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Bond strength of experimental cyanoacrylate-modified dental glass ionomer cements

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Abstract Glass ionomer cement (GIC) has been successfully used in dental field for more than 40 years. Despite numerous advantages of GIC, low bond strength and slow setting rate limited conventional GICs for use only at low stress-bearing areas. To improve bond strength to tooth, two kinds of cyanoacrylates such as ethyl 2-cyanoacrylate (EC) and allyl 2-cyanoacrylate (AC) were added in a commercial GIC. Changes in setting time of cyanoacrylate-modified GICs (CMGICs) according to the concentration of cyanoacrylates and/or *p*-toluene sulfonic acid (TSA) was investigated using a rheometer. Shear bond strength to human dentin was measured. Biocompatibility was determined by the viability of fibroblasts. Optimal concentrations for EC and TSA were 5–10% of the GIC powder and 30% of the GIC liquid, respectively. EC-based CMGIC showed twofold increase of initial bond strength compared with conventional GIC. Also, AC-based CMGIC showed three times higher bond strength and similar biocompatibility compared with the GIC. Therefore, CMGIC materials can be widely applied in dental adhesive restoration field because they showed improved bond strength and proper setting time.

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Introduction

In early 1970s, dental glass ionomer cement (GIC) was developed [1, 2]. Main components of this material were metal ionic powder and polyacrylic acid in water [3], and its setting reaction was based on the acid/base reaction between silicate glass and polyacrylic acid in water [4, 5]. GIC showed unique clinically useful properties such as biocompatibility, anticariogenic effect due to fluoride release and adhesion to moist tooth structure [6–8]. Therefore, this material has been usually used as an adhesive filling material in dentistry [9–11]. However, despite the advantages of GIC, brittleness, low tensile and initial bond strength limited conventional GIC for use only at certain low stress-bearing areas [12].

As to the setting mechanism of GIC, it is generally known that acidic degradation of glass powder results in release of cations such as Ca^{2+} and Al^{3+}, which cross-link with ionized carboxylic acid groups in polymer chains, causing the material to set by gelation. Therefore, problems of GIC are known as long setting time such as 48 h for the completion of chemical reactions and relatively low ionic bond strength between this material and tooth surface and also between the macro-chains in polymer [13].

In this study, to enhance the adhesive bond strength of GIC, two kinds of cyanoacrylates were chosen as additives because they showed exceptionally rapid adhesion to a wide range of surfaces under moist condition [14, 15]. Cyanoacrylates have been employed with varied success

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rates as a bond strength enhancer in dentin adhesives, pulp capping materials and cavity varnishes because of good biocompatibility and fast polymerization reaction in contact with moisture [16, 17]. They were also used for the bonding of fractured teeth and for the adhesion of pins to retain amalgam restorations [18–21]. As to the main merit of cyanoacrylates, it was reported that etching step of dentin to enhance micromechanical retention was not required because cyanoacrylates were rapidly polymerized upon exposure to hydroxyl ions from moisture in dentin [22–24]. It was reported that the adhesive bond between dentin and ethyl 2-cyanoacrylate (EC) was quite stable after 1-week water exposure [25], and also reported that dental resin composites were retained for 18-month period when EC was used as a bonding material [26]. Furthermore, cyanoacrylate-based dental cements that could substitute GIC, and EC-modified GIC were already confirmed to show improved monomer conversion and hardness than other dental cements [21, 27].

Allyl 2-cyanoacrylate (AC) was introduced as an advanced form of cyanoacrylate that showed improved mechanical properties including bond strength by the induced double bond in the molecule [28]. AC molecule polymerized by two mechanisms such as polymerization of cyanoacrylate by hydroxyl anions in water and light polymerization of allyl group by photo-initiator and UV light [28]. Therefore, we supposed that addition of AC in GIC would improve the bond strength and the bond stability to dentin surface than conventional cyanoacrylate because of the fast initial bond formation of cyanoacrylate by moisture in dentin and the cross-linking of the allyl group with other adjacent molecules. However, very fast setting time of this kind of cyanoacrylate due to high reactivity with hydroxyl anion should be solved before application to dental restoratives or adhesives. Recently, reaction kinetic controllers such as HCl or SO_2 gas, by inhibition of the polymerization reaction of cyanoacrylates in acidic condition, were reported [29]. However, these reaction kinetic controllers cannot be applied to certain reaction conditions such as mixing with ionic compound or solution state materials because of variable reactivity caused by various ionic circumstances.

The purposes of this study were to (1) determine the miscibility of cyanoacrylates with dental GIC; (2) evaluate the influence of *p*-toluene sulfonic acid (TSA) on the adjustment of reaction rate of EC in cyanoacrylate-modified GIC (CMGIC); and (3) determine the optimal concentrations of the additives that improved the bond strength to dentin.

In this study, optimal concentrations of EC and TSA, and AC in CMGICs, for the application to dental adhesive restorations, were determined through the evaluations of setting time, shear bond strength, micro-structural morphology, and biocompatibility.

Materials and methods

Chemical reagents

A commercial GIC (GC Fuji II, GC, Tokyo, Japan: Lot no. 0904081) was used as the starting composition. EC, TSA, cell culture reagents, camphoroquinone (CQ), 2-(dimethylamino)ethyl methacylate (DEMA), and other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA), and AC was purchased from Permabond (920; Pottstown, PA, USA). Chemicals were used without further purification.

Preparation of experimental CMGICs

For the preparation of EC-based CMGICs, TSA with the concentrations of 10, 20, and 30% (w/v) was dissolved in the liquid of the commercial GIC. 2.7 g of commercial GIC powder and 1.0 g of TSA-added GIC liquid was mixed for 20 s. After then, EC with the ratios of 5, 10, and 20 wt% of the GIC powder was added and mixed for 10 s. Unmodified commercial GIC was used as a reference. Compositions of experimental EC-based CMGICs are listed in Table 1. In case of AC-based CMGICs, 0.5 wt% of CQ and 0.5 wt% of DEMA were dissolved in the liquid of the commercial GIC. After then, AC was added and mixed for 10 s according to Table 2, and light curing was performed or not depending on the test item.

Setting time of CMGICs

To determine the setting time of CMGICs, ingredients were mixed according to the compositions in Tables 1 and 2, following the methods in "Preparation of experimental

Table 1 Ethyl 2-cyanoacrylate (EC) modified glass ionomer cements composition

Specimen	EC (in powder, %)	TSA (in liquid, %)
EC-5-0	5	0
EC-10-0	10	0
EC-20-0	20	0
EC-5-10	5	10
EC-10-10	10	10
EC-20-10	20	10
EC-5-20	5	20
EC-10-20	10	20
EC-20-20	20	20
EC-5-30	5	30
EC-10-30	10	30
EC-20-30	20	30

TSA *p*-toluene sulfonic acid

Table 2 Allyl 2-cyanoacrylate (AC) modified glass ionomer cements composition

Specimen	AC (in liquid, %)	CQ (in liquid, %)	DEMA (in liquid, %)
AC-10	10	0.5	0.5
AC-30	30	0.5	0.5
AC-50	50	0.5	0.5
AC-100	100	0.5	0.5

CQ camphoroquinone, *DEMA* 2-(dimethylamino)ethyl methacylate

CMGICs" section. In case of AC-based CMGIC, light curing was not performed. Viscosity change was measured at 23 °C in a small oscillation mode (1 Hz) on a rheometer (CVO 100, Bohlin Instruments, Worcestershire, UK) equipped with a cone/plate tools 1°/40 mm disk. The point at which a sudden change of viscose modulus (G″) occurred was set as the setting time.

Shear bond strength

Shear bond strength to dentin was determined according to the concentrations of EC and TSA (EC-5-30 and EC-10-30 in Table 1), or AC (AC-10, AC-30, AC-50, and AC-100 in Table 2). To prepare dentin surface, acryl resin embedded, freshly extracted human molar teeth were polished with 600 grit sand papers using a polishing machine (RotoPol-25; Struers, Ballerup, Denmark). Then each composition was mixed and filled in a Teflon mold (4 mm in diameter and 7 mm in height) that was laid on polished dentin surface. In case of AC-based CMGICs, filled cement was light cured for 40 s with a light-curing unit (Spectrum 800, Dentsply/Caulk, Milford, DE, USA) with an intensity setting of 400 mW/cm^2. After 10 min, the mold was removed from the cement. Specimens were divided into two groups ($n = 10$) such as 1 h group (immersed in 37 °C distilled water for 1 h) and 24 h group (immersed in the same condition for 24 h). Shear bond test was performed using a universal testing machine [30, 31]. The crosshead speed was set to 1 mm/min, and the load at the point when the specimen was deboned from dentin was determined.

Morphology and element analyses

Debonded cements from dentin after bond strength test were collected for the analyses of microstructure and element. Bonding surfaces of the GIC and CMGIC specimens (EC-5-30, EC-10-30, and AC-100) were observed with a field emission scanning electron microscope (FE-SEM: S-4700; Hitachi, Tokyo, Japan). For the element analysis of the glass core and matrix of set cement, energy dispersive spectroscopy (EDS: EX-250; Horiba, Tokyo, Japan) was performed with the FE-SEM.

Biocompatibility

For the biocompatibility test by direct contact [32], specimens of the unmodified GIC and CMGICs (EC-5-30, EC-10-30, and AC-100) were prepared with a Teflon mold (15 mm in diameter and 2 mm in height, $n = 5$). In case of AC-100, specimen was light cured for 40 s in three overlapping areas with the light-curing unit (Spectrum 800). Mold was removed after 10 min. After sterilization with by ethylene oxide (EO) gas, specimens were fixed in 24 well plates. A medical grade silicone adhesive (Silastic; Dow Corning, Midland MI, USA) was used to fix the specimen at the center of the well. Fixed specimens were rinsed three times with phosphate-buffered saline (PBS). Washed specimens were pre-wetted with cell culture medium [Dulbecco's modification of Eagle's medium (DMEM) with 10% fetal calf serum, penicillin (100 units/mL) and streptomycin (100 μg/mL) with L-glutamine (2 mM)], and kept at 37 °C and 5% CO_2 incubator for 12 h. Then, the medium was aspirated and suspension of fibroblast cells (ATCC-L929, Manassas, VA, USA) was added directly to each specimen in culture plate (2×10^5 cells in 500 μL/well). Culture well without specimen was used as a control. Relative cell viability at 4, 24, 48, and 72 h was determined and compared with that of control by using a WST-8 assay [33].

Results and discussion

In this study, setting time of the experimental CMGICs was determined first. Based on the results, compositions that showed proper setting time were further tested for the bond strength and biocompatibility.

Setting time of CMGICs

In this study, setting time was defined as the time when prepared CMGICs remained in sol state. In contrast to the polymerization of the EC-based CMGIC by moisture, the AC-based CMGIC was polymerized by two steps such as the polymerization of cyanoacrylate by moisture and light polymerization of the allyl group by visible light irradiation. Setting time of the EC-based CMGICs and the AC-based CMGICs was measured by the rheological method. Setting time of the EC-based CMGICs increased as the TSA concentration increased or the EC concentration decreased (EC-5-0: 85 ± 3, EC-5-10: 103 ± 3, EC-5-20: 121 ± 5, EC-5-30: 143 ± 3, EC-10-0: 67 ± 2, EC-10-10: 83 ± 3, EC-10-20: 96 ± 6, EC-10-30: 131 ± 5, EC-20-0: 57 ± 5, EC-20-10: 72 ± 3, EC-20-20: 80 ± 5, EC-20-30: 118 ± 5 s, Fig. 1). Based on one-way analysis of variance (ANOVA), setting time was influenced by the composition ($P < 0.05$), and the post hoc results are included in Fig. 1. Since the setting

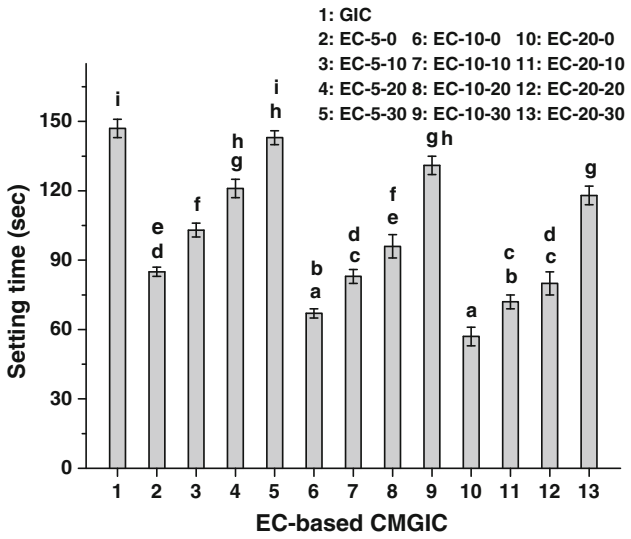

Fig. 1 Setting time of glass ionomer cement and ethyl 2-cyanoacrylate-based cyanoacrylate-modified glass ionomer cements according to *p*-toluene sulfonic acid and ethyl 2-cyanoacrylate concentrations. The same *letter* indicates the homogenous subsets based on Scheffe's multiple comparison test ($P < 0.05$)

time of the unmodified GIC was determined as 147 ± 5 s, proper setting time based on this experimental method was assumed to be around 150 s. Therefore, compositions of 5 or 10 wt% of EC with 30% (w/v) TSA were regarded as proper candidates. These compositions were further tested for bond strength.

Setting time of all of the AC-based CMGICs, under no light cured condition, was similar to that of the GIC (Fig. 2). Based on one-way ANOVA, setting time was influenced by the composition ($P < 0.05$), and the following homogenous subsets were observed based on Scheff's multiple comparison test: AC-100: 132 ± 4 = AC-50: 138 ± 3/AC-50 = AC-30: 144 ± 2/AC-10: 152 ± 4 s ('/' indicates homogenous group marker, $P < 0.05$). Setting times of the high AC concentrations (AC-50 and AC-100) were similar to that of the GIC, which suggested that some kinds of reaction regulators were already included in the commercial AC used in this study. Therefore, TSA regulator was not added in the AC-based CMGICS. Commercial AC-based adhesive was used in this study; however, further studies with pure or refined AC should be performed.

Shear bond strength of the EC-based CMGICs

Shear bond strength of the GIC as a reference and the EC-based CMGICs (EC-5-30 and EC-10-30) were measured after 1 and 24 h. After 1 h, an EC-based CMGIC showed over twofold increase of the bond strength compared with the GIC (GIC: 1.5 ± 0.2 MPa, EC-10-30: 3.1 ± 0.4 MPa, Fig. 3). Based on Scheffe's multiple comparison test, the following homogenous subsets were observed ($P < 0.05$): GIC = EC-5-30/EC-10-30. Shear bond strength values of the GIC and the EC-based CMGICs after 24 h were also different, and the following homogenous subsets were observed based on Scheffe's multiple comparison test ($P < 0.05$): GIC = EC-5-30/EC-5-30 = EC-10-30. An EC-based CMGIC showed only around 1.4-fold increased bond strength compared with the GIC (GIC: 2.9 ± 0.5 MPa, EC-10-30: 4.2 ± 0.3 MPa). Based on paired *t*-test, the shear bond strength after 1 and 24 h showed significant difference (mean shear bond strength after 1 h: 2.2 MPa < that after 24 h: 3.5 MPa, $P < 0.05$). Shear bond strength value of the GIC after 24 h of this study was similar to a previously reported value of 2.2 ± 0.8 MPa [34, 35]. We supposed that

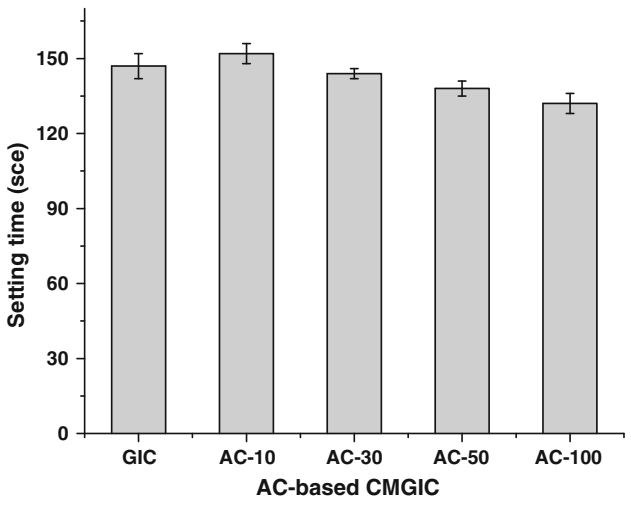

Fig. 2 Setting time of allyl 2-cyanoacrylate-based cyanoacrylate-modified glass ionomer cements according to allyl 2-cyanoacrylate concentrations

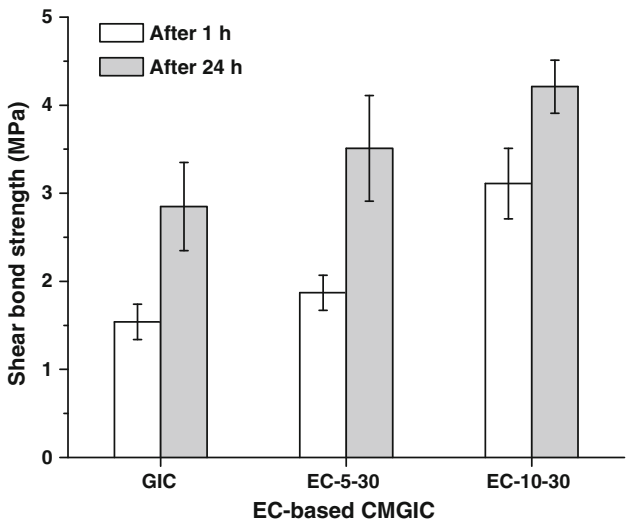

Fig. 3 Shear bond strength to dentin according to ethyl 2-cyanoacrylate concentrations

high initial bond strength of the EC-based CMGIC was due to the initial polymerization reaction of cyanoacrylate by the moisture in dentin, which was faster than the ionic reaction of the GIC.

In case of the GIC, setting reaction occurred in two steps. The first step was the cross-linking reaction by ion interactions between Ca^{2+} ion from glass core and carboxyl anion of polymer, which continued for around 3 h. Then, the second step was mutation step by substitution from Ca^{2+} to Al^{3+}. As result of the mutation step, polymer chain mobility in the cement decreased and hardness of the cement increased, which continued for around 48 h [36]. Therefore, it takes 48 h for the completion of the chemical reactions in the GIC. As another reason for the increased initial bond strength of the CMGICs, we supposed that setting shrinkage of the CMGICs decreased by the fast polymerization reaction of the CMGIC with dentin. In general, fine cracks were observed between dentin and the GIC caused by the setting shrinkage of GIC [37]. However, this phenomenon was not observed in the CMGICs of this study.

Shear bond strength of the AC-based CMGICs

Figure 4 shows the shear bond strength of the AC-based CMGICs to dentin. Based on one-way ANOVA, shear bond strength after 1 h was significantly influenced by the composition, and the following homogenous subsets were observed based on Scheffe's multiple comparison test ($P < 0.05$): GIC = AC-10/AC-10 = AC-30/AC-50/AC-100. High AC concentration compositions showed high 1 h bond strength. Also, the shear bond strength after 24 h was significantly influenced by the composition, and the and the following homogenous subsets were observed based on Scheffe's multiple comparison test ($P < 0.05$): GIC = AC-10 = AC-30/AC-50/AC-100. Based on paired *t*-test, the shear bond strength values after 1 and 24 h showed significant difference (mean shear bond strength after 1 h: 5.0 MPa < that after 24 h: 6.7 MPa, $P < 0.05$). However, when the concentration of AC was low (AC-10 and AC-30), they showed relatively low bond strength [AC-10 (1 h/24 h): 2.4 ± 0.4/3.6 ± 0.3; AC-30 (1 h/24 h): 3.3 ± 0.6/5.2 ± 0.8 MPa], because the radical initiation reaction was inhibited in acidic conditions when the AC concentration was low [38].

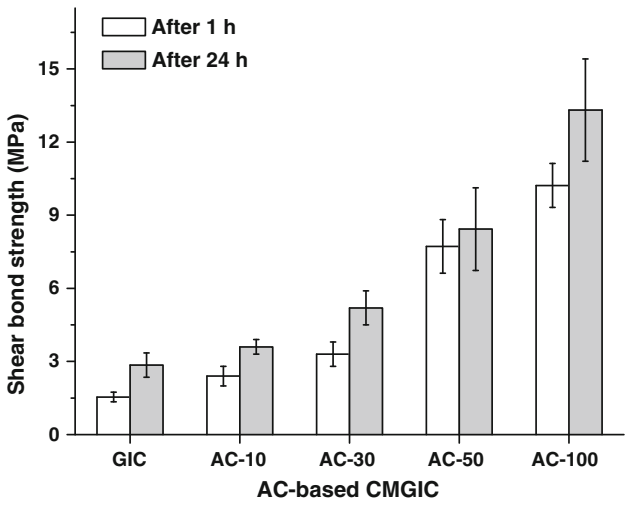

Fig. 4 Shear bond strength to dentin according to allyl 2-cyanoacrylate concentrations

Ionic bond, except for some salts, generally reveals weak binding energy than covalent bond. Also, long time is required for the termination of reaction compared with the interaction by covalent bond because of the sensitivity to the reaction conditions such as pH and temperature [35, 39]. Therefore, we supposed that the combined effect of fast initial bonding reaction to dentin by cyanoacrylate and the cross-linking of intra-molecular allyl groups by covalent bond resulted in the high initial bond strength of the AC-based CMGICs than the GIC that is set by ionic interaction.

SEM images of GIC and CMGICs with composition spectra by EDS

Morphology and composition of the set GIC and CMGICs were determined by the FE-SEM and EDS. In case of the EC-based CMGIC, study on the monomer conversion during polymerization was already performed using an infrared spectra test, and complete polymerization of EC and monomer was confirmed [21]. Therefore, it was supposed that the behavior of AC in the GIC would be similar to that of the reported EC-based CMGIC because chemical properties including polymerization mechanism of AC are similar to EC. As indicated in Fig. 5, powder particles and ionic cross-linked phase between dissolved metal cations from the glass core and polyanions in the acidic liquid were obtained. In case of the GIC and the EC-based CMGICs (Fig. 5a–c), elements for ionic interaction were observed based on spectra. Major composition of the glass core (spectrum 1) was Si, Al, O, Ca and that of its outskirt (spectrum 2) was Si, Al, O, C, Ca. Since the intensities of Si, Al, O, C, and Ca were lower in the outskirt area compared with those in the glass core, it was supposed that the matrix area was cross-linked area by the interaction between released metal cations such as Ca^{2+}, Al^{3+} and carboxyl group in polyanion [35, 39]. The AC-based CMGIC (AC-100; Fig. 5d) showed lowest intensities of Si, Al, C, O, and Ca in the outskirt area. As to the causes for these low intensities, it was supposed that ionization of glass core was inhibited by the cross-linked AC after light polymerization, and waterless condition inhibited

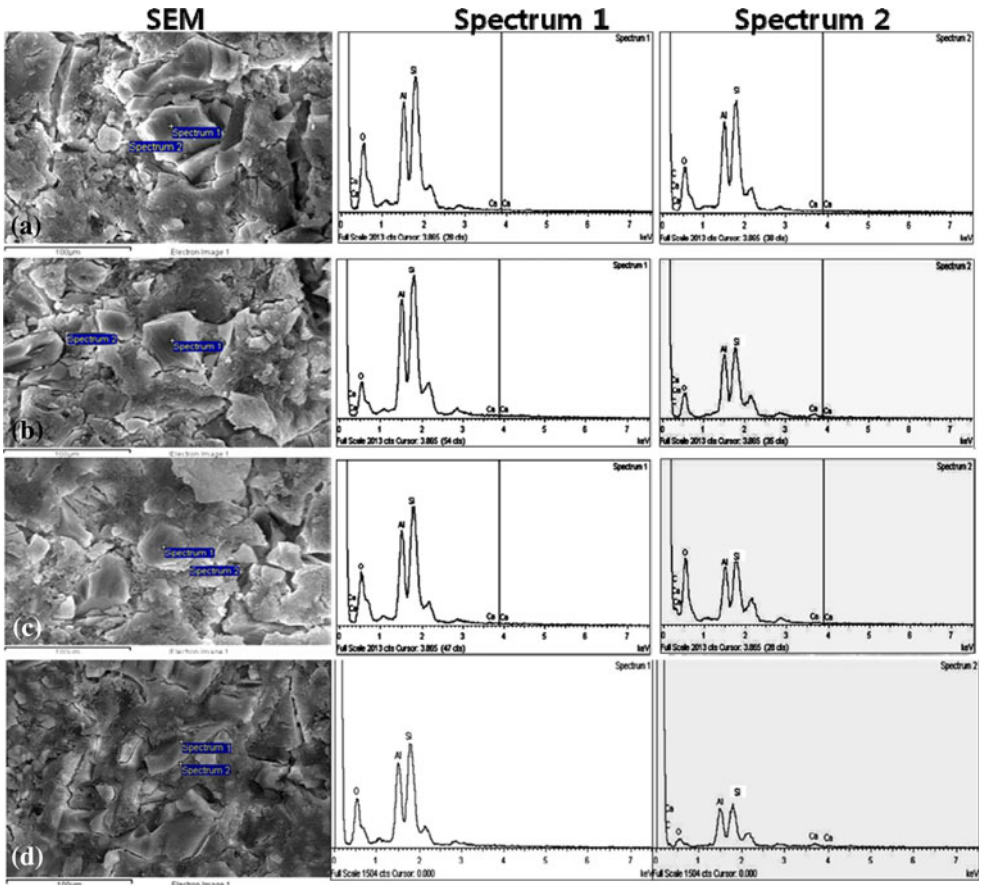

Fig. 5 SEM images of a glass ionomer cement and cyanoacrylate-modified glass ionomer cements with composition spectrum by energy dispersive spectroscopy [**a** GIC, **b** EC-5-30, **c** EC-10-30, **d** AC-100]

ionization. Nevertheless, existence of some elements from glass core was confirmed by weak peaks. It was supposed that the existence of glass core elements in the outskirt area represented good affinity of AC with glass powder; therefore, AC contributed for the improvement of bond strength of this material to dentin.

Ionic bond between carboxyl anion of the GIC liquid and Ca^{2+} ion on dentin was important to maintain the stable bond strength in water [40]; therefore, this reaction mechanism was regarded as an essential adhesion mechanism of the unmodified GIC with dentin. Based on the result of this study, cyanoacrylate did not affect reaction for the ion interaction in the GIC, and contributed to improve the bond strength by its polymerization.

Biocompatibility

Since the remaining non-reacted cyanoacrylate monomers or excess TSA after polymerization could be highly chemically reactive species [41, 42], it was concerned that these might cause unexpected problems. To confirm the presence of non-specific side effects in the body, biocompatibility test was performed. The difference in the cell viability between the unmodified GIC as the reference and the CMGICs was determined. GIC showed low cell viability (Table 3). The GIC result of this study was similar to those of previous studies [43–45]. Leaching of cytotoxic materials such as fluoride from the GICs was confirmed previously [46, 47]. There was no significant difference in the cell viability between the unmodified GIC and the CMGICs (Table 3, $P > 0.05$). EC concentration had little effect on the initial cell adhesion to the CMGICs (4 h results); however, after 48 h cell culture, increased cell proliferation on the high concentration EC specimens was observed (Table 3). Therefore, good biocompatibility of the EC-based CMGICs and an AC-based CMGIC were confirmed after comparison with that of the unmodified GIC. Although resin modified GICs based on light polymerization reaction of 2-hydroxyethyl methacrylate or

Table 3 Cell viability (%) of cyanoacrylate-modified glass ionomer cements

Specimen	Culture time			
	4 h	24 h	48 h	72 h
GIC	40 ± 5	26 ± 4	14 ± 6	10 ± 3
EC-5-30	34 ± 4	24 ± 2	14 ± 2	11 ± 1
EC-10-30	32 ± 2	24 ± 3	16 ± 1	10 ± 2
AC-100	34 ± 3	23 ± 1	14 ± 2	11 ± 1

modified polyacrylic acid have been widely used in dental clinic, one of the problems of these materials was reported as cytotoxicity by the released non-reacted resin monomer due to no complete polymerization [48, 49]. But in case of the CMGICs, this kind of problem would be reduced by the fast reaction with moisture and/or light curing.

Conclusions

Improved GICs that showed high bond strength to dentin was formulated by adding two cyanoacrylates such as EC and AC in the GIC under acidic condition. To determine the optimal composition for the CMGIC, the setting time by reaction controller, shear bond strength including initial bond strength, morphology, element analysis, and biocompatibility of the CMGICs were determined. AC-based CMGICs showed high shear bond strength to dentin than the unmodified GIC and EC-based CMGICs. Element analysis for ionic interaction and biocompatibility test was similar to that of the GIC. Future studies are needed to understand the polymerization mechanism with cyanoacrylates and to further increase the bond strength to dentin and enamel.

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