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貴財団より助成金を受領して行った研究テーマについて報告いたします。

添付資料： 研究報告書

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2. 研究テーマ

シランカップリング剤の成分と pH 値と湿潤湿気がデュアルキュア型レジン接着剤のシリカベースマシナブルセラミックスとの接着耐久性及ぼす効果

3. 成果の概要

シランカップリング剤とレジン接着剤を適切に組み合わせることで、シランカップリング剤の劣化を防止できることがわかりました。さらに、シランカップリング剤のシロキサン量は接着耐久性には影響を及ぼさず、シランカップリング剤の pH が一部、レジン接着剤のセラミックスに対する濡れ性が最も大であることが明らかになりました。

4. 研究業績

(1) 学会における発表 有

Meng X, Yoshida K, Atsuta M: Micro-shear bond strength of self-adhesive resin cement to silica-based machinable ceramic, The 2nd joint meeting of the Japan prosthodontic society and the greater New York academy of prosthodontics, Tokyo, Japan, 2007.

(2) 発表した論文 有

Meng X, Yoshida K, Atsuta M (2007) Influence of light irradiation condition on micro-shear bond strength of dual-cured resin luting agents. Dent Mater J, 26 (4): 575-581.

シランカップリング剤の成分と pH 値と湿潤湿気がデュアルキュア型レジン接着剤の
シリカベースマシナブルセラミックスとの接着耐久性及ぼす効果

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要旨

Objective. To evaluate the correlation between siloxane quantity, pH value and wettability of five silane coupling agents with resin bond durability of ceramic.

Methods. Five silane coupling agents { Monobond S (Ivoclar-Vivadent), Rely XTM Ceramic Primer (3M), Clearfil Ceramic Primer (Kuraray), GC Ceramic Primer (GC), Porcelain Liner M (Sun Medical)} were used. Their siloxane quantity, pH value and contact angle to Heliobond (Ivoclar-Vivadent) was measured irrespectively by a FTIR spectrophotometer, pH-indicator strips and a contact-angle meter. 1.5mm thick ceramic plates (ProCAD, A3) were polished and cleaned, and treated by ten combinations between five silane coupling agents and two dual-cured resin luting agents {Variolink (VLII Ivoclar-Vivadent), Linkmax HV(LMHV, GC)}. Their micro-shear bond strength were measured by after 0, 10,000, and 30,000 time thermal cycling. Data was analyzed by three-way ANOVA, four measure parameter of silane coupling agents were subjected to correlation analysis.

Results. Bond strength was significantly affected by silane coupling agents, thermal cycling, and not by resin luting agents. Significant correlation was established between contact angle and bond strength after TC30,000 of silane coupling agents in VLII and LMHV; and between pH value and bond strength of silane coupling agents in VLII.

Conclusion. The hydrolytic degradation of current dental silane for ceramic bonding might be inevitable under endurance test. The improvement of combination between silane coupling agent with resin luting agent could affect delay this hydrolytic degradation process, which is depended by the wettability to resin luting agent, partly by pH value, not by siloxane quantity of silane coupling agents.

Key Words silane coupling agent, pH, siloxane, resin luting agent, machianable ceramic, micro-shear bond strength

緒言 :

Silane as a coupling agent is used popularly in resin bond of silica-based ceramic restorative.^{1,2} Activated silane can provide a physical and chemical bond between resin luting agent and silica-based ceramic: its silanols could form a direct siloxane bridge with hydroxyls of ceramic surface, meanwhile produce crosslinked siloxane polymolecular layer which could form an interpenetrating polymer network (IPN) with resin luting agent; its organic part could take part in the polymerization with resin matrix to provide a direct covalent link with resin luting agent.³

Short-term resin bond strength to silaned ceramic could be obtained, which even could caused cohesive failure of silica-based ceramic in bond test, however this adhesive interfaces were not stable under endurance tests such as thermal cycling or long-term water storage, and different degree reduction of bond strength occurred in various dental silane coupling agents.⁴⁻⁹ Bond durability degradation is contributed to the hydrolysis of siloxane (-Si-O-Si-) in ceramic surface and IPN under water effect.^{10,11} Other field research suggested that the rate of hydrolytic damage of silane could be related to the proportion of Si_{silane}-O-Si_{silane} because the siloxane (Si_{silane}-O-Si_{silane}), siloxane is easier to break than the siloxane (Si_{silica}-O-Si_{silane}), and OH- groups could catalyze the hydrolytic reaction.¹² Miyata et al also suggested that a weaker silane coupling agent/resin bond

could result in a weaker filler/resin in composite with silanated filler.¹³

Current dental silane coupling agents have different silane concentration, activation modes, and supplemental compositions, which produces their different siloxane quantity¹⁴, pH value^{14,15}, wettability to resin luting agents. These factors could form different adhesive interface structures with resin luting agents, which might decide their water resistance. The fact that many dental silane coupling agents are used in different studies, make a correlation of data from various researchers rather difficult. A further understanding of the role of different properties of silane coupling agent can solve this ambiguity.

In this study, we attempted to explore the relationship siloxane bond quality, pH value and wettability of five commercial dental silane coupling agents with their resin bond durability to ceramic.

対象と方法 :

Table 1 Materials tested in this study (information provided by manufacturers)

Material (Abbreviation)	Chemical composition	Lot No.	Manufacturer
Silane coupler:			
Monobond S (MBS)	Ethanol 52%, water 47%, silane 1%, acetic acid	H26975	Ivoclar-Vivadent, Schaan, Liechtenstein
Rely X™ Ceramic Primer (RCP)	Ethanol 70-80%, water 20-30%, silane <1%	3UK	3M, ESPE, Seefeld, Germany
Clearfil Ceramic Primer (CCP)	Ethanol, MDP, silane (γ -MPTS) < 5%	00001B	Kuraray co., Ltd, Kurashiki, Japan
GC Ceramic Primer (GCCP)	A liquid: ethanol, silane B liquid: ethanacol, MMA, UDMA, organic acid	0601262	GC Corp., Tokyo, Japan
Porcelain Liner M (PLM)	A liquid: MMA, 10% 4-META, other B liquid: MMA, silane (γ -MPTS) 10%, other	MR1	Sun Medical Co., Ltd, Moriyama, Japan
Resin luting agent:			
Variolink II (VLII)	A3, Resin matrix: Bis-GMA, UDMA, TEGDMA. Filler: content 72.3%, mean particle size 0.7 μ m, Ba-Al-F-Si-glass	Base: H23580 Catalyst: H23432	Ivoclar-Vivadent, Schaan, Liechtenstein
Linkmax HV (LMHV)	Universal, Resin matrix: UDMA, TEGDMA. Filler: content 70%, mean particle size 0.8 μ m, F-Al-Si-glass	Base: 0601131 Catalyst: 0601131	GC Corp., Tokyo, Japan

1. 1.5 mm thick of ceramic plates (13 X 11 mm squares) Ceramic plate preparation
2. The measurement of contact angle between resin bond agent and silane ceramic surface
3. The determination of pH value in five silane coupling agents
4. The FT-IR analysis of siloxane quantity in five silane coupling agents
5. Micro-shear test of bond strength between dual-cured resin luting agent and silanated ceramic surface before and after 10,000 and 30,000 thermal cycling time.

結果 :

Three-way ANOVA analysis showed that bond strength was significantly affected by silane coupling agent and thermal cycling, not by composite luting agent. The interactions were significant between silane coupling agent/thermal cycling, resin

luting agent/thermal cycling, silane coupling agent/reisin luting agent, silane coupling agent/resin luting agent/thermal cycling.

Table 2 pH value, siloxane signal absorbance strength and mean contact angle for five silane coupling agents.

Silane coupler	Contact angle θ	pH value	Siloxane signal absorbance strength
MBS	34.0 (1.5)	4.0	0.022
RCP	27.7 (1.2)	4.0	0.035
CCP	21.7 (1.2)	1.0	0.116
GCCP	20.7 (1.1)	1.4	0.053
PLM	21.5 (0.9)	2.2	0.075

Table 3 Mean bond strength (SD) of ten combinations between five silane coupling agents and two resin luting agents after 0, 10,000 and 30,000 time thermal cycling.

* Same letters at bond strength for each resin luting agent were not significantly difference by post HocTukey test ($p < 0.05$).

Resin luting agent	Silane coupler	Thermal cycling time		
		0	10,000	30,000
VL II	MBS	24.1 (2.2) ^f	18.6 (4.3) ^{dc}	3.6 (3.5) ^a
	RCP	18.6 (2.7) ^{dc}	7.3 (2.9) ^{ab}	5.2 (3.7) ^a
	CCP	21.7 (2.0) ^{ef}	23.0 (3.3) ^{ef}	10.8 (5.3) ^{bc}
	GCCP	24.0 (4.7) ^f	23.3 (4.6) ^{ef}	13.9 (2.6) ^{cd}
	PLM	25.1 (5.4) ^f	15.3 (2.9) ^{cd}	12.1 (4.2) ^{bc}
LMHV	MBS	22.5 (2.7) ^f	19.6 (4.5) ^{ef}	5.1 (5.2) ^a
	RCP	19.8 (2.2) ^{ef}	12.3 (3.3) ^{bc}	10.1 (3.3) ^b
	CCP	20.2 (2.2) ^{ef}	17.7 (3.0) ^{def}	10.9 (3.3) ^b
	GCCP	18.7 (2.6) ^{def}	17.9 (2.9) ^{def}	14.2 (3.1) ^{bc}
	PLM	22.1 (4.1) ^f	22.3 (2.6) ^f	15.8 (3.4) ^{cde}

Table 5 Pearson's correlation coefficient and respective p value between two properties. Correlation is significant at $p < 0.05$ (2-tailed).

Composite luting agent	VL II			LMHV		
	Contact angle	pH value	Siloxane absorbance	Contact angle	pH value	Siloxane absorbance
Properties of silane couplers						
Bond strength (TC0)	-0.154 (p=0.805)	-0.318 (p=0.603)	0.052 (p=0.933)	0.525 (p=0.364)	0.428 (p=0.473)	-0.164 (p=0.792)
Bond strength (TC10,000)	-0.353 (p=0.560)	-0.738 (p=0.154)	0.458 (p=0.437)	-0.175 (p=0.778)	-0.331 (p=0.586)	0.240 (p=0.697)
Bond strength (TC30,000)	-0.947 (p=0.014)*	-0.898 (p=0.039)*	0.622 (p=0.262)	-0.910 (p=0.032)*	-0.639 (p=0.245)	0.474 (p=0.420)

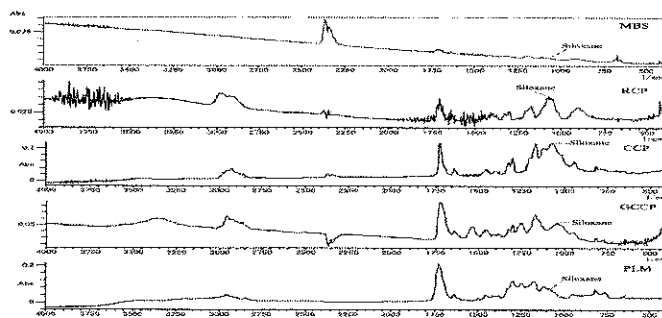


Fig 1-The FT-IR spectra of the five dental silane coupling agents. X-axis: wave number in cm^{-1} ; Y-axis: absorbance in arbitrary unit.

考察：

In this study, no silane coupling agents could maintain their role in resin bond of ceramic, and significant interaction between silane coupling agents and thermal cycling suggested that they had different hydrolytic degradation process of silane. The difference of composition in silane coupling agents could affect the hydrolytic rate of silane.

In this study, we simulated the silane film of ceramic on the KBr plate, and found that different siloxane absorbance strengths occurred in five dental silane coupling agents. This difference was not correspond their silane concentrations demonstrated by manufacturers. RCP with <1% silane had higher has siloxane absorbance strength than MBS with 1% silane, which suggested that the silane degree activation and condensation could not only depended by silane concentration, but also depended by other factor such as pH value, solvent type, hydrolysis time. Within the range of siloxane absorbance strength in this study, the difference of siloxane quantity might not cause a substantial influence on the hydrolytic degradation of silane coupling agent, because the siloxane absorbance strength of five dental silane coupling agents had any correlation with their bond strength at TC0 and 10,000 in two resin luting agents.

Five silane coupling agents have different activation modes: MBS and RCP activated by water, while CCP, GCCP and PLM activated by organic acid. So CCP, GCCP and PLM have lower pH value than MBS and RCP. Previous research showed pH value of ceramic surface and silane coupling agents could affect primary resin bond strength.¹⁶ In this study pH value of silane coupling agents had no correlation with their bond strength (TC0). After TC 30,000, the significant correlation between pH value and bond strength occurred in VL II. It might support at some extent the thought of Olmos et al¹², in which higher pH of silane coupling agent could catalyze the hydrolytic degradation of siloxane. However the correlation effect of pH value was lower than that of contact angle in VL II; even did not occur in LMHV.

Contact angle is a consequence of the inter-molecular interaction between the probing medium and solid. When two media of similar chemical composition are used to probe the surface, the one with a lower surface tension should yield a lower contact angle. VL II and LMHV are dual-cured composite resin luting agents with rather low fluidity. So we used a resin bond agent (Heliobond) as probing medium to reference the wettability of five dental silane coupling agents to resin luting agent. Comparing with pH value, contact angle showed more significant correlation with bond strength (TC 30,000) in two resin luting agents. This result further suggests that the water-resistance ability of resin bond interface to ceramic could be depended on the combination between silane coupling agent and resin luting agent. High wettability of silane coupling agent to resin luting agent helps to form their interpenetrating polymer network (IPN) and copolymerization. MBS and RCP activated by water showed lower wettability than those activated by the use of organic acid such as phosphate acid monomer. Even if under the same activation mode, solvent type and solution concentration also affected their wettability, in which RCP had higher wettability than MBS. To improve the lower wettability of MBS, the manufacturer recommends the additional use of flowable resin bond agent (Heliobond) follows the treatment of MBS. However our and other researches showed that this resolution was not more effective than the only use of MBS.^{17,18} Besides the use of organic acid, two-liquid silane coupling agents (GCCP and PLM) blend functional monomer such as MMA, UDMA into silane before the use of silane, and obtained better bond durability. This beforehand use of functional monomer might be an effective way to obtain better interpenetrating polymer network (IPN) and copolymerization between silane coupling agents and resin luting agents.

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