

Electrical shear bonding strength reduction of resin-modified glass-ionomer-cement containing ionic-liquid: Concept and validation of a smart dental cement debonding-on-demand

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With improvement of bonding strength of recent dental cement, it is difficult nowadays to remove restorations without excessive force or vibration to tooth, occasionally resulting in damage of dentin, enamel, and dental root. Therefore, “smart” dental cement indicating strong bonding and easy debonding-on-demand simultaneously is required. In this research, resin-modified glass-ionomer-cement containing an ionic-liquid, tris(2-hydroxyethyl)methylammonium methylsulfate was produced, and the shear bonding strength before and after direct current application were evaluated. The prototype cement containing 15 to 20 mass% ionic-liquid indicated simultaneously no significant reduction of shear bonding strength from that of the original cement not containing ionic-liquid, and significant reduction of bonding strength to approximately 20% of that of the original cement after direct current application of more than 2 mA/mm². The prototype cement in this research demonstrated that the concept of smart dental cement electrically debonding-on-demand is feasible.

Keywords: Glass ionomer cement, Shear bonding strength, Ionic-liquid, Smart adhesive

INTRODUCTION

Various types of dental cement have been widely used for bonding of dental restorations. With progress of dental cement, many properties have been improved¹⁾, and the improvement of mechanical properties, especially bonding strength increase is a key factor expanding the life time of dental restorations. Thus, patients today can receive great benefits from such advanced dental cements, however, they occasionally give patients some problems. In cases of, e.g., secondary caries formation or development of pulpitis near restoration, the restoration usually has to be removed for treatment. However, the excellent bonding strength of advanced dental cement is an obstacle to easy removal. To remove such restorations being bonded strongly to tooth, excessive force or vibration are applied to the restoration, which leads not only to a discomfort or pain of patients, but also to occasional damages of dentin and enamel, and, in the worst case, to root fracture. Hence, strong bonding is not necessarily excellent property of dental cement. To demonstrate the contradictory property of strong bonding and easy debonding simultaneously, “smart” dental cement debonding-on-demand is required.

Adhesives debonding-on-demand have been developed for engineering application. They have a great merit that the components assembled using the adhesive can be easily disassembled for repair and maintenance²⁾. In addition, before recycling the components, parts of different materials can be easily separated. The adhesive debonding-on-demand needs a trigger to change its

properties for easy debonding. A major trigger is heat; adhesives softened or melt at elevated temperature are most popular ones³⁾. Other triggers are, e.g., pH, light, and electric current^{2,4)}. In oral cavity, thermal trigger has a potential risk of oral mucous membrane damage. Moderate pH change and visible light is possibly safe trigger for oral mucous membrane, however, it is difficult to inhibit their working as a trigger in oral cavity in daily life. In contrast, small electric current is reasonably safe and easy to inhibit. Because the patient does not feel significant pain if the voltage is under pain-threshold⁵⁾, small current values of 0.4 mA^{6,7)}, 1 mA⁸⁾ and 5 mA⁹⁾ are adopted for the fluoride iontophoresis for tooth, and a significant electric current in oral cavity is generated only in the case of galvanic current between two different metal restorations. Thus, electric current is adopted as a trigger in this research.

A commercial product of adhesive debonding-on-demand with electric current trigger named “ElectRelease™” was reported in 2002¹⁰⁾. The basic material design of the product is epoxy resin containing ionic-liquid (IL), which gives the epoxy resin electrical conductivity. The design suggests that dental cements containing IL also indicate electrical conductivity and perform debonding-on-demand property. The authors have tried to make prototype cement based on several types of dental cement, and found that glass ionomer cement (GIC) and resin modified GIC (RMGIC) containing IL indicated significant electrical conductivity. Therefore, the authors focus on RMGIC with IL in this research, because the bonding strength is higher than that of GIC.

IL is popular material today for reaction solvents

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and battery applications¹¹⁾. In contrast, research and development of its medical application has just started and biosafety evaluation is not widely performed. A promising candidate of biosafe IL for medical application is the amino acid base IL^{12,13)}. However, it is not popular at present and difficult to prepare it for prototype cement production. Thus, a popular IL whose biosafety is not clarified is used in this research. Needless to say, various types of mechanical properties, chemical properties and biological properties of dental cement are important for clinical use, however, the objective of this paper is limited to the validation of the concept, “dental cement debonding-on-demand with electric current trigger”. Thus, prototype cements containing IL with several mixing ratios were prepared, and their bonding strength before and after electric current application were evaluated. And effects of electric current application condition were also investigated.

MATERIALS AND METHODS

Prototype cement preparation

The IL adopted in this research was tris(2-hydroxyethyl)-methylammonium methylsulfate (Fig. 1, Sigma-Aldrich Japan, Tokyo, Japan, hereinafter called THMM), because the low acute oral toxicity ($>6.400\text{ mg/kg, LD}_{50}$, rat) and no skin irritation (rabbit) as described in the safety data sheet was appropriate to produce prototype cement. The base dental cement was RMGIC (Vitremer™ 2 paste, 3M Japan, Tokyo, Japan). The mixing ratios of THMM in weight were 10% (VT10), 15% (VT15), 20%

(VT20), and 25% (VT25) in this paper. The THMM was mixed manually with 2 cement pastes (a base paste and a catalyst paste) simultaneously using polymer spatula and mixing paper.

Specimen preparation for shear bonding strength evaluation

To evaluate the shear bonding strength (σ_s) of a dental cement, σ_s between restoration and dentin/enamel is most important. However, in this paper, σ_s between metal and metal was evaluated, because the objective of this paper is focused on the validation of the σ_s reduction with electric current trigger. Besides, the high cost of THMM required downsizing of specimen. Thus, two small Cu plates ($4^w\text{ mm} \times 2^t\text{ mm} \times 20^l\text{ mm}$) were used to prepare specimen. The square bonding area ($4\text{ mm} \times 4\text{ mm}$) was roughened using sandblast (alumina particles of $50\text{ }\mu\text{m}$ diameter at a pressure of 0.4 MPa for appropriate time: uniformity of surface roughness was confirmed visually), rinsed ultrasonically in distilled water for 5 min, and the two plates were bonded each other to form T letter in the setting mold as shown in Fig. 2. The pair of plate were pressed for 5 min to set cement thickness $15\text{ }\mu\text{m}$, and the excess cement was removed manually. The specimens were, then, kept for 24 h in air at room temperature for curing. Twenty-four hours might be insufficient for saturation of curing^{14,15)}, however, the σ_s values after curing for 24 h were reasonably high to validate the effect of current application on σ_s .

Current application to specimen

Direct current of 5, 10, 15, and 19 V was applied for 30 or 120 s to the specimen using programmable power supply (Type 7651, Yokogawa Electric, Tokyo, Japan) as shown in Fig. 3. The anode/cathode setting is also shown in Fig. 3. The current value change over time was recorded using digital multimeter (Type TY720, Yokogawa Electric), and the total charge density to the specimen was calculated from time-integrated current value. To analyze the effects of intermittent current application, interval time between current applications of 19 V for 30 s was set to 15, 30 and 60 s, and the current value change was also recorded.

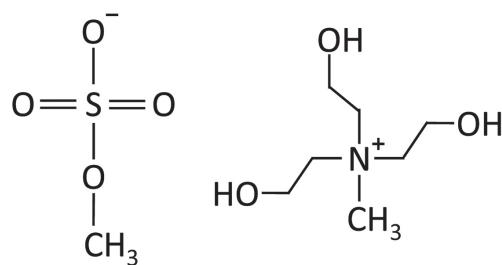


Fig. 1 Structural formula of THMM.

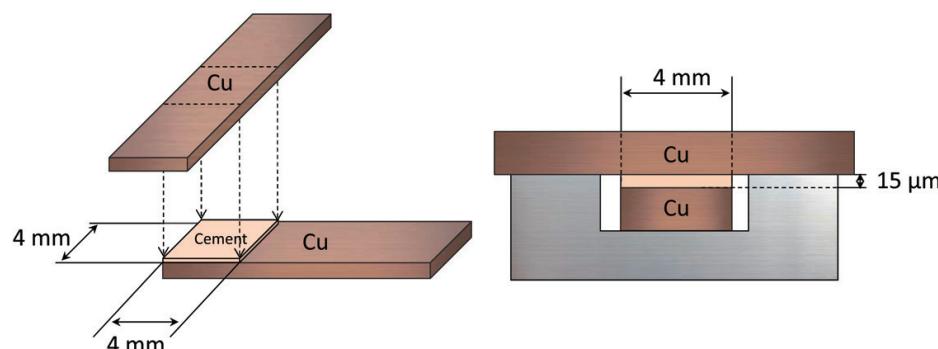


Fig. 2 Design and preparation of specimen for shear bonding strength test.

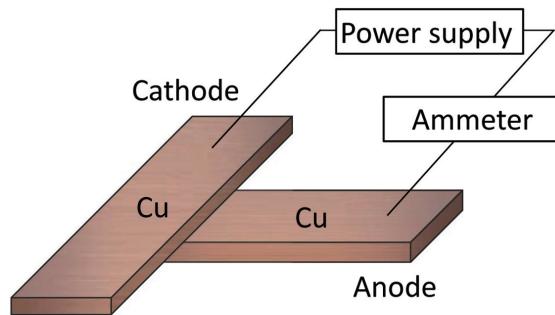


Fig. 3 Setting of electric current application to specimen.

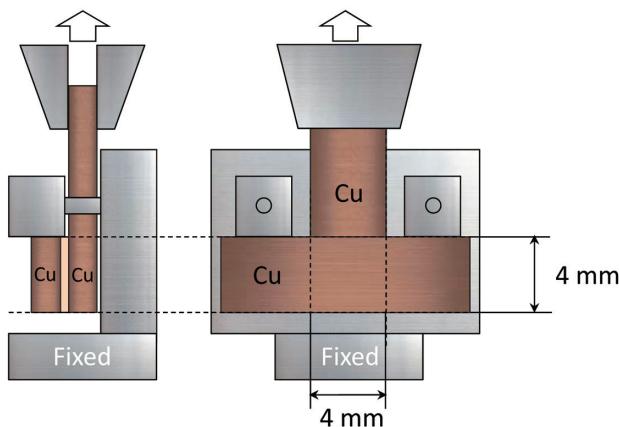


Fig. 4 Specimen setting for shear bonding strength test.

Bonding strength evaluation

Universal test machine (AG-1kNX, Shimadzu, Kyoto, Japan) was utilized for σ_s evaluation. The specimen setting in tensile test jig was shown in Fig. 4. The σ_s was calculated as follows;

$$\sigma_s = P/S$$

where σ_s is the shear bonding strength, P is the load at the fracture, and S is the bonding area, 16 mm² in this paper. σ_s of specimen bonded using RMGIC not containing THMM (VT00) was also evaluated as a control, and σ_s of specimen before and after current application were evaluated. The number of each specimen was 7 to 15.

Fracture surface observation

After σ_s evaluation, fracture surfaces of the specimen were captured by a digital camera using automatic white-balance and automatic exposure.

Statistical evaluation

σ_s data were statistically analyzed by Steel-Dwass Test using EZR software (Saitama Medical Center, Jichi Medical University, Japan)¹⁶⁾ to compare the means of the different groups. The statistical significance was accepted at the 0.01 confidence level.

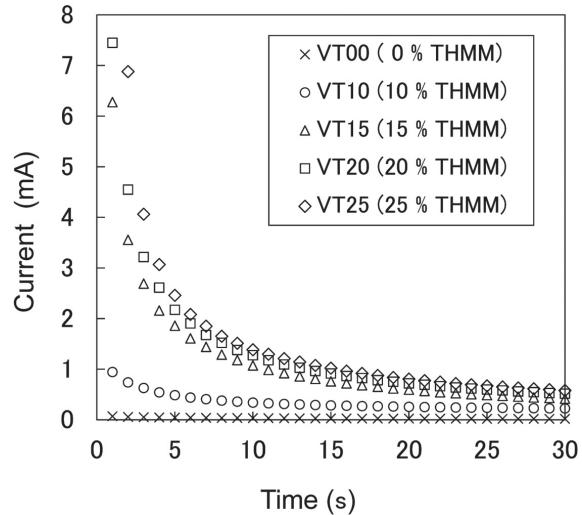


Fig. 5 Current change during constant voltage of 19 V application.

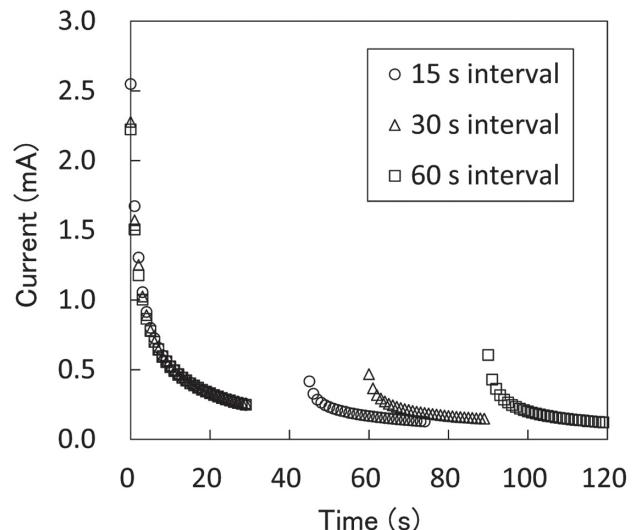


Fig. 6 Current change during constant voltage of 19 V application with intervals on VT15.

RESULTS

Current change during current application

Figure 5 shows typical current value change over time during constant voltage of 19 V application of each specimen. Specimen not containing THMM (VT00) showed nearly zero initial current, and no change during voltage application. With increasing mixing ratio of THMM, initial current values were increased, and current values of each specimen reduced exponentially over time. The charge density calculated increased with increasing mixing ratio of THMM.

Figure 6 shows typical current value change before and after intervals during current application of 19 V to

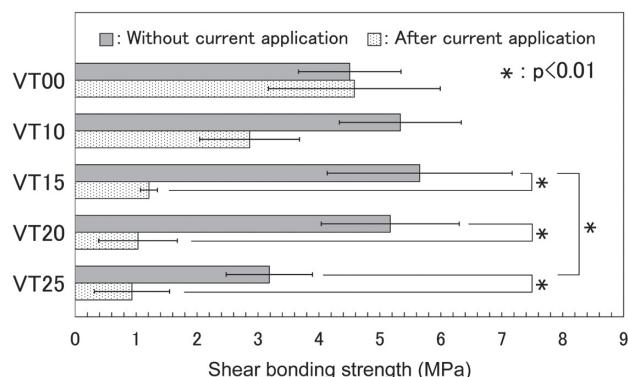


Fig. 7 Average shear bonding strength before and after current application.
Error bar shows standard deviation.

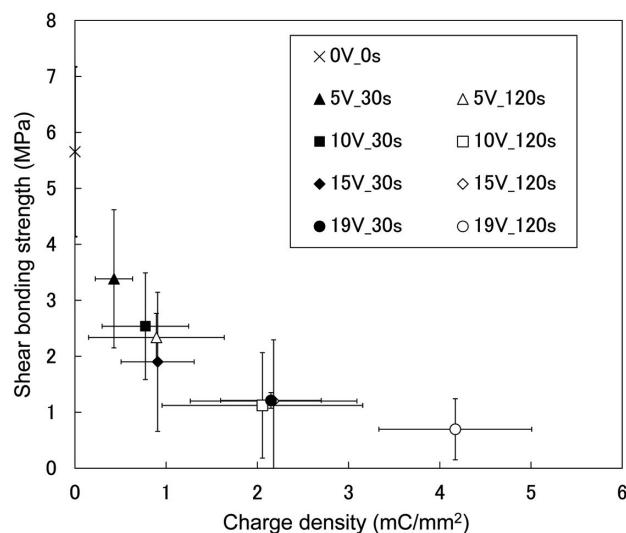


Fig. 8 Effect of charge density on shear bonding strength of VT15.
Current condition indicates voltage and time of applied current.

VT15 specimen. The initial current value after intervals were higher than the final value of the initial current application, and the increment from the final value increased with increasing interval time.

Shear bonding strength

Figure 7 shows σ_s of each sample before and after current application of constant voltage of 19 V for 30 s. There was no significant difference between σ_s of each specimen containing THMM less than 20% before current application, and σ_s of VT25 showed significant decrease from that of VT15. There was no significant difference between σ_s of VT00 and VT10, before and after current application. In contrast, there was significant difference between σ_s of VT15, VT20, and VT25 before and after current application.

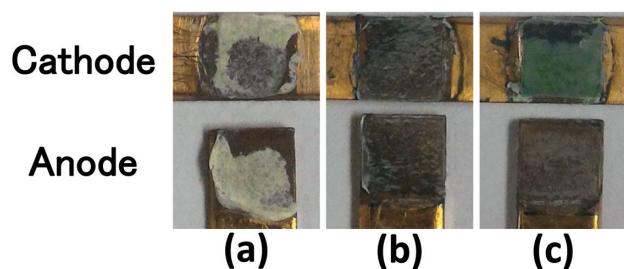


Fig. 9 Fracture surfaces after shear bonding test.
(a) VT00, (b) VT15 before current application, (c) VT15 after current application.

Charge density effect of shear bonding strength

Figure 8 shows charge density effect of σ_s of VT15 specimen. σ_s showed exponential decrease with increasing charge density from 0 mC/mm² to approximately 4 mC/mm². Voltage value and applied time of current did not affect directly on σ_s .

Fracture surface after shear bonding strength test

Figure 9 shows the fracture surfaces after shear bonding strength tests of VT00, VT15 before and after current application of 19 V for 30 s. Cement residue was observed on both anode and cathode of VT00 and VT15 before current application, indicating the fracture was cohesive fracture. In contrast, cement residue was not observed on the anode of VT15 after current application, indicating the fracture was interfacial fracture on anode. In addition, only the cement residue on the cathode of VT15 after current application showed greenish surface.

DISCUSSION

Current change during current application

The basic contents of RMGIC are poly acrylic acid and copolymers, water-soluble polymers and polymerizable monomers, glass fillers, tartaric acid, and water¹⁷. Since the prototype RMGIC contains both water and THMM, both electronic conductivity and ionic conductivity contribute to the current value¹⁸. The two conductivity, however, was not evaluated separately in this paper, but the total ability conducting electric current was evaluated qualitatively as "electrical conductivity". Although the matrix of cured RMGIC is water-based poly acrylic acid gel, VT00 in this paper did not show electrical conductivity. This result is not incompatible with the fact that tartaric acid is contained in the cement before curing, because tartaric acid is expended in acid-base reaction for curing. In contrast, the prototype RMGIC containing THMM in this study showed electrical conductivity clearly, and with increasing THMM content, the electrical conductivity also increased. These results suggest that the matrix gel containing THMM converted to electrolyte known as ion gel¹⁹, and that the prototype RMGIC containing higher THMM showed higher

electrical conductivity. Although the ion concentration in matrix gel was not evaluated in this research, the ion concentration and electrical conductivity of the prototype RMGIC containing higher THMM should be higher as reported in a previous study²⁰.

With increasing current application time, the current values were decreased from the initial value. Candidates of electro-chemical reactions on electrode during current application²¹ are;

1. Cu ion release on anode
2. Hydrogen gas evolution on cathode
3. Ion migration in matrix gel^{18,22}

One other candidate of change in matrix gel affecting on the electrical conductivity is;

No cement residue was observed on anode, and that the surface color of cement residue on cathode changed to green after current application. This color change suggests that Cu ion was released from anode, and that some kind of Cu compound was generated at the interface between anode and RMGIC, or Cu ion was dissolved into matrix gel of RMGIC. The Cu compound was not analyzed in this paper, however, the compound could change the interfacial bonding between anode and RMGIC, resulting in acceleration of fracture on the anode surface. Effects of Cu ion dissolution into matrix gel on σ_s was not clarified, however, Cu ion elution led to elimination of a part of anode surface, resulting in damage of interfacial bonding on the anode. The damage of interfacial bonding also reduced the electrical connection through the interface, resulting in the reduction of current value over time. Hydrogen gas evolution could not be observed during the current application, because it was difficult to find a gas evolution in solid and non-transparent electrolyte. It could also damage the interface bonding between cathode and RMGIC, however, the damage was not severe, because bonding at the cathode interface was stronger than that at the anode interface. Further investigation is required to clarify the effects of chemical reaction during current application in detail.

The electrical conductivity was recovered after interval of current application. Since the potential electro-chemical reactions on anode and cathode are irreversible, the electrical conductivity recovery was caused by the ion migration in matrix gel. With current application, anions and cations in matrix gel were migrated and polarized, resulting in reduction of electrical conductivity of ion gel²³. During the interval after current application, anions and cations polarized diffused in the matrix gel over time, and the electrical conductivity recovered.

Effects of THMM addition on shear bonding strength

Since the basic curing mechanism of GIC is acid-base reaction, THMM potentially affects GIC curing, resulting in acceleration or deceleration of curing. In this study, curing time after specimen preparation was set to 24 h, which might be insufficient for saturation of curing. In case that curing after 24 h was insufficient, acceleration of curing can be observed after 24 h in specimens

containing THMM. Although no significant difference was observed between σ_s of specimen containing THMM less than 20% before current application, the average value increased with increasing THMM content from 0 to 15%. This increment might be caused by the acceleration.

Since THMM is not an adhesive monomer, it should have no contribution to increase σ_s , but may decrease σ_s , because the composition of RMGIC decreases with increasing THMM composition. However, σ_s of only VT25 showed significant decrease from that of VT15. Note that RMGIC contains water, and ions of THMM should preferentially dissolve in water. Therefore, small amount of THMM can be contained in the matrix gel as a solution. In contrast, large amount of THMM cannot be fully contained as a solution, and might be dispersed in matrix gel as independent liquid droplets. Such liquid droplets can reduce the matrix gel network density, resulting in reduction of gel strength. The fracture before current application was cohesive fracture, therefore, reduction of gel strength led to reduction of σ_s .

Effects of current application on shear bonding strength
The fracture after current application changed from cohesive fracture to interfacial fracture on anode, suggesting that the mechanism of σ_s reduction was not the reduction of gel strength, but reduction of interfacial bonding strength on anode. Therefore, candidate mechanisms of σ_s reduction were electro-chemical reactions on anode. As discussed in section 4.1., Cu ion release and/or potential Cu compound generation damaged the interfacial bonding between RMGIC and anode, resulting in σ_s reduction. Thus, large amount of charge density should promote the σ_s reduction. For larger amount of charge density, higher THMM content is effective. While, due to the high cost of THMM, its content in RMGIC should be minimized. Therefore, the best THMM content in this paper was summarized to be 15% in this paper.

The THMM content in RMGIC is not the only dominant factor affecting on the σ_s reduction, but also the charge density is a dominant factor. Therefore, for σ_s reduction, high voltage current application has an advantage to save the time for application. However, high voltage application in oral cavity might damage teeth and oral mucous membrane, or give the patient significant pain. Thus, low voltage application under pain-threshold for a long time is more safe and comfortable. Nevertheless, current value after long time current application is limited. These limitations suggest low voltage application for long time is not the best current application condition. One possible better condition is a discontinuous current application. Current value can be recovered after interval of current application, which suggests current application for long time containing intervals might be more effective than continuous current application for the same time.

Future work

The THMM utilized in this study is not guaranteed to be

sufficiently biosafe in oral cavity. For clinical application, more biosafe IL is required. The authors have evaluated RMGIC containing few types of IL, and found all of them could indicate σ_s reduction after current application, promising that RMGIC containing future biosafe IL will also indicate σ_s reduction after current application. Evaluation of chemical properties of RMGIC containing IL is also required, especially, dissolution test of IL from RMGIC is most important. Even in the case of biosafe IL, dissolution of IL from RMGIC leads to decrease of electrical conductivity and difficulty in effective current application.

The other major type of dental cement today is resin-based cement. It is widely utilized in clinic because of its excellent properties. One of the properties is its bonding strength: The bonding strength of several products of resin-based cement is significantly higher than that of RMGIC²⁴⁻²⁷. Higher bonding strength of dental cement, however, increased the risk of occasional damages of dentin and enamel, and root fracture. Therefore, smart resin-based dental cement debonding-on-demand is much more required. The authors have tried to develop smart resin-based cement, and found that it requires different material design from RMGIC. The potential largest difference between the two cement is hydrophilicity of matrix; matrix of resin-based cement is hydrophobic and that of RMGIC is hydrophilic. The development of smart resin-based dental cement debonding-on-demand needs further research to overcome the difference.

Since the specimen bonded in this study was metal, it was easy to apply a current to the smart dental cement. The authors suppose that the effective clinical applications of smart dental cement are, *e.g.*, bonding between metal core and metal crown, and metal fixture and metal abutment of dental implant. In addition, since teeth is electrical conductive object, bonding between teeth and metal bracket also can be an application. In contrast, it is not easy to apply a current to cement between metal and resin or ceramics. To apply a current to cement between, *e.g.*, metal core and resin crown, specially designed crown containing electrical pathway inside is required. Most difficult target is cement between resin/ceramics and resin/ceramics. In case that the mechanism of σ_s reduction is the electrochemical reaction on anode, the smart dental cement might have no effect on this target. For such difficult targets, smart dental cement with other type of trigger should be developed.

CONCLUSIONS

The prototype RMGICs containing IL were produced and their properties were evaluated. They indicated the following properties.

1. They indicated electrical conductivity with containing IL, and the conductivity was increased with increasing IL content.
2. Their shear bonding strength to Cu plate did not change significantly before current application under 20% IL content.

3. Their shear bonding strength to Cu plate decreased significantly after current application over 15% IL content.

4. Their shear bonding strength after current application depended on the charge density.

These results suggest that RMGICs containing IL is a candidate of smart dental cement indicating practically sufficient shear bonding strength and easy debonding-on-demand with electric current, simultaneously.

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