Bond Strength of Organic Cements to Tooth Structure — Effect of Various Mordants on Bonding to Dentin —

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The bond strength of glass ionomer cement to dentin treated with cleanser and subsequently mordants was measured to develop the best treating system. Also, the effect of the chosen system on the bonding of five other cements to dentin was investigated.

The bond strength of glass ionomer cement to dentin subjected to 37°C water immersion for 1 day was improved by using 0.5 M maleic acid and three mordants containing Fe (III) ion. Particularly, 10 % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ solutions greatly improved the bonding.

Although the bond strength of three other polycarboxylate-based cements such as polycarboxylate and glass ionomer cements was improved using 0.5 M maleic acid and 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, that of two resin cements to dentin was not improved.

Key words: Mordant, Bonding, Cement

INTRODUCTION

Polycarboxylate and glass ionomer cements have a lower bonding strength to cut dentin than to cut enamel. This is caused by the difference in their structure or by the formation of smear layer on the dentin surface after cutting. However, some researchers reported that sorption of some cations (Fe (III), Ca (II), Al (III) and Sn (II))^{1,2)} onto the dentin surface after removing smear layer using a cleanser such as a citric acid solution is available for improving the bonding of cements.

Previously³⁾, we described that the application of 10 % citric acid as a cleanser and 10 % ferric chloride as a mordant improved the bonding of the glass ionomer cement to cut dentin after immersion in 37°C water for 1 day.

In this study, the bond strength of the glass ionomer cement to dentin treated with a new cleanser and subsequently mordants was measured to develop the best treating system. Also, the bond strength of the other glass ionomer, and two polycarboxylate and adhesive resin cements to dentin treated with the chosen system was measured to investigate their effect on the bonding of these cements.

Furthermore, analysis of elements on the dentin surface and observation of morphology of dentin surface before and after treatment were performed by SEM or EPMA.

MATERIALS AND METHODS

Cleanser and mordants :

Table 1 shows the cleanser and the mordants.

Preparation of specimen for bond strength :

Table 1 Bond strength of glass ionomer cement to dentin treated with 0.5M maleic acid and various mordants

mordant	(%)	bond strength (kg/cm ²)		abbr.
control		37.6	(9.28)	Cont.
0.5M maleic acid		31.9	(5.29)	Maleic
FeCl ₃ •6H ₂ O	10	100.9	(15.87)	FeCl-10
Fe(NO ₃) ₃ •9H ₂ O	1	27.9	(4.85)	FeNO-1
	5	58.4	(12.17)	FeNO-5
	10	71.4	(9.14)	FeNO-10
	20	60.2	(6.63)	FeNO-20
Fe ₂ (SO ₄) ₃ •XH ₂ O	1	41.4	(4.94)	FeSO-1
	10	55.3	(18.32)	FeSO-10
	20	49.6	(7.65)	FeSO-20
	30	33.0	(5.21)	FeSO-30
FeNH ₄ (SO ₄) ₂ •12H ₂ O	1	19.2	(6.05)	FeNH-1
	10	113.5	(12.28)	FeNH-10
	20	25.8	(12.99)	FeNH-20
Fe(NH ₄) ₂ H(C ₆ H ₅ O ₇) ₂	5	28.6	(4.78)	FeNHC-5
	10	23.6	(3.69)	FeNHC-10
Fe(NH ₄) ₃ (C ₂ O ₄) ₃ •3H ₂ O	10	36.6	(3.52)	FeNHO-10
CuCl ₂ •2H ₂ O	1	31.4	(12.78)	CuCl-1
	5	34.9	(9.83)	CuCl-5
	10	40.3	(6.93)	CuCl-10
Co(NH ₄) ₂ (SO ₄) ₂ •6H ₂ O	2	34.6	(6.72)	CoSO-2
	5	38.7	(5.28)	CoSO-5
	10	34.0	(4.08)	CoSO-10
AlNH ₄ (SO ₄) ₂ •12H ₂ O	2	40.6	(4.01)	AlSO-2
	5	41.5	(4.47)	AlSO-5
	10	43.6	(5.38)	AlSO-10
KAl(SO ₄) ₂ •12H ₂ O	2	41.3	(4.86)	KAl-2
	5	40.3	(5.88)	KAl-5
	10	41.1	(8.39)	KAl-10

The values in parentheses are the standard deviation.

Bovine teeth were embedded with acrylic resin in a cylindrical metal mold (Fig. 1). Teeth were polished with 600-grit SiC paper under running water, rinsed with distilled water and dried under a light stream of air for 30 min.

The dry polished teeth were treated with cleanser and subsequently the mordants. All treated teeth were cleaned and dried after each treatment by the methods described above. Tape with a 6 mm diameter hole was placed onto the dentin surface and a plastic tube (5 mm diameter) was put through the hole of the masking tape. A cement mixed according to the directions of the manufacture was filled into the tube. Thirty minutes after the cement was applied, the tape and the plastic tube were removed.

Measurement of bond strength :

The bond strength after immersion in 37°C water for 1 day was measured using a tensile shear testing apparatus (Fig. 2). The bond strength of cements to untreated dentin was used as a control.

Preparation of specimens for SEM observation and EPMA analysis :

Fig. 1 Diagram of specimen.

Fig. 2 Tensile shear testing apparatus.

Specimens with a 1 mm thick dentin surface were cut out of the dentin, and treated in the same way as described above for SEM and EPMA. Additionally, the treated 1 mm thick dentin specimens were split to take a side view of thickness of precipitate layer by SEM. Specimens were fixed in a 5 % glutaraldehyde-0.25 M cacodylate buffer at room temperature for 3 hours and dehydrated through a graded series of ethanol. After replacement of ethanol with isoamil acetate, specimens were dried with liquid carbon dioxide using a critical point dryer. Specimens were then coated with gold/palladium for SEM and with evaporated carbon for EPMA.

Determination of cps ratio :

The cps ratios were determined as previously described³⁾.

RESULTS

Bond strength :

Table 1 shows the bond strength of Fuji Ionomer to the dentin surface treated with

Table 2 The statistical analysis of the bond strength using Scheffe's multiple comparison test

abbr.				
FeNH-10				
FeCl-10				
FeNO-10				
FeNO-20				
FeNO-5				
FeSO-10				
FeSO-20				
AlSO-10				
AlSO-5				
FeSO-1				
KAl-2				
AlSO-2				
CuCl-10				
CoSO-5				
KAl-10				
KAl-5				
Cont.				
FeNHO-10				
CuCl-5				
CoSO-2				
CoSO-10				
FeSO-30				
Maleic				
CuCl-1				
FeNHC-5				
FeNO-1				
FeNH-20				
FeNHC-10				
FeNH-1				

The bars indicate no significant difference ($p > 0.05$) between the data connected.

cleanser and mordants after immersion in water at 37°C for 1 day. The bond strength was analyzed by Scheffe' multiple comparison test (Table 2).

When dentin was treated with cleanser and with mordants [10 % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 10 % $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 10 % $\text{Fe NH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], the bond strength was higher than that of the control.

Table 3 shows the bond strength of five cements to dentin treated with 0.5 M maleic acid and with 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Although the bond strength of one glass ionomer and two polycarboxylate cements to the treated dentin was significantly higher than that of the control ($p < 0.05$), the bond strength of two resin cements was not significantly different from that of the control ($p > 0.05$).

SEM observation :

Figure 3 shows the dentin surface and the morphology of fracture dentin surface after application of the cleanser and four mordants. The smear layer was clearly removed with 0.5 M maleic acid. Although a layer of precipitate was observed on the dentin surface where three mordants were applied, it was not observed after application of the other mordant.

EPMA analysis :

Table 3 Bond strength of six dental cements to dentin before and after treating with 0.5M maleic acid and with 10% $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

dental cement	bond strength (kg/cm^2)	
	before (control)	after
Fuji Inomer Type I *	37.6 (9.26)	113.5 (12.28)
Hy-Bond Ionomer**	42.8 (7.17)	97.2 (18.03)
Live Cenera*	27.6 (5.22)	56.1 (12.40)
Hy-Bond Carbo cement**	52.2 (8.48)	78.3 (9.49)
Panavia EX†	41.2 (12.26)	29.6 (4.31)
Chemiace††	26.5 (10.03)	38.9 (8.30)

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** SHOFU INC., Kyoto, Japan

† KURARAY, Okayama, Japan

†† SUN MEDICAL, Kyoto, Japan

Fig. 3 SEM micrograph of dentin surface and fracture dentin surface treated with 0.5 M maleic acid and with four mordants.

a: 0.5 M maleic acid

b: 0.5 M maleic acid and 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

c: 0.5 M maleic acid and 10 % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

d: 0.5 M maleic acid and 10 % $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

e: 0.5 M maleic acid and 10 % $\text{Fe}(\text{NH}_4)_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$

Table 4 The cps ratios of adsorbed elements on the dentin surface

mordants	cps ratios	elements
10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.050	Fe
10% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.142	Fe
10% $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{XH}_2\text{O}$	0.057	Fe
1 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.026	Fe
10% $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.061	Fe
20% $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.039	Fe
10% $\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$	trace	Fe
10% $\text{Fe}(\text{NH}_4)_3(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$	trace	Fe
10% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.018	Cu
10% $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.001	Co
10% $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.001	Al
10% $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.020	Al

Table 4 shows the cps ratios of each element on dentin surface. Although the range of cps ratios of Cu $K\alpha$, Co $K\alpha$, Al $K\alpha$ are from 0.001 to 0.020, the range of those of Fe $K\alpha$ are large and dependent upon the kind of anion in the substance.

DISCUSSION

The bonding of the glass ionomer cement to dentin was improved by using cleanser and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as previously described³⁾. In this study, the influence of various mordants on the bonding of cements to dentin without smear layer was investigated.

As shown in Table 1, some mordants improved the bond strength of Fuji Ionomer to dentin. Particularly, 10 % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ greatly increased the bond strength of this cement. All the mordants that improved the bonding of the cement had Fe (III) ion. Additionally, their ability of depositing ferrous compounds onto the dentin surface is excellent because the cps ratio of Fe on the dentin surface is higher, and precipitation on the dentin surface is observed after application of these mordants. Therefore, these results demonstrate that ions supplied from a mordant can play an important role in the bonding of the cements to dentin. However, since the ability of depositing a chemical compound onto the dentin surface is dependent upon the kind of substance used as a mordant and variation of concentration of a mordant in a mordant solution, and also because the mordant showing the highest cps ratio does not give the highest bond strength to the cement, the selection of the mordant and adjustment of the concentration of mordant in the solution are very important to obtain an excellent mordant available for improvement of bonding of the cement.

As shown in Table 3, the bond strength of polycarboxylate-based dental cements such as glass ionomer and polycarboxylate cements was improved by using 0.5 M maleic acid followed by 10 % $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. However, the bonding of two resin cements was not improved. It is known that the setting reaction mechanisms of glass ionomer, polycarboxylate and two adhesive resin cements are different from each other⁴⁻⁶⁾. If the ions supplied from the mordant adversely affect the setting reaction of the resin cements, the bonding of the cement can never be improved by the mordant treatment. This might be one of the

reasons for the uselessness of the mordants for the resin cements in this study. The treatment, however, may enhance the bonding of these cements to dentin, if some other curing systems of them are developed.

CONCLUSION

A cleanser (0.5 M maleic acid) and various mordants were prepared to develop the best treating system to improve the bond strength of glass ionomer cement to dentin. Also, the effect of the chosen system on the bonding of five other cements to dentin was investigated.

The bond strength of Fuji Ionomer after immersing in 37°C water for 1 day was improved by using 0.5 M maleic acid and three mordants containing Fe (III) ion. Particularly 10 % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 10 % $\text{FeNH}_4 (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ greatly increased the bond strength of Fuji Ionomer cement. However, other mordants containing Fe (III), Cu (II), Co (II) or Al (III) ions did not improve the bond strength significantly. This shows that the selection of mordant and adjustment of concentration of mordant are very important for improvement of the bonding of the cement.

Although the bond strength of three other polycarboxylate-based dental cements such as polycarboxylate and glass ionomer cements was increased by using 0.5 M maleic acid and 10 % $\text{FeNH}_4 (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, that of two adhesive resin cements was not improved by these mordants.

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歯科用アマルガムとその構成相の生理食塩水中での腐食挙動に関する研究

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従来型及び高銅型アマルガムとそれらの構成相の0.9%食塩水中での腐食挙動を、電気化学的方法によって検討した。

電位走査法によって電位-電流曲線を求めた結果、Sn, Sn₈Hg, Ag₃Sn, Cu₆Sn₅では、同じ電位付近に、1つのアノードピークと2つのカソードピークがみられ

た。又、両アマルガムは、2つのアノードピークと3ないし4つのカソードピークがみられた。

従来型アマルガムを-1.5 Vから+0.5 Vまでアノード走査後、X線マイクロアナライザーで分析した結果、Sn-Cl richな腐食生成物が観察された。

有機セメントの歯質への接着性に関する研究

その2 象牙質への接着力に与える各種のモダントの効果について

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最良の表面処理システムを開発する目的で、グラスアイオノマーセメントと、クレンザー及び各種のモダントを用いて処理した象牙質との接着力を測定した。また上記の結果から選ばれた表面処理システムが、他の5種のセメントの接着力に与える影響についても検討を加えた。その結果、37度水中に1日浸漬した後の接着力は、0.5モルのマレイン酸とFe(III)イオンを含む3種のモダントを用いると増加し、中でもモダントに10%

塩化第二鉄、10%硫酸第二鉄アンモニウムを用いると特に大きく増加した。また、カルボキシレートセメントやグラスアイオノマーセメントのような、ポリカルボン酸をベースにした有機セメントの象牙質への接着力は、0.5モルマレイン酸と10%硫酸第二鉄アンモニウムによる表面処理によって大きく増強されたが、2種のレジンセメントについては、増強効果はなかった。