The Effect of Water or Wax-based Binders on the Chemical and Morphological Characteristics of the Margin Ceramic-Framework Interface

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ABSTRACT

This study evaluated the effect of binder choice in mixing ceramic powder on the chemical and morphological features between the margin ceramic-framework interfaces. Titanium and zirconia frameworks (15x5x0.5 mm3) were veneered with margin ceramics prepared with two different binders, namely a) water/conventional or b) wax-based. For each zirconia framework material, four different margin ceramics were used: a- Creation Zi (Creation Willi Geller International); b- GC Initial Zr (GC America); Triceram (Dentaurum); and d- IPS emax (Ivoclar Vivadent). For the titanium framework, three different margin ceramics were used: a- Creation Ti (Creation Willi Geller International); b- Triceram (Dentaurum); and c- VITA Titaniumkeramik (Vita Zahnfabrik). The chemical composition of the framework-margin ceramic interface was analyzed using Energy Dispersive X-ray Spectroscopy (EDS) and porosity level was quantified within the margin ceramic using an image program (ImageJ) from four random areas (100 x 100 pixels) on each SEM image. EDS analysis showed the presence of Carbon at the margin ceramic-framework interface in the groups where wax-based binder technique was used with the concentration being the highest for the IPS emax ZirCAD group. While IPS system (IPS ZirCAD and IPS Emax) presented higher porosity concentration using wax binder, in the other groups wax-based binder reduced the porosity of margin ceramic, except for Titanium - Triceram combination.

INTRODUCTION

Metal-ceramic fixed-dental prosthesis (FDP) present ceramic fractures of ~2% over 7 years or ~3% to 4% over 10 years in clinical use.[1] The use of all-ceramic crowns has grown in recent years because of their superior properties in terms of aesthetics and biocompatibility as opposed to their metal-ceramic counterparts.[2-4] Thus, several reinforced ceramic materials using CAD/CAM processes have been introduced in reconstructive dentistry as frameworks, such as zirconia-based ceramics, in an attempt to improve the mechanical support to the veneer ceramics.[5] In fact, the bilayered interfaces must present sufficient adhesion to transmit load from the veneer to the framework materials.[6] In addition, the framework material

should have a higher coefficient of thermal expansion than that of the veneering ceramic, maintaining this layer intact under compression.[7] Nonetheless, exposure of the framework ceramic (delamination) and chip-off fractures (chipping) of the veneering ceramic were described as the most frequent reason for failures associated with veneered zirconia FDPs.[8] These cracks developed in service are also localized at the margin area and would be seen as a localized cracking or chipping, resulting from the combination of residual tensile stress and/or water influence.[5,9] Some factors such as thickness and mechanical properties of framework and veneer ceramic, nature of the applied load, residual stresses induced during firing process and inadequate adhesion and thereby dislodgement of the FDP are associated with the stress state created in all-ceramic FDPs.[10]

During the last few decades, efforts have been made to improve the mechanical and chemical properties of veneer ceramics as well as the application techniques such as injection techniques under pressure resulting in lower intrinsic defect,[11] or using bonder prior to application of veneering the ceramic on the framework that could eliminate thermal stresses.[1] In the conventional layering technique, margin ceramics are used to reduce the marginal porosities, improving fit and mechanical properties and increase the bond strength at the framework-margin ceramic interface in order to resist the stresses and thereby prevent ceramic crack formation at the cervical region. Conventional methods on the other hand are based on mixing margin ceramic powder with distilled water or a special modelling liquid supplied by the manufacturers to form condensable slurry. The slurry is then applied under vibration over a ceramic or metal framework and subsequently fired under vacuum, increasing density. However, using this process, porosity and defects are often present even in fired thin ceramics in the cervical region, which significantly affects the mechanical properties and optical quality.[12] In addition, a recent study showed the negative influence of liquid-based binders (modelling liquid, distilled water and alcohol) on polycrystalline zirconia ceramics that significantly affected grain microstructure[13] that may also result in degradation of zirconia in the presence of moisture.[14]

The use of a wax-based binder with ceramic powder is extensively used in industrial ceramic procedures but reports of its use in reconstructive dentistry is limited.[15,16] In order to employ slurries effectively during veneering, it is important to use a binder that provide stability, appropriate viscosity of a slurry and adequate green stage strength of the products prior to firing.[16] Previous studies have demonstrated that variables such as sintering time, temperature, atmospheric pressure and viscosity of the ceramic had a significant effect on the fracture toughness and porosity concentration of the ceramic.[12,17] Other researchers also reported that mixing liquid, powder/liquid ratio and the technique used to form the slurry could affect the ceramic properties and their microstructure.[17-20] However, no information is available comparing liquid systems with a wax-based binder on the porosity or physical properties of dental veneer ceramics on ceramic- and metal-based frameworks.

The objective of this study was to evaluate the effect of water or wax-based binders on the chemical and morphological characteristics of margin ceramic-framework interface. The hypothesis tested was that the use of a wax-based binder could produce more homogeneity in the margin ceramic after sintering compared with the use of conventional powder-liquid slurry.

MATERIALS AND METHOD

SPECIMEN PREPARATION

Titanium alloy and zirconia framework materials (IPS emax ZirCAD, Ivoclar, Schaan, Liechtenstein; and ICE zircon, Zirconzahn, Bruneck, Italy) were used in combination with different ceramics. For each zirconia framework material, four different margin ceramics were used: a- Creation Zi (Creation Willi Geller International, Switzerland); b- GC Initial Zr (GC America, USA); Triceram (Dentaurum, Germany); and d- IPS emax (Ivoclar Vivadent, Liechtenstein). For the titanium framework, three different margin ceramics were used: a- Creation Ti (Creation Willi Geller International, Switzerland); b- Triceram (Dentaurum, Germany); and c- VITA Titaniumkeramik (Vita Zahnfabrik, Germany). In order to condense the ceramic, two different binders were used, namely a conventional water-based binder (modelling liquid) and wax-based binder (n=3 per group).

FABRICATION OF FRAMEWORKS

One dental technician fabricated all ceramic specimens using a stainless steel mould (15 mm x 5 mm x 0.5 mm). For titanium blocks (Dentaurum GmbH & Co. KG Turnstrasse 3175228 Ispringen, Germany), an agar impression was made from the inner part of the stainless steel mould and duplicated with wax. Wax sprues (Horus, Herpo Produtos Dentários Ltd, São Paulo, Brazil) were attached perpendicular to one end of the template and were connected to a central wax rod (Wax Wire for Casting Sprues, Dentaurum, Pforzheim, Germany). The assembly was mounted in a silicone ring and poured with alumina and magnesia-based investment material (Rematitan®Ultra, Dentaurum JP Winkelstroeter KG, Pforzheim, Germany) that was mixed at a ratio of 100 g powder to 14 ml liquid. After the investment material set, silicone ring and the sprue former were separated from the investment mold. Metallic frameworks were cast in commercially pure titanium in an electrical induction furnace (Rematitan®Autocast, Dentaurum) under argon gas.

All specimens were adjusted according to the dimensions of the stainless steel mould and ultrasonically cleaned (Quantrex 90, L&R Ultrasonics, Kearny, NJ) for 5 min in ethanol and dried by oil-free air spray for 30 s.

APPLICATION OF CERAMIC LAYER

Veneer ceramics were condensed at a thickness of 0.5 mm on the zirconia and titanium frameworks. The ceramic slurry was placed in small portions using a spatula, condensed inside the mould and vibrated manually. The excess fluid was removed with soft absorbent paper (Kimwipes Lite 200, Kimberly Clark Corp., Roswell, GA).

With the wax-based binder technique, ceramic powder was mixed with white modelling wax (S-U-SHADE-SET, Schuler-Dental GmbH & Co, Ulm, Germany) using a heated spatula according to each manufacturer's recommendations. Then, the ceramic slurry was condensed inside the mould using a spatula and vibrated manually.

The ceramic specimen was carefully removed from the mould allowed to dry and sintered in the furnace (Dental-Keramikoven, Dekema GmbH, Freilassing, Germany) following the firing process recommended by each manufacturer of the margin ceramic *(Table 1)*. The specimens were tried in the mould for minor adjustments and ultrasonically cleaned for 5 min in ethanol and dried using oil-free air spray for 30 s.

Chemical and morphological analyses of the framework-margin ceramic interface

The chemical composition of the framework-margin ceramic interface was analyzed using Energy Dispersive X-ray Spectroscopy (EDS) (INCA, Oxford instruments, Oxford, United Kingdom) *(Figure 1)*.

In order to quantify the porosity level in percentage within the margin ceramic, an image program (ImageJ, National Institutes of Health, Bethesda, USA) was used. The analysis was performed following a filter sequence allowing the image program to quantify the porosity. Four random areas (100 x 100 pixels) on each SEM image were analyzed for porosity level. The specimens were then gold sputtered and analyzed under the Scanning Electron Microscope (SEM) (LEO1450VP/LEO-Zeiss, England).

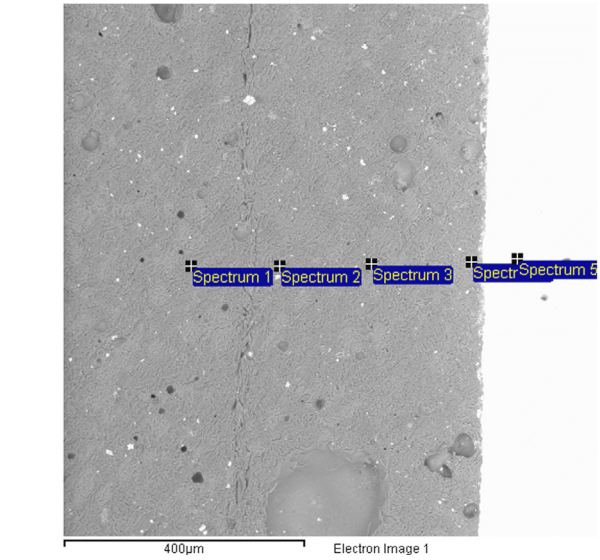


Figure 1: The elemental analysis was achieved from a line profile of 5 spots across the margin ceramic-framework interface using EDS.

Table 1. Firing procedures of the dental ceramics tested. ST: Starting temperature, DT: Drying time, FT: Final temperature, TRI: Temperature rate of increase, HT: Holding time.

Margin Ceramics	ST (°C)	DT (min)	TRI (°C/min)	Vacuum pressure	FT (°C)	HT (min)
Creation Ti	450	4	45	Yes	810	1
Vita Titankeramik	400	6	53	Yes	770	1
Triceram Ti	500	6	55	Yes	785	1
GC Initial Zr	450	4	45	Yes	830	1
Creation Zr	450	4	45	Yes	860	1
Triceram Zr	500	6	55	Yes	790	1
IPS Emax Ceram	403	4	50	Yes	800	1

Table 2. Elemental composition of the specimens at the margin ceramic (a- Creation Zi; b- GC Initial Zr, c- Triceram, d- IPS emax, e- Creation Ti, f- Triceram, g- VITA Titaniumkeramik) and framework materials interfacial area fabricated using either conventional process (c) or wax-based binder (w) analyzed using energy dispersive X-ray spectroscopy analysis.

		C		O		Na		Al		Si		K		Ca		Ti		Zr		Ba		Zn		Mg		Fe	
		c	w	c	w	c	w	c	w	c	W	c	w	c	w	c	w	c	w	c	w	c	w	c	w	c	w
Ice Zirconia Tranlucent	A	-	-	51.8	48.4	5.2	4.5	7.2	7.5	25.6	26.5	5.3	6.3	0.4	-	-	-	4.9	6.8	-	-	-	-	-	-	-	-
	B	-	3.8	49.4	46.9	7.0	6.2	5.6	5.1	24.0	25.0	4.8	4.6	1.7	1.2	-	-	6.3	7.2	1.1	-	-	-	-	-	-	-
	C	-	-	53.4	53.4	6.7	6.7	3.7	3.7	23.9	23.9	2.5	2.6	0.7	0.6	-	-	6.8	6.9	2.3	2.2	-	-	-	-	-	-
	D	-	9.5	48.8	47.2	5.3	5.1	8.6	3.7	22.5	22.8	4.9	3.8	1.4	0.9	0.6	0.5	7.9	5.3	-	-	-	1.1	-	-	-	-
IPS emax ZirCAD	A	-	5.2	51.1	37.9	3.6	3.1	7.7	6.0	23.0	22.4	8.3	7.6	-	1.3	-	-	6.3	14.9	-	1.2	-	-	-	-	-	0.3
	B	-	-	51.0	51.1	5.4	5.3	6.4	6.5	20.2	20.2	4.2	4.2	1.1	1.0	0.5	0.5	10.8	10.8	-	-	0.3	0.3	-	-	-	-
	C	-	-	47.1	51.8	4.8	5.1	5.1	6.7	17.8	22.6	4.9	3.1	1.1	1.1	-	-	14.8	8.1	4.3	2.0	-	-	-	-	-	-
	D	-	12.0	42.1	47.6	3.8	3.0	6.1	3.3	20.7	21.0	3.8	2.8	1.9	1.1	0.4	0.5	9.1	8.4	-	-	-	0.2	-	-	-	-
Titanium	E	-	-	52.1	47.8	5.6	4.2	3.3	4.5	25.3	25.7	3.4	4.0	2.8	2.9	7.6	10.7	-	-	-	-	-	-	-	-	-	0.4
	F	-	-	53.0	53.0	4.2	4.2	4.2	4.2	20.9	20.9	5.4	5.3	0.8	0.8	11.5	11.5	-	-	-	-	-	-	-	-	-	-
	G	-	-	44.4	52.1	4.8	4.5	5.9	5.7	24.0	20.9	4.7	4.4	1.3	0.6	14.5	10.7	-	-	-	-	0.9	-	0.3	-	-	-

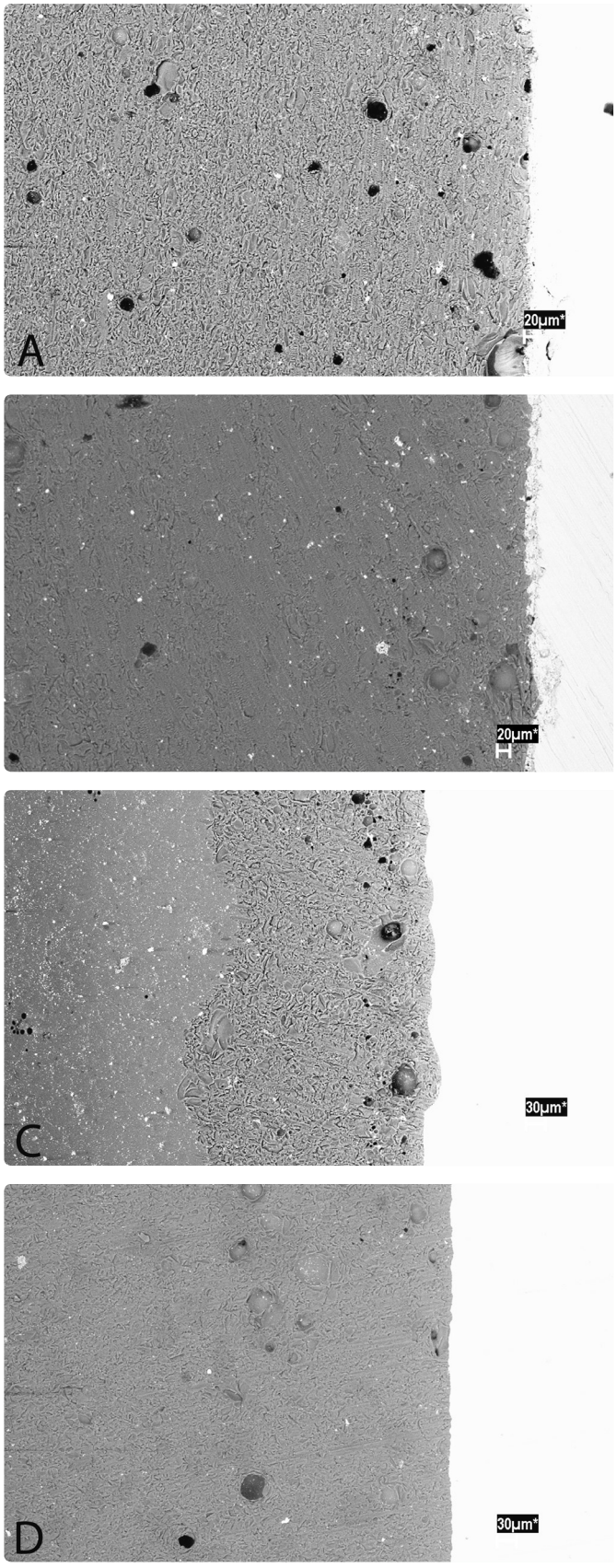
RESULTS

EDS analysis showed the presence of Carbon at the interface between the margin ceramics and framework in the groups where wax-based binder technique was used *(Table 2)*. The Carbon concentration was the highest in the IPS emax ZirCAD group *(Table 2)*.

While IPS system (IPS ZirCAD and IPS Emax) presented higher porosity concentration using wax binder, in the other groups wax binder reduced the porosity of margin ceramic, except for Titanium – Triceram combination *(Table 3, Figures 2a-d)*.

Table 3. Porosity level (%) within the margin ceramic-framework interface quantified by the image program.

Groups (Framework-Margin Ceramic)	Porosity (%)	
	Conventional	Wax
Ice - Creation	28.4 ± 2.7	7.7 ± 2.1
Ice - Initial	11.2 ± 2.6	5.2 ± 1
Ice - IPS Emax	4.2 ± 1.7	9.2 ± 2.2
Ice - Triceram	8.3 ± 1.9	6.1 ±1.7
IPS Zircad - Creation	4 ± 2.1	4.6 ± 1.1
IPS Zircad - IPS Emax	10.1 ± 3.7	16.4 ± 23.6
IPS Zircad - Triceram	5.9 ± 1.4	6.6 ± 0.5
IPS Zircad - Initial	9.4 ± 2.3	32.5 ± 19
Titanium - Creation	8.1 ± 2.7	4.4 ± 1.1
Titanium - Triceram	11.6 ± 2	18.6 ± 9.4
Titanium - Vita	10.3 ± 4.1	4.9 ± 2



Figures 2a-d: Representative images of different margin ceramic-framework interfaces with varying degrees of porosities: a) Titanium + Creation Ti (conventional technique); b) Titanium + Creation Ti (wax-based binder); c) IPS emax ZirCAD + GC initial Zr (conventional technique); d) IPS emax + GC initial Zr (wax-based binder).

DISCUSSION

With the introduction of the metal-ceramic materials for the FDPs, a metal-free zone concept in the labial margin was introduced through modifying the framework.[2] On the other hand, in order to eliminate the metal shine through, pressable ceramic systems were introduced in clinical practice because of their ease of manipulation, favourable mechanical properties and lower porosity compared to that of traditional feldspathic ceramics. Likewise, pressable ceramics provide better control of dimensional stability and the possibility to be used without a metal copin that increased the demand for this option clinically.[9] However, extensive FDPs demand higher mechanical properties of the framework where metal-ceramics are still the choice of materials.

In the present study, the interaction between margin ceramics and different titanium- and zirconia-based framework materials were evaluated when the slurry margin ceramics were applied with water- or wax-based binder. The ceramics prepared with the wax-binder presented higher homogeneity than the ceramics prepared with modelling liquid in some material combinations. Thus, the hypothesis of this present study was partially accepted.

During firing process of ceramics, many important step take place one of which is the binder removal. In fact, complete elimination of non-ceramic components within the slurry is desirable through diffusion from the framework to the surface. However, conventional liquids used to form the ceramic slurry seem to have negative effect on the microstructure of zirconia-based framework.[13] In addition, it is assumed that the drying time, temperature protocol and material type used in the process have a significant effect on the porosity of the overlying ceramic. Consequently, the porosity and defects decrease the mechanical and optical properties of the ceramic. Porosity in the marginal region may decrease translucency due to highly scattered light and also act as crack initiators with high stress concentration, decreasing strength in tension and shear.[12,21,22] Most of the current all-ceramic FDP systems, including those with high-strength frameworks fabricated using CAD⁄CAM system, are bilayered structures[10,11] When the restorations are loaded during service, delamination problems of veneered ceramics usually occur at the marginal part of the FDP.[23]

Regarding the binder choice in this investigation, previous studies have reported that no residue wax-based binder was present above temperatures of 600oC.[24,25] However, when wax was mixed with ceramic powder, this kinetic parameter may have been different, justifying the presence of carbon at the margin-framework interface in some specimens which was more material dependent. The presence of carbon, mainly on the region away from the framework, suggests that the firing protocol requires modification for the ceramic that uses a wax-based binder. Furthermore, no additional studies exist that investigated pre-heating temperature or drying time performed with ceramics processed using a wax-based binder, which may otherwise provide a method to reduce the carbon concentration. Of the groups where wax-based binder was used, only Ice Zirconia - Creation Zir, Ice Zirconia - Triceram Zir, GC Initial Zr-Fs, IPS emax ZirCAD - Triceram Zir, IPS emax - IPS emax ceram presented carbon free interfaces. Although other ceramics have final temperature of slightly lower or even than these ceramics (770-950)°C, they presented carbon. This indicates that final temperature is not decisive for the complete elimination of wax contaminants. Ceramics with starting temperature between 400 to 500°C but temperature rate of increase ranging between 45-55°C but not exceeding 55°C could prevent presence of wax contamination.

Future research efforts should be directed to modify the firing procedures for the margin ceramics using wax-based binder. Also, mechanical studies should elucidate whether the presence of carbon could diminish durability of margin ceramics.

CONCLUSIONS

The use of a wax-based binder to mix the liquid with ceramic powder resulted in more Carbon in the margin ceramic compared to conventional technique without the use of wax where the former technique decreased the percentage of porosity in the ceramics tested except for IPS ZirCAD and IPS Emax and Titanium - Triceram combination.

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