin: the composite resin remnant on the ceramic specimen was < 1/3 of its cross-sectional area
- Cohesive failure within the ceramic or composite resin: the composite resin remnant on the ceramic specimen was > 2/3 of its cross-sectional area
- Mixed failure which is a combination of adhesive and cohesive failures: the composite resin remnant on the ceramic specimen was between 1/3 to 2/3 of its cross-sectional area.

FTIR was conducted to analyze the changes in chemical composition of Clearfil ceramic primer, silane, and 10-MDP at 24 hours and 6 months after opening the bottle. The solutions were analyzed on NaCl plate by Bomem analyzer (Bomem Hartmann and Brau, MB-Series, Quebec, Canada). All spectra with 4 cm^{-1} resolution in the range of 400 - 4000 cm^{-1} were recorded. To obtain the desired spectra, 5 scans were performed for each solution (the device was capable of performing 22 scans/minute).

Three-way ANOVA was applied to analyze the effects of type of ceramic primer, type of ceramic, and time on μSBS. The adjusted Bonferroni test was used for pairwise comparisons. The Kolmogorov-Smirnov test was applied to assess the normality of data distribution and the Levene's test was used to analyze the homogeneity of variances. All statistical analyses were carried out using SPSS version 21 at level of significance of 0.05.

RESULTS

Table 2 presents the mean μSBS of the study groups. Considering the normal distribution of data as confirmed by the Kolmogorov-Smirnov test ($P > .05$) and homogeneity of variances as confirmed by the Levene's test ($P > .05$), three-way ANOVA was applied to analyze the effects of type of ceramic primer, type of ceramic, and time on μSBS. The results showed significant interaction effects of type of ceramic primer and time ($P = .046$, F = 4.062), and also type of ceramic primer and ceramic type ($P = .001$, F = 11.955) on μSBS. Also, the effect of time on μSBS was significant ($P = .008$, F = 7.263). No other significant effects were

Table 1. Characteristics of the materials used in this study

Material	Chemical composition	Lot no.	Manufacturer
Clearfil ceramic primer	80% WT < ethanol, 5% WT > 3-trimethoxysilylpropyl methacrylate, 10-MDP	240009	Kuraray Noritake Dental Inc., Tokyo, Japan
Silane	3-(methacryloyloxy) propyltrimethoxy silane	10182637	Alfa Aesar Inc., Ward Hill, MA, USA
10-MDP	1% WT MDP, ETOH	160606	Kuraray Noritake Dental Inc., Tokyo, Japan
Valux Plus resin composite	Resin: Bis-GMA, TEG DMA Filler: 66% WT silica or zirconia (volume)	N763201	3M ESPE, St. Paul, MN, USA

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Table 2. Mean µSBS (MPa) of the study groups (n = 15)

Ceramic primer	Ceramic type	Time	Mean	Std. deviation
Clearfil single-bottle	Zirconia	24 hours	26.95	6.139
		6 months	24.49	8.183
	Feldspathic porcelain	24 hours	28.61	11.123
		6 months	18.13	4.618
Two-bottle experimental	Zirconia	24 hours	19.11	3.590
		6 months	18.29	4.312
	Feldspathic porcelain	24 hours	26.36	6.367
		6 months	25.32	11.445

noted ($P > .05$).

The adjusted Bonferroni test was then applied for pairwise comparisons, which showed that in use of single-bottle Clearfil ceramic primer, the µSBS of both ceramic types significantly decreased at 6 months ($P = .001$ for both). However, the effect of time on the µSBS provided by the two-bottle experimental primer was not significant in any ceramic type ($P > .05$, Table 3).

The adjusted Bonferroni test was also used for pairwise comparisons of µSBS provided by single-bottle and two-bottle primers in each ceramic group. The results showed that the µSBS values to zirconia provided by single-bottle primer at 24 hours ($P = .003$) and 6 months ($P = .017$) were significantly higher than the corresponding values provided by the two-bottle experimental primer. The difference in µSBS to feldspathic porcelain provided by single-bottle and two-bottle primers was not significant at 24 hours ($P = .383$). However, the µSBS to feldspathic porcelain

provided by single-bottle primer was significantly higher than that provided by two-bottle primer at 6 months ($P = .014$).

Table 3 presents the results regarding the mode of failure. The majority of failures were mixed at both 24 hours and 6 months in use of both primers, except for porcelain/single-bottle primer/24-hour group, which showed that cohesive failure within the porcelain was the dominant mode. Figure 2 shows different modes of failure.

Figures 3 – 5 show the FTIR spectra of single-bottle primer, silane, and 10-MDP at 24 hours and 6 months. The peaks at 2840-3000 cm^{-1} were related to C-H vibrations. The peak at 1719 cm^{-1} indicated the carbonyl group (C=O) vibrations, and the peak at 1638 cm^{-1} was related to the vinyl (C=C) group vibrations. Also, the peaks at 1297 cm^{-1} and 1325 cm^{-1} wavelengths indicated ester functionality. The peaks at 1167 cm^{-1} and 1192 cm^{-1} were related to vibrations of ester

Table 3. Frequency of different modes of failure in the study groups

Ceramic primer type	Ceramic type	Time	Mode of failure		
			Adhesive	Cohesive	Mixed
Clearfil single-bottle	Zirconia	24 hours	3 (20%)	1 (6.7%)	11 (73.3%)
		6 months	6 (40%)	0 (0.0%)	9 (60%)
	Porcelain	24 hours	2 (13.3%)	8 (53.3%)	5 (33.3%)
		6 months	5 (33.3%)	3 (20%)	7 (46.7%)
Two-bottle experimental	Zirconia	24 hours	2 (13.3%)	0 (0.0%)	13 (86.7%)
		6 months	6 (40%)	0 (0.0%)	9 (60%)
	Porcelain	24 hours	3 (20%)	4 (26.7%)	8 (53.3%)
		6 months	4 (26.7%)	3 (20%)	8 (53.3%)

Fig. 2. Modes of failure; (Left) adhesive; (Right) cohesive; (Middle) mixed.

(C-O-C in ester group) while the peaks at 1089 cm^{-1} and 818 cm^{-1} were related to symmetrical and asymmetrical vibrations of Si-O-CH3. The peak at 941 cm^{-1} was related to the vinyl group vibration.

Single-bottle ceramic primer: as shown in Figure 2, the peaks at 3300 - 3400 cm^{-1} which were related to O-H vibrations in Si-OH and water were more extensive at 6 months than at 24 hours, such that the area under the curve of this peak almost doubled at 6 months. Also, a new peak formed at 1697 cm^{-1} at 6 months, which was related to vibrations of carbonyl group bonded to hydroxyl group in Si-OH and water. A new peak also formed at 1087 cm^{-1} at 6 months, which was related to formation of siloxane oligomer (Si-O-Si), indicating degradation of active silane. A peak at 2835 cm^{-1}, which was observed at 24 hours and was related to the vibrations of CH in Si-O-CH3, completely disappeared at 6 months. In other words, it was hydroxylated and eventually oligomerized over time. This process decreased the 815 cm^{-1} wavelength over time, due to degradation of Si-O-CH3 in silane, which was replaced with formation of siloxane. The peaks at 1719 cm^{-1} which were related to vibrations of carbonyl group (C=O) in methacrylate did not significantly change after 6 months. The peaks at 1297, 1321, 1192, and 1167 cm^{-1} related to ester groups did not significantly change at 6 months either.

Silane: as shown in Figure 3, a slight increase in peak was noted at 3450 cm^{-1} after 6 months, which was insignificant compared to the same peak in the single-bottle primer. No significant change was noted in the peaks at 1638 cm^{-1} (vinyl group), 1194 cm^{-1} and

1167 cm^{-1} (vibrations of C-O-C ester), and 1089 cm^{-1} (Si-O-CH3) after 6 months. In total, the magnitude of changes was much smaller than those in single-bottle primer at 6 months.

10-MDP: for the pure 10-MDP, the peak at 1718 cm^{-1} was related to methacrylate group, and the peak at 1034 cm^{-1} was related to phosphate group.[6] As shown in Figure 4, a slight reduction at 1713 cm^{-1} was noted at 6 months compared with 24 hours.

DISCUSSION

This study assessed the effect of storage time on chemical structure of a single-bottle and a two-bottle experimental ceramic primer and μSBS of composite to ceramic. It was hypothesized that by separation of acidic monomer from silane and their packaging in different bottles, and mixing immediately before use, the problems related to limited shelf-life of single-bottle ceramic primers due to gradual formation of oligomers following hydrolysis and dehydration condensation as the result of exposure to acidic catalyst may be eliminated.[4,7-11]

The results showed that the μSBS of composite to both ceramic types by single-bottle ceramic primer was significantly affected by storage and significantly decreased after 6 months, but this effect was not significant for the two-bottle experimental primer for any of the ceramic types. Thus, the null hypothesis of the study, which stated that long storage time does not have a detrimental effect on single-bottle primers, was rejected.
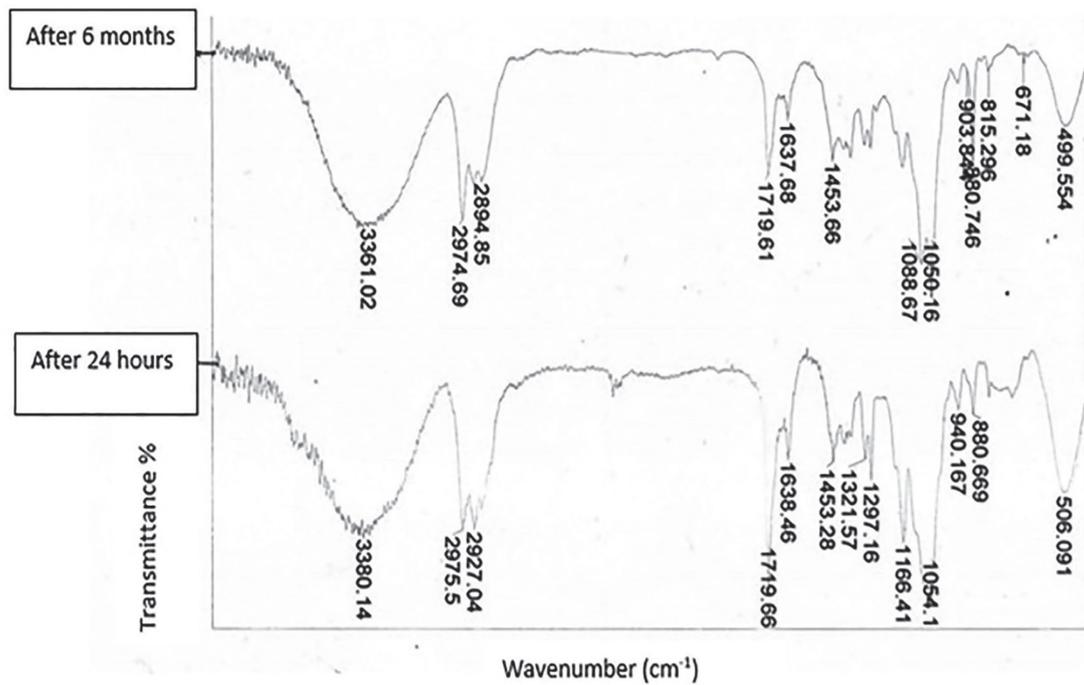
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Fig. 3. FTIR spectra of Clearfil single-bottle ceramic primer at 24 hours (lower spectrum) and 6 months (the upper spectrum).
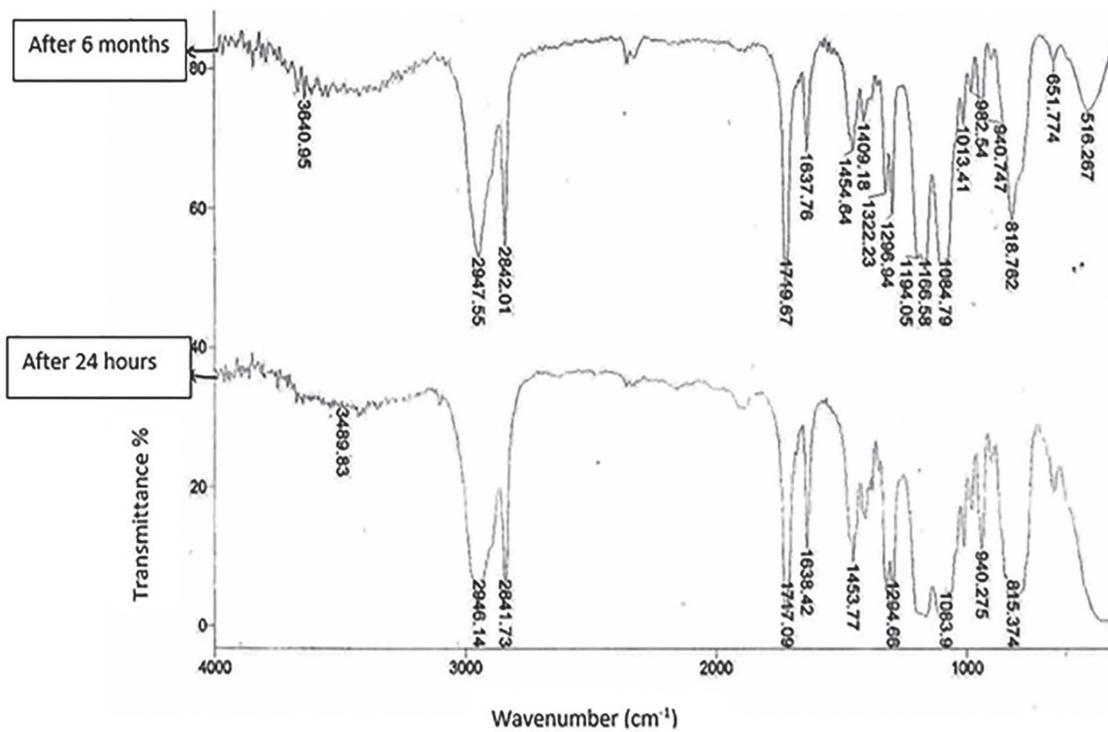

Fig. 4. FTIR spectra of silane at 24 hours (lower spectrum) and 6 months (upper spectrum).
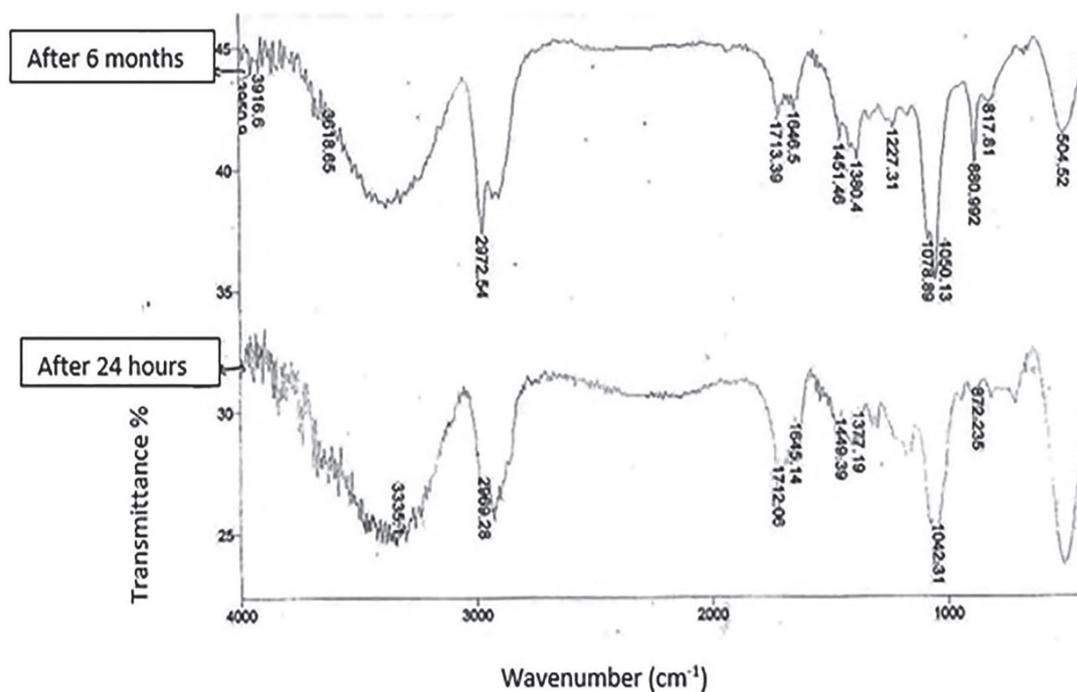
Fig. 5. FTIR spectra of 10-MDP at 24 hours (lower spectrum) and 6 months (upper spectrum).

For preparing ceramic substrates in this study, just ceramic primer was used to avoid interfering factors such as damage to the ceramic surface and even fracture possibility due to pressure caused by mechanical methods such as sandblasting, silica coating or acid etching.[12] It is also reported that by using phosphate monomers as activator in ceramic primer solution[13] or silane,[14] pretreatment of ceramic surface with acid does not increase the durability of the resin cement bond to silicon oxide ceramics.

The main objective of this study was to assess the influence of time on efficacy of ceramic primer. Consequently, other adhesive agents were excluded from the study, with the ceramic primer solution being the sole focus. Moreover, given the presence of MDP monomer in the ceramic primer, this product can potentially serve as a polymer coupling agent.

In the present study, a 4% WT solution of silane was used in combination with 10-MDP solution, as the resulting concentration of 2% falls within the concentration range of silane present in most ceramic primers, which typically have concentrations ranging from 1 to 5% WT.[7,10] Based on the results of Maleknejhad

Yazdi *et al*., which demonstrated that a concentration of 10% WT 10-MDP provides the best outcomes in bond strength and degree of conversion,[5] the concentration of this substance in the experimental solution was increased to 20% WT so that after mixing with a diluted silane solution, the final concentration would reach 10%.

In the present study, after combining the silane solution and 10-MDP, the solution was allowed to activate for 2 minutes. Previous studies have reported complete hydrolysis of silane 24 hours after mixing with an acid.[4] Nevertheless, the hydrolysis process can occur after application on the ceramic surface due to its acidic nature and the catalytic effect of a silica-rich substrate. Therefore, waiting for 24 hours after mixing the freshly prepared solution is not necessary.[8]

According to the results of this study, the μSBS of composite to both ceramic types by single-bottle ceramic primer was significantly affected by storage and significantly decreased after 6 months, but this effect was not significant for the two-bottle experimental primer for any of the ceramic types. These re-

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sults were in line with those of Yoshihara *et al*.,[7] who showed that an experimental primer made of fresh silane with adhesive right before application on glass ceramic surface provided higher bond strength when used immediately compared with its delayed application. Similar results were obtained in other *in vitro* studies on the bond strength of silane-containing universal adhesives to composite[15] and lithium disilicate ceramics.[16-18] Ghasemi *et al*.[19] reported a significant reduction in bond strength to zirconia 6 months after opening a single-bottle ceramic primer. Several studies compared single-bottle (pre-hydrolyzed) and two-bottle (hydrolysis occurs after mixing of the two bottles) primers, and showed optimal performance of both types;[4,10,20-22] although it was demonstrated that the atmospheric temperature was not suitable for pre-hydrolyzed silane,[21] and stability of silane in single-bottle systems was lower due to formation of oligomers.[4,10,21,22] In other words, following hydrolysis in single-bottle systems, silane undergoes dehydration condensation and forms oligomers which cannot bond to glass ceramics.[4,7] This can explain the reduction in bond strength of single-bottle ceramic primers over time. However, in two-bottle systems, due to packaging of acid and silane in two separate bottles, hydrolysis occurs at a much lower pace.

The present study revealed higher bond strength of single-bottle primer to zirconia at both 24 hours (P = .003) and 6 months (P = .017). For feldspathic porcelain, this difference was not significant at 24 hours (P = .383) but at 6 months, the bond strength of two-bottle primer was significantly higher due to significant reduction of bond strength of single-bottle primer (P = .014). Hooshmand *et al*.[4] and Yoshihara *et al*.[7] found no significant difference in bond strength of primers to feldspathic porcelain and glass silica, respectively. However, some other studies reported lower bond strength in use of two-bottle primer at room temperature compared with single-bottle pre-hydrolyzed primer.[20,21,23] This finding may be due to limited reactions at room temperature, such that by a temperature rise, hydrolysis reactions are completed in two-bottle primers, the residual solvent is eliminated, and the bond strength increases comparable to single-bottle primer.[22] The condense structure of silanol plays an important role in performance of si-

lane primer. These structures in pre-hydrolyzed primers are better coupling agents compared with their analogues in two-bottle primers, which can also explain lower efficacy of coupling function in two-bottle primers.[20] Anagnostopoulos *et al*.[20] explained that lower bond strength in two-bottle primers was due to the use of higher concentrations of silane and subsequent formation of a thicker layer of condensed silanol, compared with single-bottle primers. On the other hand, Aoki *et al*.[24] assessed the effect of acids on hydrolytic durability of ceramic primers and showed that by an increase in acid hydrolysis, the contact angle of primer on the surface decreased, and wetting of substrate increased. This finding can explain higher bond strength of zirconia specimens treated with single-bottle primer in the present study. Also, 10-MDP might have undergone some changes in the process of concentration in the present study, affecting the bond strength of experimental ceramic primer to zirconia.

In the present study, the standard deviation values were higher in feldspathic porcelain than zirconia, similar to the study by Hooshmand *et al*.[4] This finding may be due to the fact that feldspathic porcelain specimens in the present study were manually prepared, and could have defects due to operator errors, inadequate condensation, or inadequate dehydration and presence of voids in their structure, while the zirconia specimens were fabricated by the computer-aided design/computer aided manufacturing system, and were then sintered.

Assessment of the mode of failure in the present study showed that mixed failure was dominant in all groups and both primers, and no significant change occurred in any group over time, which was in agreement with the results of Ghasemi *et al*.[19] and Hooshmand *et al*.[4] Some cohesive failures in porcelain specimens were also noted, which could have been due to inherently low cohesive strength of porcelain and non-uniform load distribution at the interface due to micro-shear test.

FTIR analysis of single-bottle primer showed esterification of primer at 6 months. Also, the results indicated that the primer was hydroxylated and oligomerized over time. Degradation of silane and its replacement with siloxane was also noted. Sol-

vent evaporation was found as well. These results were similar to those reported by Hooshmand et al.,[4] Ghasemi et al.[19] and Yoshihara et al.[7] However, the present results showed less changes in the composition of ceramic primer over time, compared with the study by Ghasemi et al.,[19] which may be due to the fact that this ceramic primer was freshly obtained from the manufacturer in the present study and was immediately tested (unlike the study by Ghasemi et al.[19]). Also, a separate fresh bottle was opened for FTIR. In the present study, the primary formulation of silane in ceramic primer changed to silanol. In fact, formation of Si-O-Si and its related peak at 1087 cm^{-1} indicated degradation of active silane such that silanol was attached to its silanol coupling agent, indicating degradation of primer. Moreover, CH_3O- was replaced with O-H.

The FTIR spectra of silane solution showed no significant change over time. Insignificant changes were attributed to the effects of solvent as discussed by Goto.[25]

The FTIR spectra of 10-MDP only showed a slight reduction at 1713 cm^{-1}. The 10-MDP molecule is hydrolyzed into methacrylic acid and 10-hydroxydecyl dihydrogen phosphate; this monomer is converted to phosphoric acid and a 10-carbon alcohol over time.[26]

In total, the FTIR results showed hydrolysis and degradation of single-bottle ceramic primer over time, which can explain the reduction in bond strength. This result was in agreement with previous findings in this regard.[4,7,20] To overcome this problem, some studies suggested mixing of fresh silane with primer or adhesive (two-component primer) right before application on the ceramic surface.[4,7]

This study had some limitations. Aside from the limitations of *in vitro* studies, microshear test was used in this study. Other bond strength tests are recommended for future studies to obtain more accurate results. Also, only FTIR was conducted in the present study. Future studies should perform nuclear magnetic resonance spectroscopy in addition to FTIR to further scrutinize the changes in composition of primers over time. Last but not least, future studies should schedule longer follow-ups to assess the behavior of primers after longer storage periods.

CONCLUSION

Within the limitations of this study, the results showed that the µSBS of composite to feldspathic porcelain and zirconia with the use of Clearfil single-bottle ceramic primer depended on its storage time, and significantly decreased after 6 months. This finding was confirmed by FTIR assessment; however, this was not the case for the two-bottle experimental primer neither for bonding to zirconia nor to feldspathic porcelain. The single-bottle primer generally yielded higher bond strength than the two-bottle primer. In conclusion, the problems of limited shelf-life of single-bottle primers may be partly overcome by the application of two-bottle ceramic primers.

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