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Polymerization of resin cements by self-curing with or without adhesive treatment

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The primary aim of this study was to determine whether there is a difference in degree of conversion (DC) between resin cements polymerized with an adhesive and those without an adhesive. The secondary aim was to compare interfacial gap of zirconia restoration when resin cements are self-cured. The DC of resin cement was measured without adhesive treatment continuously for 15 min and at 24 h. The DC was measured again after light-curing or self-curing adhesive treatment. For interfacial gap evaluation, inlay cavities were prepared on extracted third molars. Zirconia restorations were fabricated and cemented with the resin cement. After thermo-cycling, interfacial gap at the restoration-tooth interface was investigated using swept-source optical coherence tomography (SS-OCT) imaging. The DC of resin cement with adhesive treatment differed depending on the adhesive, cement, and polymerization method ($p<0.05$). Interfacial gap was different depending on the adhesive and cement ($p<0.05$).

Keywords: Resin cement, Degree of conversion, Adhesive, Interfacial gap

INTRODUCTION

Resin cements are gaining popularity as luting materials for zirconia restorations. There are some clinical situations in which light-curing of resin cement is not feasible, such as metal crowns, thick zirconia restorations, or root canal posts. In these cases, polymerization of resin cement is achieved primarily by a self-curing process. It is known that the mechanical properties of self-cured resin cements are generally inferior to those of light-cured ones[1].

Resin cement is a type of resin composite, which means application and polymerization of an adhesive are required before cement placement. Traditionally, two bottles of adhesive, a base and a catalyst, are provided for self-curing of adhesive. Self-adhesive resin cement (SAC) does not require adhesive treatment because it includes acidic functional monomers in its paste. Some SAC manufacturers recommended their primer be applied to prepared teeth (G-Cem One primer, GC, Tokyo, Japan; Clear Bond Quick Universal, Kuraray Noritake, Tokyo, Japan). For conventional resin cement, some manufacturers claim that their single-bottle adhesives can polymerize both the adhesive and the cement through a "touch-cure" self-curing process (Tooth primer, Panavia V5 cement, Kuraray Noritake; Single Bond Universal adhesive, RelyX Ultimate cement, 3M ESPE, St. Paul, MN, USA). In single-bottle systems, the accelerators are included in the adhesive for self-curing of the cement paste, and activators are present in the cement paste for self-curing of the adhesive.

An inherent problem of self-curing resin systems is the acid-base reaction between the acidic monomers in the adhesive and the basic amine in the cement paste[2]. The pH of tooth adhesives is known to be around 1.0–2.5 to demineralize the tooth surface for bonding[3]. The optimal pH of tertiary amine activity to accelerate self-curing is approximately 4.5[4]. Inhibition of polymerization can occur not only at the tooth-adhesive interface but also in the oxygen-inhibited layer of the resin-restoration interface[5,6]. Chemically cured adhesives have thick oxygen inhibition layers, which are more sensitive to the acid-base concentration[5,7]. This problem has prompted the development of alternative redox systems that are less sensitive to acidity.

Applying an adhesive to a tooth can decrease or increase the polymerization of the resin cement. The basic amine component of resin cement can be neutralized by the acidity of the adhesive, which interferes with polymerization. After applying an adhesive, polymerization of the resin cement can be enhanced by an accelerator in the adhesive. The degree of conversion (DC) of resin cement impacts the bond strength and long-term stability[8]. In terms of the polymerization method of the adhesive, it can be light-cured or self-cured. Self-curing adhesives are available in

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either one-bottle or two-bottle formulations. Therefore, it is wondered if these adhesive treatments can lead to decreased or increased polymerization of resin cement.

Other factors can affect the ability of resin cement to bond to teeth. Acidity can be neutralized to some degree by the buffering capacity of tooth materials. The wet/dry condition can be an important factor in the polymerization of both adhesives and resin cements[9,10]. The polymerization speed of resin cement can affect the longevity of the restoration. If the polymerization rate is too low, premature occlusal biting can weaken the restoration-tooth interface. It is also wondered if one-bottle and two-bottle adhesives may exhibit different polymerization speeds and bonding abilities.

A lower bond strength can create a micro-gap at the cement space between the tooth and restoration. As a non-invasive imaging method to detect micro-gaps, micro-computed tomography (micro-CT) and optical coherence tomography (OCT) can be used[11-13]. Both tomography systems can provide 3D reconstructive images within a few micrometer resolutions[11,14]. Micro-CT is a useful method to evaluate the interfacial gap at a restoration-tooth interface[15]. Due to the penetrating ability of X-rays, micro-CT enables the evaluation of a restoration or tooth irrespective of its shape or depth. As for the drawbacks, tracers such as silver nitrate should be infiltrated to identify a micro-gap[12]. OCT system can provide real time visualization without tracers or X-ray exposure. Swept-source optical coherence tomography (SS-OCT) offers superior image resolution and scanning speeds by using a wavelength-tuned laser[14,16]. However, OCT has light-penetrating limitation when capturing an image. The imaging depth of SS-OCT systems is known to be in the range of about 2 mm[14].

The primary objective of this study was to determine if polymerization of resin cements differed by use of adhesive. The secondary objective was to compare interfacial gaps on prepared teeth when resin cement was self-cured with adhesive treatments.

The null hypotheses are as follows:

1. There is no difference in the DC when resin cements are polymerized with or without an adhesive treatment.
2. When zirconia restoration is cemented with different adhesives and self-curing resin cements, there is no difference in interfacial gap at the restoration-tooth interface.

MATERIALS AND METHODS

Experimental steps of this study

The first step is to measure the pH of each adhesive for tooth treatment. The second step is to measure the DC of resin cement with or without an adhesive. The final step is to compare the interfacial gaps of zirconia restoration by self-curing resin cement with different adhesive treatments on prepared teeth.

Measurement of adhesive pH

Measurement of pH followed a procedure described by Sanares *et al.*[17]. Adhesives do not usually dissociate into ions, which are required to measure the pH value. For the ionized form, a glass vial holding 3 mL of 70% ethanol and 30% water was prepared. Next, 2 mL of adhesive was added to the glass vial, which was then mixed and stirred continuously for 1 min. The pH value of the adhesive solution was measured at room temperature (23±1°C) by a digital pH meter (SevenCompact pH meter S210, Mettler Toledo, Greifensee, Switzerland). The pH value was measured three times for each adhesive, and the mean was calculated.

Measurement of the DC for self-curing resin cement without adhesive treatment

The setup for the measurement of DC is illustrated schematically in Fig. 1. A clear polyethylene film 0.2 mm thick that served as a spacer was prepared with a hole and placed on a cover glass. Resin cement was mixed according to the manufacturer's instructions and placed into the hole. Then resin cement was covered by another cover glass to remove excess cement (Fig. 1).

The specimen was mounted on a customized metal holder and placed in a Fourier transform infrared spectrometer (Nicolet S10 FTIR spectrometer, Thermo, Madison, WI, USA). Infrared spectra data were obtained using OMNIC and TQ analyst EZ software (Thermo). As soon as the specimen was mounted, the area of the peak uncured (peak area [u]) was measured. Collection of spectra was set between 6,140 and 6,200 cm^{-1} using FTIR in transmission mode. The peak area was at 6,165 cm^{-1}, corresponding to vinyl stretching[18]. Continuous measurement of infrared spectra, which was the area of the peak cured (peak area [c]), was initiated 3 min after mixing of the cement began. No light-curing was applied and a dark cover allowed the cement to self-cure. The collection setup was two scans per spectrum at a resolution of 4 cm^{-1}. Collection of spectra absorbance continued for 15 min. The DC was calculated by the following:

$$DC\ (\%)=[1-(\text{peak area [p]}/\text{peak area [u]})]\times 100\%$$

where [p] and [u] stand for polymerized and unpolymerized, respectively.

Peak area [u] was calculated by averaging 12 absorbance measurements during the first 30 s, immediately after the mixed cement specimen was mounted. Peak area [p] was measured continuously and the DC was calculated by averaging 12 absorbance measurements at 3, 5, and 15 min after initiation of measurement. Because the DC measurement (peak area [p]) began 3 min after mixing the cement, the DCs at 3, 5, and 15 min actually indicate the DCs at 6, 8, and 18 min after the initiation of cement mixing. The specimen was stored in dark and dry conditions at 23±1°C. After 24 h, the DC at 24 h was measured and calculated in the same way. Six specimens were made and measured for each group (n=6).

Measurement of DC for self-curing resin cement after light-curing adhesive treatment

A clear polyethylene film with the same hole was

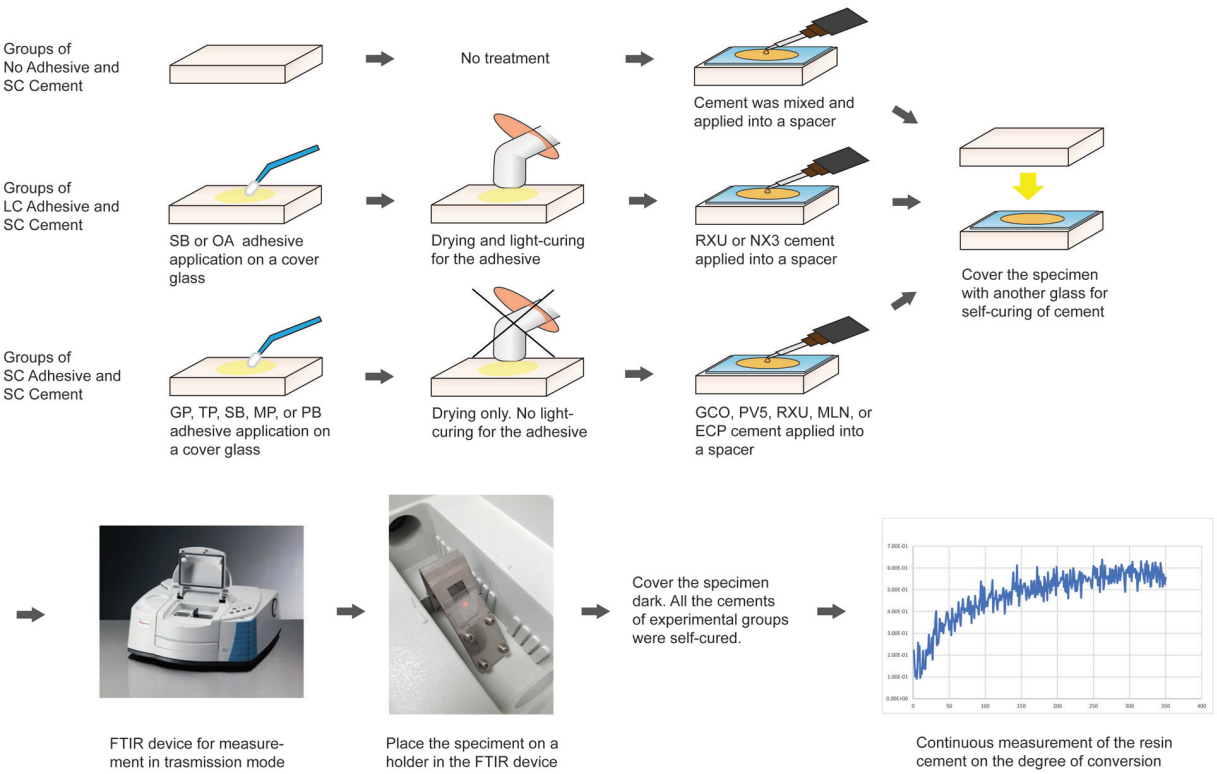

Fig. 1 Experimental procedure for continuous measurement of the DC of resin cement. SC and LC indicate self-curing and light-curing.

prepared and positioned on a cover glass. Before placing the resin cement, an adhesive was applied on the cover glass. Single Bond Universal (3M ESPE) and Optibond All-In-One (Kerr, Brea, CA, USA) were used for group 1 and group 2 (Table 1). The adhesive was dried and light-cured for 10 s by a light-curing unit (Elipar DeepCure-S, 3M ESPE). Resin cement was then mixed and placed using the same method described above. Six specimens were made and the DC was calculated.

Measurement of DC for self-curing resin cement after self-curing adhesive treatment

As shown in Table 1, there are two types of adhesive mixing systems: one-bottle and two-bottle. For the one-bottle adhesive system (GP, TP, and SB in Table 1), the adhesive was applied to a cover glass. For the two-bottle adhesive system (MP and PB), drops of adhesives A and B were mixed and then applied to a cover glass. The adhesive was dried and no light-curing was performed. Resin cement was then mixed and placed following the same method. Six specimens were made and the DC was calculated.

Measurement of DC for light-curing resin cement with or without adhesive treatment

For the light-curing cement group with adhesive treatment, each adhesive was applied on a cover glass. The adhesive was dried, light-cured, or self-cured as described above (Table 1). The peak area [u] was measured after the resin cement was mixed and mounted in the spectrometer. The resin cement was then light-cured for 20 s and infrared spectra (peak area [c]) was measured continuously for 15 min. After 24 h, the spectra were collected again. For the light-curing cement group without adhesive, the DC measurement was performed in the same way without application of the adhesive. Six specimens were made and measured for each group.

Measurement of interfacial gap on zirconia restoration

1. Tooth preparation

The setup employed in this study is illustrated schematically in Fig. 2. The use of teeth was approved by an institutional review board under the number of VC21TISI0022. Fifty-four extracted human third molars were kept in a 0.5% chloramine solution at 4 °C. The occlusal surface of the tooth was flattened with a trimmer and SiC papers. Cylindrical class I cavities were prepared. The preparation dimensions were 3.2±0.2 mm in diameter and 1±0.1 mm in depth.

2. Zirconia inlay fabrication and treatment on the restoration surface

Inlays were fabricated with a 100 μm cement space after optical scanning of the preparation (Medit Identica hybrid scanner, Medit, Seoul, Korea). Zirconia disks (Katana-HT, Kuraray Noritake Dental) were used to mill the inlay. Zirconia inlays were made using a Roland

Table 1 Cement, adhesive material, application method, and the pH of each adhesive

Group	Resin cement (code)	Cement type	Manufacturer	Adhesive (code)	Number of bottles	Adhesive application method	Curing for adhesive	pH of adhesive
Experimental group with light-curing of adhesive								
1	RelyX Ultimate (RXU)	DC	3M ESPE, St. Paul, MN, USA	Single Bond Universal (SB)	One	Apply for 10 s and dry	LC	3.06
2	NX3 Nexus (NX3)	DC	Kerr, Brea, CA, USA	Optibond All-in-one (OA)	One	Apply for 10 s and dry	LC	2.61
Experimental group with self-curing of adhesive								
3	G-CEM One (GCO)	DC	GC, Tokyo, Japan	No adhesive	NA	NA	NA	NA
4	G-CEM One (GCO)	DC	GC	G-CEM One Primer (GP)	One	Apply for 10 s and dry	SC	2.31
5	Panavia V5 (PV5)	DC	Kuraray Noritake, Tokyo, Japan	Tooth Primer (TP)	One	Apply for 10 s and dry	SC	2.74
6	RelyX Ultimate (RXU)	DC	3M ESPE	Single Bond Universal (SB)	One	Apply for 10 s and dry	SC	3.06
7	Multilink N cement (MLN)	SC	Ivoclar vivadent, Schaan, Liechtenstein	Multilink N Primer A and B (MP)	Two	Mix A and B, apply for 10 s, and dry	SC	A: 7.95 B: 2.15
8	Estecem plus cement (ECP)	DC	Tokuyama, Tokyo, Japan	Palfique Universal Bond A and B (PB)	Two	Mix A and B, apply for 10 s, and dry	SC	A: 2.62 B: 8.21

DC, LC, and SC indicate dual-curing, light-curing, and self-curing.
Number of bottles is the number of adhesive bottles in each adhesive system.
NA: Not applicable.

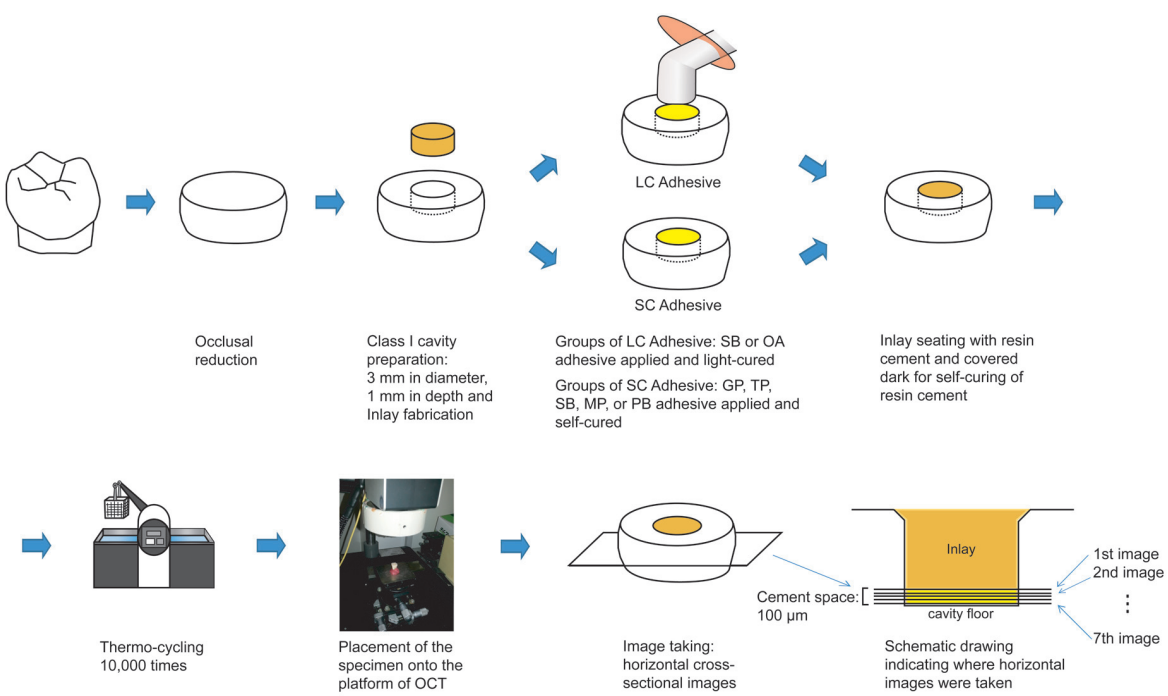

Fig. 2 Experimental procedure for interfacial gap (HB%) measurement of self-curing resin cement using SS-OCT.

milling machine (DWX-51D, Roland DG). The milled inlays were sintered in a furnace. After sintering, the inlays were finished for fitting into the cavity. The internal surface of the inlay was air-abraded by 50 μm aluminum oxide particles (Hi Aluminas, Basic material, Renfert, Germany). The inlays were cleaned ultrasonically in water and dried.

3. Restorative procedure of zirconia inlay cementation

This experiment evaluated the effect of different adhesive treatments and self-curing cements on interfacial gap. The cements of the experimental groups were self-cured under eight different conditions (six teeth for each group).

For groups 1 and 2, the adhesive was light-cured and the cement was self-cured (Table 1). For group 1, Single Bond Universal (SB, 3M ESPE) was applied to the cavity and light-cured for 10 s. After RelyX Ultimate cement (RXU, 3M ESPE) was mixed and loaded, the restoration was seated. No light-curing was applied for self-curing of the cement. For group 2, Optibond All-In-One (OA, Kerr) was applied and light-cured. After NX3 Nexus cement (NX3, Kerr) was mixed and loaded, the restoration was seated. The specimen was stored in a dark room at 100% humidity and a temperature of 23±1°C.

For group 3, the restoration was cemented by a SAC without any adhesive treatment. After the prepared cavity was cleaned[19], G-CEM One cement (GCO, GC) was mixed and loaded. From group 4 to group 8, after adhesives were applied, all adhesives and cements were self-cured. For group 4, G-CEM One primer (GP) was applied to the tooth. G-CEM One cement was mixed and loaded. For group 5, Tooth Primer (TP) in a Panavia V5 (Kuraray Noritake) was applied. Panavia V5 cement (PV5) was mixed and loaded. For group 6, Single Bond Universal (SB) was applied. RelyX Ultimate cement (RXU) was mixed and loaded. For group 7, Multilink N Primer A and B (MP, Ivoclar vivadent, Schaan, Liechtenstein) were mixed and applied. Multilink N cement (MLN) was mixed and loaded. For group 8, Palfique Universal Bond A and B (PB, Tokuyama, Tokyo, Japan) were mixed and applied. Estecem Plus cement (ECP, Tokuyama) was mixed and loaded. The restoration seating procedure was the same. The specimen was stored in the same conditions as in groups 1 and 2.

The LC-control group was cemented by light-curing of both the adhesive and conventional resin cement. SB adhesive was applied to the prepared tooth. Mild air was blown and the adhesive was light-cured for 10 s. After RXU cement was mixed and loaded into the cavity, the inlay was positioned and light-cured for 20 s. The specimen was stored in the same conditions as those of the experimental groups (six teeth for the group).

4. Thermo-cycling procedure

Each tooth specimen was kept in water at room temperature (23±1°C) after 24 h of the finishing cementation process. Each specimen was then thermo-cycled 10,000 times (Thermal cycling tester RB 508, R&B, Daejeon, Korea), which were estimated to simulate clinical functions of around one year[20]. The teeth were immersed in water bathes of 5°C and 55°C. The dwell time was 30 s and the transfer time was 5 s. After thermo-cycling, the teeth were stored in water at 23±1°C.

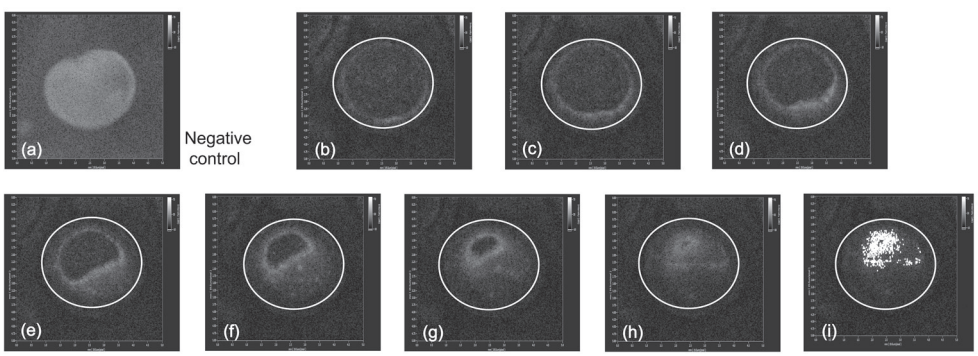

Fig. 3 SS-OCT images for interfacial gap measurement.
(a) An image of the cement space of the negative control (without cement): horizontal cross-sectional image. (b) The first horizontal cross-sectional image of a specimen in one experimental group. Luting material had a similar intensity value to that of dentin. The white circle represents the border of a prepared cavity. The first image of (b) was taken parallel to the cavity floor at the level of 5 μm down from the inlay base. (c) The second image was taken parallel at the level of 15 μm down from the first image. (d–h) The 3rd, 4th, 5th, 6th and 7th image, respectively, was taken parallel at the level of 15 μm down from the previous image. (i) The same image as in (h) processed by GapAnalyzer. The white dots on the image (i) are brighter pixels which have a higher signal intensity than the threshold to indicate micro-gaps. To calculate the interfacial gap (HB%) on image (i), the areas of white dots were measured and then divided by the circle area. On the image of (i), the HB% was calculated to be 15.1%.

5. Acquisition and analysis of images by SS-OCT

OCT images were acquired by SS-OCT (IVS-2000, Santec, Komaki, Japan). The specimen was positioned on the OCT device platform. In the horizontal cross-section, the first SS-OCT image was captured parallel to the cavity floor at 5 μm below the inlay base. The second image was taken 15 μm below the first image. Seven images for each specimen were taken at 15 μm intervals in a 100 μm cement space (Fig. 2).

Interfacial gap at the interface was evaluated by image analysis software (ImageJ ver. 1.52, National Institutes of Health, Bethesda, MD, USA). If there is a micro-gap at the restoration-tooth interface, air or water may exist. When light of OCT transverses the air or water at the interface, a portion of light is reflected at a different angle. The refractive index of air is 1.0, that of water 1.3, and that of a tooth or resin composite 1.5–1.6[21]. The axial resolution was 7 μm in hard tissues and resin composites. A micro-gap at the interface is visualized as a bright spot or cluster on an SS-OCT image (Fig. 3). The high brightness (HB%) parameter was created to indicate a micro-gap. HB% was defined as

Table 2 The mean of DC (%) at each measurement time when each cement is polymerized with or without adhesive application

DC of each cement with or without light-curing adhesive							
Cement (code)	Cement polymerization method	Adhesive	Adhesive polymerization	3 min	5 min	15 min	24 h
RelyX Ultimate (RXU)	SC	No		32.0 (2.4)^{e,f}	34.9 (3.0)^{c,d}	42.2 (2.3)^{a}	68.3 (2.7)^{a,b}
	SC	SB	LC	28.6 (3.3)^{c,d,e}	32.7 (3.1)^{b,c}	41.4 (2.6)^{a}	68.1 (2.0)^{a,b}
	LC	No		68.0 (2.6)^{l}	70.4 (2.2)^{m}	71.0 (2.7)^{g}	76.9 (2.0)^{c,d,e,f,g}
	LC	SB	LC	68.9 (2.5)^{l}	70.8 (2.5)^{m}	72.1 (2.5)^{g}	77.5 (3.0)^{c,d,e,f,g,h}
NX3 Nexus (NX3)	SC	No		32.6 (2.4)^{e,f}	40.0 (2.1)^{d,e}	55.2 (2.5)^{b,c}	74.9 (2.6)^{c,d,e,f}
	SC	OA	LC	37.3 (2.4)^{f}	43.8 (3.2)^{e,f}	55.0 (2.8)^{b,c}	75.2 (2.3)^{c,d,e,f,g}
	LC	No		56.0 (2.7)^{i,j,k}	58.5 (2.5)^{j}	63.2 (2.6)^{e,f}	78.9 (2.5)^{e,f,g,h}
	LC	OA	LC	56.6 (2.5)^{j,k}	59.1 (2.6)^{j,k}	62.9 (2.9)^{e,f}	78.9 (2.9)^{e,f,g,h}
DC of each cement with or without self-curing adhesive							
G-Cem One (GCO)	SC	No		45.3 (2.6)^{g,h}	49.3 (2.9)^{f,g,h}	56.5 (3.2)^{b,c}	72.0 (2.9)^{a,b,c}
	SC	GP	SC	50.7 (2.5)^{h,i}	53.9 (2.7)^{h,i,j}	60.0 (2.7)^{c,d,e}	76.3 (3.3)^{c,d,e,f,g}
	LC	No		52.6 (2.5)^{i,j}	57.2 (2.3)^{j}	62.6 (2.1)^{e,f}	78.7 (2.2)^{e,f,g,h}
	LC	GP	SC	52.3 (2.0)^{i,j}	56.7 (2.3)^{i,j}	62.4 (2.1)^{d,e,f}	78.4 (2.4)^{d,e,f,g,h}
Panavia V5 (PV5)	SC	No		7.72 (2.8)^{a}	30.1 (3.4)^{a,b,c}	52.0 (3.1)^{b}	72.1 (2.9)^{a,b,c}
	SC	TP	SC	28.5 (3.4)^{c,d,e}	46.2 (2.2)^{f,g}	57.7 (2.5)^{c,d,e}	75.0 (3.5)^{c,d,e,f}
	LC	No		44.6 (2.9)^{g}	49.4 (2.6)^{f,g,h}	58.8 (2.5)^{c,d,e}	76.7 (2.5)^{c,d,e,f,g}
	LC	TP	SC	46.0 (2.4)^{g,h}	51.1 (2.3)^{g,h,i}	60.3 (2.8)^{c,d,e}	77.1 (2.3)^{c,d,e,f,g,h}
RelyX Ultimate (RXU)	SC	No		32.0 (2.4)^{e,f}	34.9 (3.0)^{c,d}	42.2 (2.3)^{a}	68.3 (2.7)^{a,b}
	SC	SB	SC	25.7 (2.8)^{c,d}	28.3 (2.7)^{a,b}	38.6 (3.0)^{a}	67.0 (2.4)^{a}
	LC	No		68.0 (2.6)^{l}	70.4 (2.2)^{m}	71.0 (2.7)^{g}	76.9 (2.0)^{c,d,e,f,g}
	LC	SB	SC	67.5 (2.0)^{l}	69.1 (2.4)^{l,m}	70.2 (2.9)^{g}	76.4 (2.4)^{c,d,e,f,g}
Multilink N (MLN)	SC	No		15.4 (3.0)^{b}	39.0 (2.5)^{d,e}	67.6 (2.5)^{f,g}	77.6 (2.9)^{c,d,e,f,g,h}
	SC	MP	SC	29.4 (3.0)^{d,e}	46.5 (3.2)^{f,g}	70.5 (2.5)^{g}	78.8 (3.5)^{e,f,g,h}
	LC	No		68.4 (2.5)^{l}	69.4 (2.3)^{l,m}	71.7 (2.4)^{g}	79.9 (2.1)^{e,f,g,h}
	LC	MP	SC	68.6 (2.6)^{l}	69.9 (2.2)^{l,m}	72.0 (2.4)^{g}	80.4 (2.1)^{f,g,h}
Estecem Plus (ECP)	SC	No		14.8 (2.4)^{b}	25.7 (2.8)^{a}	56.8 (3.2)^{b,c,d}	72.9 (2.8)^{b,c,d}
	SC	PB	SC	23.6 (2.1)^{c}	31.1 (3.3)^{a,b,c}	59.7 (2.8)^{c,d,e}	74.6 (2.8)^{c,d,e}
	LC	No		58.9 (2.6)^{k}	64.3 (2.0)^{k,l}	67.4 (2.5)^{f,g}	80.9 (2.4)^{g,h}
	LC	PB	SC	60.1 (2.4)^{k}	65.1 (2.8)^{l,m}	69.2 (2.0)^{g}	82.7 (2.5)^{h}

Numbers in parentheses are standard deviations.
SC indicates self-curing of cement or adhesive, LC does light-curing.
No indicates no adhesive application.
Values followed by the same lowercase letters in each column are not significantly different (One-way ANOVA and Tukey's test, $p>0.05$).

the percentage of brighter pixels with a signal intensity greater than the threshold value[22]. Pixels of higher signal intensity above the threshold were measured on the image using a plug-in program, GapAnalyzer[23,24]. Seven horizontal cross-sectional images were obtained from each specimen (Figs. 2 and 3) and the mean percentage of high brightness (HB%) per sample was calculated.

Statistical analysis

All statistical analyses were conducted in SPSS software at an alpha significance level of 0.05 (IBM SPSS Statistics v22, IBM, Redmond, WA, USA). After the normal distribution of the DC measurements was checked, Levene's test was used to test for homogeneity of variance ($p>0.05$). To verify the difference between the DC with adhesive and that without adhesive, one-way ANOVA and Tukey's test were conducted (comparison

Table 3 The mean of high brightness values (HB%) using each adhesive and cement

	Groups of light-curing adhesive and self-curing cement		Groups of self-curing adhesive and self-curing cement						LC-control group
Adhesive Cement	LC SB SC RXU	LC OA SC NX3	No adhesive SC GCO	SC GP SC GCO	SC TP SC PV5	SC SB SC RXU	SC MP SC MLN	SC PB SC ECP	LC SB LC RXU
HB%	$18.8^{b,c}$ (2.4)	$20.3^{c,d}$ (2.5)	$20.9^{d,e}$ (2.1)	$19.0^{b,c}$ (2.4)	18.3^{b} (2.7)	22.4^{e} (2.4)	$19.6^{b,c,d}$ (2.0)	$19.7^{b,c,d}$ (2.1)	14.9^{a} (2.6)

LC indicates light-curing of adhesive or cement. SC does self-curing.
Higher HB% indicates higher interfacial gap.
The result of HB% is the mean (n=42, each group), with standard deviation in parentheses.
Values marked by the same lowercase letters are not significantly different (one-way ANOVA and Tukey's test, $p>0.05$).

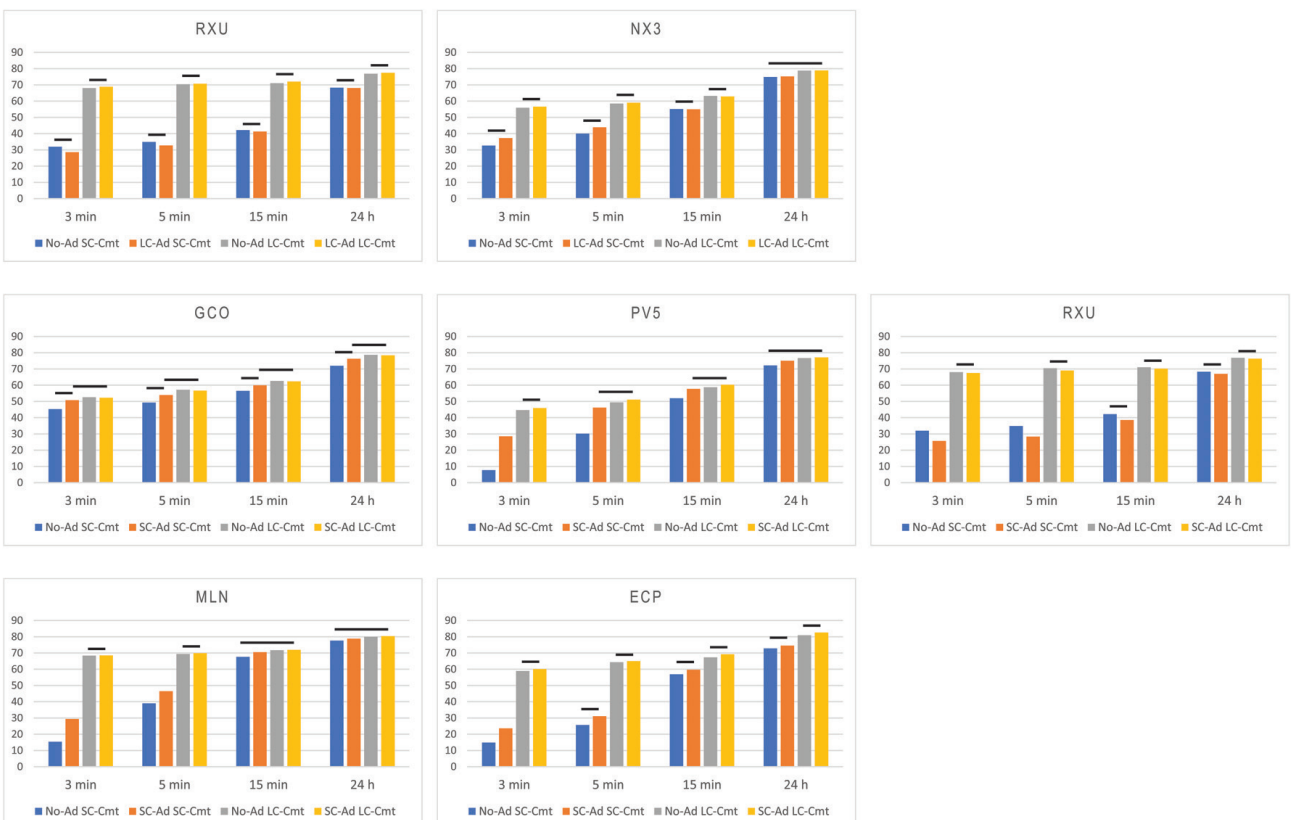

Fig. 4 The mean DC (%) when each cement is polymerized with or without the adhesive application.
Each bar indicates no statistically significant difference. No-Ad: no adhesive applied, LC-Ad: Light-curing of Adhesive, SC-Ad: Self-curing of Adhesive, SC-Cmt: Self-curing of Cement, LC-Cmt: Light-curing of Cement.

between the first and second row results of DC and between the third and fourth row results of DC in each cement, Table 2).

To compare the interfacial gap of zirconia restoration, parametric statistical tests were used (Shapiro–Wilk test, $p>0.05$). To test the homogeneity of variance, Levene's test was used ($p>0.05$). The HB% of interfacial gap was evaluated using a one-way ANOVA to compare the effects of different adhesives and cements. Tukey's test was performed for multiple comparison (Table 3).

RESULTS

The pH of each adhesive is presented in Table 1. All the single bottle adhesives indicate acidic pH. For adhesive that comprised two bottles to be mixed, one adhesive was acidic and the other was neutral.

Table 2 and Fig. 4 show the mean DC when each cement was polymerized with or without adhesive treatment at 3, 5, and 15 min and 24 h. When the cement was light-cured, the DC with adhesive did not differ from that without adhesive at each time (comparison between the third and fourth row results of each cement in Table 2).

When the cement was self-cured, the DC of PV5, RXU, MLN, and ECP with self-curing adhesive was different from that without adhesive at 3 min (comparison between the first and second row results in Table 2). The DC of PV5, MLN, and ECP with self-curing adhesive was higher than that without each adhesive at 3 min; however, the DC of RXU with self-curing adhesive was lower than that without it at 3 min. The DC of PV5, RXU, and MLN was different at 5 min. The DC of PV5 and MLN with self-curing adhesive was higher than that without adhesive at 5 min. The DC of RXU with self-curing adhesive was lower than that without it at 5 min. The DCs of the cements did not differ at 15 min, with the exception of PV5. The DCs of all the cements did not differ at 24 h regardless of application of the adhesive.

The interfacial gap result was expressed as HB%, with higher values indicating higher micro-gap (Table 3). Representative horizontal images for each group are presented in Fig. 5. After one-way ANOVA and Tukey's analyses, differences in HB% were found when the cement was self-cured. (Table 3, $p<0.05$). All the groups of self-curing cement showed higher interfacial gap than that of light-curing cement (LC-control). When RXU cement was self-cured, the interfacial gap with light-curing SB adhesive was lower than that with self-curing SB. GCO demonstrated lower interfacial gap when its primer (GP) was applied. The interfacial gap using single-bottle self-curing adhesives (GP, TP, and SB) exhibited similar or higher than that using two-bottle ones (MP and PB, Table 3).

DISCUSSION

The first null hypothesis was rejected because there was a difference in the DC when resin cements were self-cured with or without the adhesive. The second null hypothesis was also rejected because interfacial gap (HB%) of some self-cured cements differed from that of

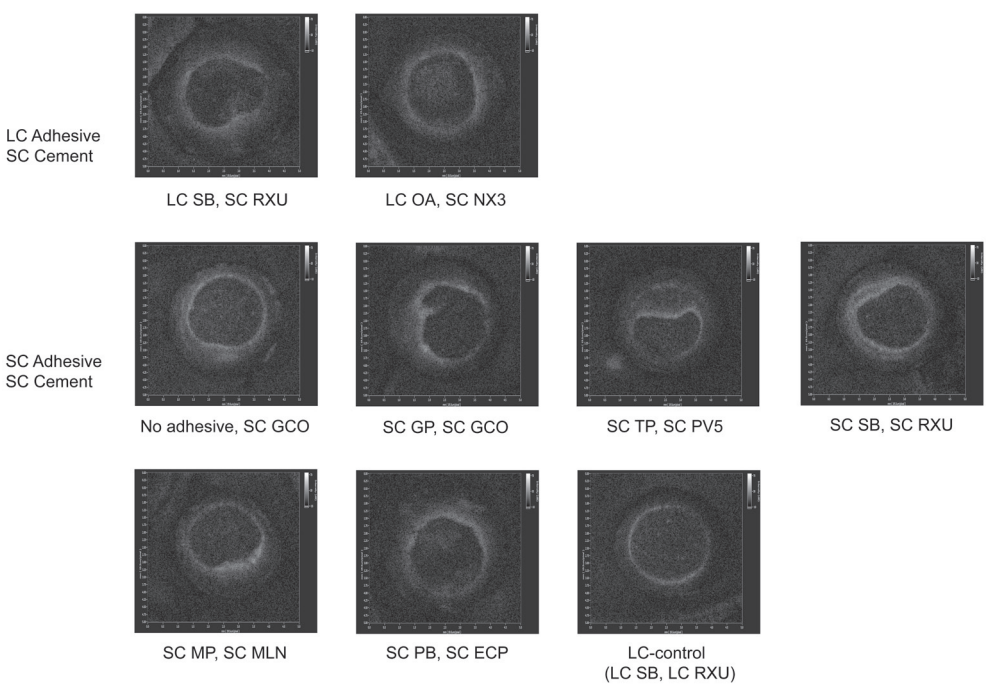

Fig. 5 Representative horizontal-cut images at the cement space.
The white dots or clusters on each image are brighter pixels that have low refractive index to indicate micro-gaps. LC indicates light-curing and SC does self-curing.

other cements.

When the DC of self-curing cement with light-curing adhesive was compared that without adhesive, no difference was found (Table 2). OA is reported to be a hydrophilic adhesive[25]. A study using OA showed that hydrophilic adhesives lead to high shear bond strengths when a conventional resin cement is light-cured; however, the bond strength drops significantly if the resin cement is self-cured[25]. A hydrophobic bonding resin layer, which has been placed in the final process in a three-step adhesive, is known to be more reliable and improves the bond strength[26,27]. NX3 cement is known as an amine-free resin cement. In this experiment, light-cured OA did not interfere with self-curing of NX3 in terms of the DC. The interfacial gap of self-curing NX3 with OA was similar or higher than that of other self-curing cements (Table 3).

Under the conditions used in this experiment, the self-curing adhesive generally made the resin cement polymerize more rapidly at the beginning of the self-curing process. The DC of self-curing cements after 24 h showed no statistical difference between those with and those without the adhesive (Table 2). Delayed polymerization gives water time to be absorbed from dentin through osmosis[9,28], which can lead to lower bond strength with tooth material[29]. Water infiltration can inhibit self-curing of resin cement as well as the adhesive layer[30,31]. An oxygen inhibition layer is inevitably formed when the adhesive is polymerized in air. There is competition between scavenging of free radicals by the oxygen and new radical generation by the initiators and accelerators[17]. Some studies reported that light application to the resin cement generates abundant free radicals rapidly, which can suppress the acid-base reaction between the adhesive and the cement[17,29,32].

GCO is a self-adhesive resin system, which does not require an additional adhesive. As mentioned earlier, an adhesive is recommended to be applied for prepared tooth before using a SAC. GP contains the functional monomers of 4-methacryloxyethyl trimellitic acid (4-MET) and 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP)[33]. In terms of polymerization speed, self-curing of GCO was relatively rapid. From the manufacture's information, GCO does not include a tertiary amine in its paste but a fluoroaluminosilicate glass filler is found in in paste-A[33]. To neutralize initially acidic conditions, a glass-ionomer concept can be applied[34]. The acid-base reaction of the acidic functional monomer and the basic inorganic filler in the cement can lead to neutralization[35]. GP includes functional monomers and a "touch-cure" catalyst, which could result in lower interfacial gap and higher polymerization during the initial period of self-curing (Tables 2 and 3).

PV5 is an amine-free resin cement system and includes TP, a one-bottle adhesive. Mixed cement paste self-cures very slowly when TP is not applied, particularly during the early stage of polymerization (Fig. 4). The polymerization of PV5 cement paste is dependent on the chemical-cure accelerator in TP[36]. Yoshihara *et al*. reported a vanadium compound served as a novel chemical accelerator within TP, based on the results of X-ray fluorescence analysis[36]. Their study showed that cement paste-A contains hydroperoxide, instead of benzoyl peroxide (BPO), as a chemical cure initiator for the adhesive and cement. A previous version of this cement (Panavia F2.0, Kuraray Noritake) adopted the BPO/tertiary amine/sulfinic acid system[32]. This cement system is known for its ED primer, with acidic monomers in primer-A and aromatic sodium sulfinate co-initiators in primer-B. Although sulfinic acid can be used with tertiary amines, the acidic functional monomers reportedly neutralize the tertiary amines, which can result in lower DCs[5,32,37].

RXU is an amine-free cement and a study showed RXU was dependent on light-curing[38]. The DC and polymerization rate of RXU were low with self-curing but were high with light-curing (Table 2). SB treatment without light-curing, *i.e.*, self-curing SB, showed an interesting result. The DC of self-curing RXU after self-curing SB was significantly lower than that of self-curing RXU without SB at 3 and 5 min (Table 2). The DC of self-curing RXU with self-curing SB became similar to that without SB at 15 min and 24 h. These results indicate that SB, which has not been polymerized by light-curing, may interfere with polymerization of RXU during the initial self-curing process. According to the manufacturer, SB can be self-cured because the catalyst paste of RXU includes a dual-cure activator for SB adhesive. However, the results indicate that polymerization of RXU can be inhibited if SB is not light-cured. This system is recommended for use with light-curing of the adhesive and cement.

MLN cement was used as a conventional self-curing system, which includes a two-bottle mixing adhesive. Primer-A of MLN includes water and primer-B has acidic monomers, which can prevent methacrylates from being hydrolyzed under aqueous acidic condition[4,39]. Primer-A also includes sodium-benzene sulfinate for polymerization under acidic pH[4]. The polymerization of MLN with its adhesive resulted in a higher DC at 3 and 5 min compared with that without the adhesive, which indicates the cement can be polymerized more rapidly by the adhesive. ECP uses a borate catalyst instead of aryl sulfinate. One research showed that the polymerization of an adhesive including a borate initiator was not affected by the acidity of the functional monomer[40]. According to the manufacturer, the borate initiator is decomposed by acidic functional monomers and transformed into a borane compound that produces free radicals. PB contains a peroxide that accelerates the degradation of borane compounds and serves as an active chemical initiator. Although PB accelerates the DC of ECP, the polymerization rate during the initial period was relatively low compared with other cements (Table 2 and Fig. 4).

One of the limitations in this study involves the temperature under which the DC was measured by FTIR. The DC measured in the lab can differ from that measured at body temperature. Another limitation is the dry/wet conditions under which each experiment was

carried out. The DC of resin cement was measured under a dry condition using a FTIR device; however, the resin cement is actually polymerized under wet conditions in a tooth. It was reported that both temperature and humidity significantly affect the mechanical properties and bond strengths of resin composites[10]. The third limitation of this study is zirconia restoration design: zirconia is usually used for tooth coverage restoration. However, the scan dimension of the SS-OCT device was 5×5 mm. Therefore, the restoration was designed to be class I restoration of 3 mm diameter. Regarding preparation depth, it was reported that bond strength at superficial dentin is higher than that at deep dentin[41]. After occlusal reduction and preparation, the depth of inlay cavity was 1 mm at the similar level for all the groups. The restoration was designed to have a standardized form of internal cavity for the interfacial gap comparison.

Interfacial gap (HB%) can represent the bonding quality of the tooth and restoration[42]. To compare the interfacial gaps of self-curing adhesive and cement, one-bottle self-curing adhesive systems (GP, TP, and SB) were compared to two-bottle self-curing adhesive ones (MP and PB). Interfacial gaps of GP and TP were similar to those of MP and PB (Table 3). The results showed that one-bottle GP and TP were effective for reducing the micro-gap by touch-cure activation of cement. When RXU cement was self-cured, interfacial gap of self-curing SB was higher than that of light-curing SB (Table 3). In the experiment of DC measurement, SB which was polymerized by self-curing interfered with polymerization of RXU (Table 2). This lower DC with self-curing SB can be a reason for the higher interfacial gap of RXU with self-curing SB. Moreover, interfacial gap of light-curing SB was significantly reduced when RXU cement was light-cured (LC-control). It is thought that all the single-bottle adhesives are not always effective using touch-cure activation of cement paste.

In terms of polymerization method of the resin cement by light- or self-curing, previous studies showed that light-cured cements achieved higher mechanical properties and polymerization compared with self-cured ones[43-45]. Light curing can initiate a multitude of growth centers and create a polymer with a high cross-linking density, while relatively few growth centers by self-curing can result in a more linear polymer[46,47]. It has been proposed that the adverse chemical interaction is dependent on the curing speed of cement[29,32]. Although the accelerators in the adhesive can make the cement self-cure faster during the initial polymerization, the DC and polymerization speed were not as high as those achieved by light-curing.

CONCLUSION

Resin cement showed different DCs depending on the polymerization method of cement and adhesive treatment. When an adhesive was applied on the tooth material, some resin cements can be polymerized more rapidly at the beginning of the self-curing process. The final DC with an adhesive after 24 h did not differ from that without an adhesive. Although self-curing of resin cement was enhanced by accelerators in the adhesive, the degree and speed of polymerization were not as high as those of light-curing. When resin cement was self-cured, interfacial gap was different depending on the adhesive and resin cement.

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CONFLICT OF INTEREST

The authors declare no competing interests.

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