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ORIGINAL ARTICLE

Light curing through glass ceramics: effect of curing mode on micromechanical properties of dual-curing resin cements

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Abstract

Objectives The aim of this study was to investigate micromechanical properties of five dual-curing resin cements after different curing modes including light curing through glass ceramic materials.

Materials and methods Vickers hardness (VH) and indentation modulus (Y_{HU}) of Panavia F2.0, RelyX Unicem 2 Automix, SpeedCEM, BisCem, and BeautiCem SA were measured after 1 week of storage (37 °C, 100 % humidity). The resin cements were tested following self-curing or light curing with the second-generation light-emitting diode (LED) curing unit Elipar FreeLight 2 in Standard Mode (1,545 mW/cm^2) or with the third-generation LED curing unit VALO in High Power Mode (1,869 mW/cm^2) or in XtraPower Mode (3,505 mW/cm^2). Light curing was performed directly or through glass ceramic discs of 1.5 or 3 mm thickness of IPS Empress CAD or IPS e.max CAD. VH and Y_{HU} were analysed with Kruskal–Wallis tests followed by pairwise Wilcoxon rank sum tests (α=0.05).

Results RelyX Unicem 2 Automix resulted in the highest VH and Y_{HU} followed by BeautiCem SA, BisCem, SpeedCEM, and finally Panavia F2.0. Self-curing of RelyX Unicem 2 Automix and SpeedCEM lowered VH and Y_{HU} compared to light curing whereas self-curing of Panavia F2.0, BisCem, and BeautiCem SA led to similar or significantly higher VH and Y_{HU} compared to light curing. Generally, direct light curing resulted in similar or lower VH and Y_{HU} compared to light curing through 1.5-mm-thick ceramic discs. Light curing through 3-mm-thick discs of IPS e.max CAD generally reduced VH and Y_{HU} for all resin cements except SpeedCEM, which was the least affected by light curing through ceramic discs.

Conclusions The resin cements responded heterogeneously to changes in curing mode. The applied irradiances and light curing times adequately cured the resin cements even through 1.5-mm-thick ceramic discs.

Clinical relevance When light curing resin cements through thick glass ceramic restorations, clinicians should consider to prolong the light curing times even with LED curing units providing high irradiances.

Keywords Luting resins · Polymerization · Light intensity · Radiant exposure · Surface hardness · Indentation modulus

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Introduction

Resin cements currently available on the market can be divided into three categories: (1) etch-and-rinse adhesive resin cements (cements used after application of an etch-and-rinse adhesive system including separate acid etching), (2) self-etch adhesive resin cements (cements used after application of a self-etch adhesive system), and (3) self-adhesive resin cements ("self-adhering" cements used without application of any adhesive system) [1]. Some etch-and-rinse and self-etch adhesive resin cements and most self-adhesive resin cements are so-called dual-curing, i.e. they offer self-curing as well as light curing abilities. Thus, dual-curing resin cements can be used for luting non-transparent restorations, such as porcelain-fused-to-metal crowns or bridges where (except at the margins) light curing is excluded and self-curing is essential, but they can also be used for luting semi-transparent restorations such as glass ceramic inlays or onlays where light curing is possible to a certain extent.

Previous studies have shown that light curing advantageously influenced the physico-chemical properties of dual-curing resin cements, i.e. light curing generally led to improved mechanical properties (higher surface hardness or indentation modulus) [2, 3] or to higher degree of conversion [4–6] than did self-curing alone. However, when light curing through glass ceramics, the irradiance of the light curing unit strongly decreases with increasing thickness of the ceramic material [7–9]. Consequently, when using dual-curing resin cements for luting restorations made of glass ceramics, either a potent self-curing initiator system or a high irradiance of the light curing unit and/or a long light curing time is needed for satisfactory curing. Today, the majority of light curing units is based on the light-emitting diode (LED) technology [10, 11]. LED curing units with a single high-powered diode (second-generation LED curing units [10]; blue diode, single peak) typically reach irradiances of 1,200 to 1,500 mW/cm^2. Currently, an LED curing unit with multiple diodes (i.e. a third-generation LED curing unit [10]; violet/blue diodes, polywave) is on the market (VALO, Ultradent), which reaches irradiances of more than 3,500 mW/cm^2 [4] depending on the chosen mode. In a previous study, the authors of the present study investigated (a) to what extent the increased irradiances of the third-generation LED curing unit VALO compared to a second-generation LED curing unit were transmitted through a leucite-reinforced and a lithium-disilicate glass ceramic material for computer-aided design/manufacturing (CAD/CAM) and (b) whether/to what extent the increased irradiances influenced degree of conversion (DC) of five dual-curing resin cements when cured according to 16 curing modes [4]. The curing modes comprised self-curing, direct light curing, and light curing through 1.5- or 3-mm-thick discs of the two above-mentioned glass ceramic materials. Measurements of DC in this previous study were applied to directly investigate the effect of curing mode on the organic polymer component of the resin cements. However, resin cements should also possess enhanced mechanical properties (determined by the organic as well as inorganic/filler component) in order to support the overlying restoration and to resist functional stress over time. Besides, among micromechanical properties, measuring the surface microhardness in particular has been shown to be a useful method to indirectly investigate polymer network conversion of a given resin composite material [12–14]. Thus, the aim of the present study was to measure surface microhardness (Vickers hardness; VH) and indentation modulus (Y_{HU}) after 1 week of storage of the same five dual-curing resin cements when cured according to the same 16 curing modes as used in the previous study mentioned above. The null hypothesis was that all five resin cements would yield similar VH and Y_{HU} regardless of the curing mode. Additionally, for each resin cement, VH and Y_{HU} of the present study were correlated with DC of the previous study.

Materials and methods

Preparation of ceramic discs

One block of a leucite-reinforced glass ceramic material (IPS Empress CAD, size C14, shade LT A3; Ivoclar Vivadent, Schaan, Liechtenstein) and one block of a lithium-disilicate glass ceramic material (IPS e.max CAD, size C14, shade LT A3; Ivoclar Vivadent) were used for the ceramic discs. The block of the IPS e.max CAD ceramic material was tempered in a Programat EP 5000 furnace (Ivoclar Vivadent) using the standard program recommended by the manufacturer (G9 Crystal/Glaze, program P81). From the two blocks of ceramic material, discs were cut using a low-speed diamond saw (Isomet, Lake Bluff, IL, USA). The ceramic discs were then polished under water-cooling on both sides with a polishing device (Leco VP 100; Leco Instrumente GmbH, Mönchengladbach, Germany) and silicon carbide papers (Leco abrasive discs; Leco) of descending grit size (#320 to #1200). During polishing, the thickness of the ceramic discs was monitored with a digital micrometer (Mitutoyo ID-U1025; Mitutoyo, Kawasaki, Japan). The discs were polished until thicknesses of 1.5 or 3.0 mm were reached (one ceramic disc per thickness of each of the two ceramic materials) since these two thicknesses were considered clinically relevant.

Resin cements and curing modes

One dual-curing, self-etch adhesive resin cement (control) and four dual-curing, self-adhesive resin cements were used. Detailed information about the resin cements is listed in Table 1. The self-etch adhesive resin cement (Panavia F2.0) was hand mixed according to the manufacturer's instruction with a 1:1 ratio of paste A and paste B. The four self-adhesive resin cements (in Automix syringes) were used with the mixing tips delivered by the manufacturers, and the first ~1 cm of resin cement of each new Automix syringe was discarded. Resin cements which needed to be stored in the refrigerator were taken out 1 h before use.

The five resin cements were cured according to the 16 curing modes listed in Tables 2 and 3. Self-curing of the self-etch adhesive resin cement Panavia F2.0 was either performed with addition of ED Primer II or without (Tables 1, 2, and 3). When self-curing of Panavia F2.0 was performed with ED Primer II, liquid A and liquid B were mixed according to the manufacturer's instruction with a 1:1 ratio. A droplet of mixed ED Primer II was added to paste A and B of Panavia F2.0 with a probe and hand mixed. Light curing was carried out with the second-generation LED curing unit Elipar FreeLight 2 (3M ESPE, Seefeld, Germany) in Standard Mode (i.e. without exponential/soft start; mean irradiance: 1,545 mW/cm^2) and with the third-generation LED curing unit VALO (Ultradent, South Jordan, UT, USA) in High Power Mode (mean irradiance: 1,869 mW/cm^2) or in Xtra Power Mode (mean irradiance: 3,505 mW/cm^2). Irradiance was measured using a MARC Resin Calibrator radiometer device (BlueLight Analytics Inc., Halifax, NS, Canada). In order to have near identical radiant exposures (irradiance×light curing time; J/cm^2) with the three modes of the LED curing units, the light curing time was varied (Tables 2 and 3), and radiant exposures were 61.8 J/cm^2 for the Elipar FreeLight 2 in the Standard Mode, 59.8 J/cm^2 for the VALO in the High Power Mode, and 63.1 J/cm^2 in the Xtra Power Mode. Through the ceramic discs of 1.5 and 3 mm thickness and for the Elipar FreeLight 2 in the Standard Mode, resultant radiant exposures were (for IPS Empress CAD/IPS e.max CAD) 10.3 J/cm^2/8.4 J/cm^2 through 1.5-mm-thick ceramic discs and 2.7 J/cm^2/2.0 J/cm^2 through 3-mm-thick ceramic discs. For the VALO in the High Power Mode, radiant exposures were (for IPS Empress CAD/IPS e.max CAD) 10.6 J/cm^2/8.5 J/cm^2 through 1.5-mm-thick ceramic discs and 3.0 J/cm^2/2.2 J/cm^2 through 3-mm-thick ceramic discs. Finally, for the VALO in the Xtra Power Mode, radiant exposures were (for IPS Empress CAD/IPS e.max CAD) 11.4 J/cm^2/8.9 J/cm^2 through 1.5-mm-thick ceramic discs and 3.2 J/cm^2/2.2 J/cm^2 through 3-mm-thick ceramic discs [4]. During light curing of the resin cements (groups EF, VH, and VX; Tables 2 and 3), the tip end of the light curing units was either in contact with the Mylar strip (when directly light cured) or in contact with the ceramic discs.

Measurement of micromechanical properties

Resin cement specimens (500 μm in height and ~10 mm in diameter) were produced using a metal mould. The mould was placed on reusable, roughened plastic slides, filled with one of the five resin cements (Table 1), and covered with a Mylar strip. The top side of the resin cement was made flush with the mould by use of a small glass slide. This slide was removed, and the resin cement was cured according to one of the 16 curing modes previously described (Tables 2 and 3). Custom-made jigs had been made of acrylic resin (Paladur, pink shade; Heraeus Kulzer, Hanau, Germany) in order to ensure that the ceramic discs and the tip end of the light curing units were placed in the same position on the metal mould for all specimens. For each of the five resin cements and 16 curing modes, ten specimens were produced at constant room temperature (20 °C). Immediately after production, each specimen was placed in a black photo-resistant box at 100 % humidity, and the boxes were stored in an incubator at 37 °C (Memmert UM 500, Schwabach, Germany) for 1 week. After storage, the Mylar strip was removed and the micromechanical properties VH (in N/mm^2) and Y_{HU} (in GPa) were simultaneously measured with a microhardness indenter (Fischerscope H100C, Helmut Fischer GmbH, Sindelfingen, Germany) in analogy to DIN 50359-1:1997 [15] as previously described [2]. All measurements were performed in a force-controlled mode for 50 s with the test load increasing and decreasing between 0.4 and 500 mN at a constant speed. Five VH and Y_{HU} measurements were made on the top surface of each specimen (one measurement in the centre and four measurements towards the periphery). The five measurements per specimen were averaged, and thus, ten VH and ten Y_{HU} mean values for each of the five resin cements and 16 curing modes were used for statistical analysis.

Statistical analysis

VH and Y_{HU} of all resin cements and curing modes were analysed using a non-parametrical ANOVA model with four fixed factors according to Brunner and Munzel [16]. The four fixed factors were the following: (1) resin cement (i.e. the five resin cements), (2) curing mode (i.e. self-curing, Elipar FreeLight 2 Standard Mode, VALO High Power Mode, VALO Xtra Power Mode), (3) type of ceramic (i.e. no ceramic, IPS Empress CAD, IPS e.max CAD), and (4) ceramic thickness (i.e. no ceramic, 1.5 mm thickness, 3 mm thickness). The non-parametrical ANOVA model was followed by Kruskal–Wallis tests and pairwise Wilcoxon rank sum tests (significance level α=0.05). No correction for multiple testing was done, and thus, results must be considered exploratively. To quantify the relation between DC of the previous study [4] and VH or Y_{HU} of the present study, the DC-, VH-, and Y_{HU}-medians were determined for all 16 curing modes of a given resin cement. From these medians, Spearman rank correlation coefficients were calculated. The statistical analysis was performed with SAS 9.2 (SAS Institute Inc., Cary, NC, USA) and with R version 2.15.2 (The R Foundation for Statistical Computing, Vienna, Austria; www.R-project.org).

Results

The non-parametrical ANOVA model showed that all four factors had a statistically significant effect on VH and on Y_{HU} (p<0.0001). Kruskal–Wallis tests found significant differences between the resin cements as well as significant differences between curing modes within each resin cement. Mean values and standard deviations as well as the results of the post hoc pairwise Wilcoxon rank sum tests are shown in Table 2 for VH and in Table 3 for Y_{HU}.

Table 1 Resin cements used (manufacturers' information)

Panavia F2.0	LOT-Nr: 00509A (paste A)/00096B (paste B)	
Kuraray Medical Inc., Okayama, Japan	Paste/paste	
Type of resin cement	Dual-curing, self-etch adhesive resin cement	
	Paste A	Paste B
Methacrylates	% volume n.a./% weight n.a.	% volume n.a./% weight n.a.
Type of methacrylates	10-Methacryloyloxydecyl dihydrogen phosphate (MDP)	Hydrophobic aromatic dimethacrylate
	Hydrophobic aromatic dimethacrylate Hydrophobic and hydrophilic aliphatic dimethacrylate	Hydrophobic and hydrophilic aliphatic dimethacrylate
Filler	Total filler content: 59 % volume/79 % weight	
Filler particle size	0.04–19 µm	
Panavia F2.0 ED Primer II Kuraray Medical Inc., Okayama, Japan	LOT-Nr: 00303A (liquid A)/00177B (liquid B) (group SC* only)	
Type of adhesive system	Self-etch adhesive system	
	Liquid A	Liquid B
Contents	2-Hydroxyethyl methacrylate (HEMA)	*N*-Methacryloyl-5-amino-salicylic acid
	MDP	Water
	N-Methacryloyl-5-amino-salicylic acid Water	Catalysts/co-initiators
	Accelerators	
RelyX Unicem 2 Automix	LOT-Nr: 439129	
3M ESPE, Seefeld, Germany	Paste/paste (Automix)	
Type of resin cement	Dual-curing, self-adhesive resin cement	
	Base	Catalyst
Methacrylates	30–50 % weight (% volume n.a.)	20–30 % weight (% volume n.a.)
Type of methacrylates	Triethylene glycol dimethacrylate (TEGDMA) Methacrylates with phosphoric acid groups	(Substituted) dimethacrylates
Filler	Total filler content: ~70 % weight (% volume n.a.)	
Filler particle size	90 %~12.5 µm	
SpeedCEM	LOT-Nr: P35471	
Ivoclar Vivadent AG, Schaan, Liechtenstein	Paste/paste (Automix)	
Type of resin cement	Dual-curing, self-adhesive resin cement	
	Base	Catalyst
Methacrylates	23.3 % weight (% volume n.a.)	26 % weight (% volume n.a.)
Type of methacrylates	Urethane dimethacrylate (UDMA), TEGDMA, polyethylenglycol dimethacrylate (PEG-DMA), methacrylated phosphoric acid esters	

Table 1 (continued)

Filler	75 % weight (% volume n.a.)	2.2 % weight (% volume n.a.)
	Total filler content: ~40 % volume	
Filler particle size	0.1–7 µm (mean: 5 µm)	
BisCem	LOT-Nr: 1100008747	
Bisco Inc., Schaumburg, IL, USA	Paste/paste (Automix)	
Type of resin cement	Dual-curing, self-adhesive resin cement	
	Base	Catalyst
Methacrylates	>30 % volume (% weight n.a.)	>10 % volume (% weight n.a.)
Type of methacrylates	Bisphenol A-glycidyl methacrylate (Bis-GMA)	Phosphate acidic monomers
	Dimethacrylates	
Filler	Total filler content: >50 % volume (% weight n.a.)	
Filler particle size	n.a.	
BeautiCem SA	LOT-Nr: 101206	
Shofu Inc., Kyoto, Japan	Paste/paste (Automix)	
Type of resin cement	Dual-curing, self-adhesive resin cement	
	Paste A	Paste B
Methacrylates	% volume n.a./% weight n.a.	% volume n.a./% weight n.a.
Type of methacrylates	UDMA	UDMA
		HEMA
		Carboxylic and phosphonic acid monomer
Filler	Total filler content: 60–70 % weight (% volume n.a.)	
Filler particle size	n.a.	

n.a. not applicable (no further/detailed information of manufacturer available)

Table 2 Mean values and standard deviations of the Vickers hardness (VH) of the five resin cements according to the groups of curing mode as well as results of the pairwise Wilcoxon rank sum tests (significance level α=0.05; identical letters indicate no statistically significant differences between the groups within one resin cement)

Resin cement		Panavia F2.0	RelyX Unicem 2 Automix	SpeedCEM	BisCem	BeautiCem SA
Light curing unit	Groups of curing mode (n=10 per group and resin cement)	VH (N/mm^2)	VH (N/mm^2)	VH (N/mm^2)	VH (N/mm^2)	VH (N/mm^2)
(n.a.; self-curing)	Group SC* (Panavia F2.0 only)	39.9 (3.5) b	(n.a.)	(n.a.)	(n.a.)	(n.a.)
(n.a.; self-curing)	Group SC	62.0 (6.3) a	38.9 (11.2) g	9.6 (4.4) j	37.8 (2.9) abcd	35.6 (1.5) d
Elipar FreeLight 2 (3M ESPE) Standard Mode 40 s (2×20 s)	Group EF1 (direct; through Mylar strip)	17.7 (1.5) gh	62.9 (2.4) bcde	30.1 (1.9) fgh	38.0 (2.3) abcd	37.7 (1.8) c
	Group EF2 (IPS Empress CAD 1.5 mm)	18.1 (1.1) g	63.7 (1.6) bc	31.7 (1.9) def	38.0 (2.4) abc	39.6 (1.4) b
	Group EF3 (IPS Empress CAD 3 mm)	13.0 (0.8) j	56.8 (1.6) f	30.1 (1.6) gh	32.3 (2.0) e	27.1 (2.3) ef
	Group EF4 (IPS e.max CAD 1.5 mm)	16.7 (1.6) h	62.0 (1.5) de	30.0 (1.2) g	36.9 (1.8) cd	38.2 (1.4) bc
	Group EF5 (IPS e.max CAD 3 mm)	11.3 (0.6) k	45.8 (3.8) g	28.3 (1.4) i	31.1 (2.6) e	24.5 (1.6) g
VALO (Ultradent) High Power Mode 32 s (8×4 s)	Group VH1 (direct; through Mylar strip)	22.7 (2.8) ef	62.5 (4.3) abcde	31.8 (1.0) cde	38.4 (1.8) abc	42.2 (1.0) a
	Group VH2 (IPS Empress CAD 1.5 mm)	27.1 (2.0) c	64.7 (2.5) ab	35.7 (1.0) a	39.6 (2.0) ab	42.2 (1.2) a
	Group VH3 (IPS Empress CAD 3 mm)	18.0 (1.3) g	62.4 (2.3) de	34.4 (1.0) b	38.2 (3.1) abc	29.2 (3.8) e
	Group VH4 (IPS e.max CAD 1.5 mm)	25.0 (1.5) d	63.8 (2.1) abcd	35.4 (1.3) a	37.7 (2.7) abcd	39.3 (1.4) bc
	Group VH5 (IPS e.max CAD 3 mm)	15.2 (1.2) i	58.0 (2.4) f	32.5 (1.3) cd	35.3 (2.4) d	25.0 (2.6) fg
VALO (Ultradent) Xtra Power Mode 18 s (6×3 s)	Group VX1 (direct; through Mylar strip)	18.7 (2.0) g	63.5 (1.9) b	28.0 (2.3) hi	37.5 (2.0) bcd	41.5 (1.3) a
	Group VX2 (IPS Empress CAD 1.5 mm)	24.5 (1.7) de	65.8 (1.8) a	32.8 (2.4) bcd	38.7 (2.5) abc	42.9 (2.5) a
	Group VX3 (IPS Empress CAD 3 mm)	17.9 (1.2) gh	61.4 (1.9) e	31.1 (2.2) cdefg	36.4 (2.5) cd	28.2 (1.8) e
	Group VX4 (IPS e.max CAD 1.5 mm)	21.8 (1.2) f	63.9 (2.5) abcd	31.9 (2.1) cdef	39.5 (2.1) a	39.2 (1.7) bc
	Group VX5 (IPS e.max CAD 3 mm)	13.1 (1.2) j	57.3 (3.3) f	30.8 (1.2) efg	31.8 (1.6) e	23.7 (2.3) g

n.a. not applicable

When comparing VH and Y_{HU} of the five resin cements, RelyX Unicem 2 Automix generally produced the highest VH and Y_{HU}, followed by BeautiCem SA, BisCem, and SpeedCEM, and finally Panavia F2.0. With regard to curing mode, self-curing (groups SC) of RelyX Unicem 2 Automix and SpeedCEM led to significantly lower VH and Y_{HU} than did the groups involving light curing (groups EF, VH, and VX). Self-curing of BisCem and BeautiCem SA (groups SC) led to VH and Y_{HU} in a similar range as the VH and Y_{HU} in groups involving light curing of the two resin cements (groups EF, VH, and VX). For Panavia F2.0, self-curing without ED Primer II (group SC) resulted in significantly higher VH and Y_{HU} compared not only to self-curing with ED Primer II (group SC*) but also compared to all groups involving light curing of Panavia F2.0. Considering all five resin cements, direct light curing through a Mylar strip (groups EF1, VH1, and VX1) generally led to similar or significantly lower VH and Y_{HU} compared to VH and Y_{HU} in groups where light curing had been performed through ceramic discs of 1.5 mm thickness. When light curing had been performed through discs of 3 mm thickness, Panavia F2.0, RelyX Unicem 2, and BeautiCem SA predominantly showed a significant reduction in VH. Light curing through discs of 3 mm thickness also led to a significant reduction in Y_{HU} for Panavia F2.0 and BeautiCem SA regardless of the ceramic material whereas RelyX Unicem 2 Automix predominantly showed a significant reduction in Y_{HU} when light curing had been performed through 3-mm-thick discs of IPS e.max CAD. BisCem showed a significant reduction in VH when light cured through 3-mm-thick discs of IPS e.max CAD. However, light curing through ceramic discs did not affect Y_{HU} of BisCem regardless of the thickness and the material. SpeedCEM was the least affected by light curing through ceramic discs and very often showed higher VH and similar Y_{HU} compared to when directly light cured through a Mylar strip.

The Spearman rank correlation coefficients between DC of the previous study [4] and VH or Y_{HU} of the present study are presented in Table 4 for each resin cement. For Panavia F2.0, RelyX Unicem 2 Automix, and SpeedCEM slight or moderate, positive correlations were found. BeautiCem SA showed strong positive correlations. Finally, BisCem showed a moderate, positive correlation between DC and VH but no correlation between DC and Y_{HU}.

Discussion

In the present study, VH and Y_{HU} of resin cements were investigated with a microhardness indenter when cured

Table 3 Mean values and standard deviations of the indentation modulus (Y_{HU}) of the five resin cements according to the groups of curing mode as well as results of the pairwise Wilcoxon rank sum tests (significance level α=0.05; identical letters indicate no statistically significant differences between the groups within one resin cement)

Resin cement		Panavia F2.0	RelyX Unicem 2 Automix	SpeedCEM	BisCem	BeautiCem SA
Light curing unit	Groups of curing mode (n=10 per group and resin cement)	Y_{HU} (GPa)	Y_{HU} (GPa)	Y_{HU} (GPa)	Y_{HU} (GPa)	Y_{HU} (GPa)
(n.a.; self-curing)	Group SC* (Panavia F2.0 only)	6.9 (1.0) bc	(n.a.)	(n.a.)	(n.a.)	(n.a.)
(n.a.; self-curing)	Group SC	9.0 (1.1) a	7.1 (1.3) h	3.1 (0.9) h	7.5 (0.6) a	6.9 (0.4) d
Elipar FreeLight 2 (3M ESPE) Standard Mode 40 s (2×20 s)	Group EF1 (direct; through Mylar strip)	5.2 (0.4) e	10.0 (0.2) cd	6.8 (0.3) cdef	6.7 (0.6) def	8.0 (0.3) bc
	Group EF2 (IPS Empress CAD 1.5 mm)	5.1 (0.3) e	10.2 (0.3) bc	6.7 (0.2) def	6.8 (0.6) bcdef	8.1 (0.5) abc
	Group EF3 (IPS Empress CAD 3 mm)	4.0 (0.3) h	9.4 (0.3) f	6.7 (0.3) def	6.5 (0.5) f	6.2 (0.5) ef
	Group EF4 (IPS e.max CAD 1.5 mm)	4.9 (0.3) e	9.8 (0.4) de	6.6 (0.3) ef	6.7 (0.8) bcdef	7.9 (0.2) c
	Group EF5 (IPS e.max CAD 3 mm)	3.7 (0.2) i	8.3 (0.7) g	6.3 (0.2) g	6.8 (0.2) ef	5.7 (0.4) g
VALO (Ultradent) High Power Mode 32 s (8×4 s)	Group VH1 (direct; through Mylar strip)	6.2 (0.7) cd	10.0 (0.4) bcd	6.9 (0.2) cde	7.2 (0.4) abc	8.5 (0.2) a
	Group VH2 (IPS Empress CAD 1.5 mm)	6.9 (0.5) b	10.3 (0.4) ab	7.2 (0.3) a	7.0 (0.5) abcdef	8.2 (0.4) ab
	Group VH3 (IPS Empress CAD 3 mm)	5.1 (0.4) e	10.2 (0.2) bc	7.2 (0.2) a	7.3 (0.5) ab	6.3 (0.7) e
	Group VH4 (IPS e.max CAD 1.5 mm)	6.5 (0.6) bcd	10.2 (0.2) bc	7.2 (0.3) ab	6.8 (0.4) def	8.0 (0.2) bc
	Group VH5 (IPS e.max CAD 3 mm)	4.6 (0.2) f	9.5 (0.5) ef	7.0 (0.2) bc	7.0 (0.4) abcd	5.9 (0.6) efg
VALO (Ultradent) Xtra Power Mode 18 s (6×3 s)	Group VX1 (direct; through Mylar strip)	5.3 (0.5) e	10.2 (0.4) bc	6.5 (0.3) fg	7.2 (0.4) abcd	8.5 (0.3) a
	Group VX2 (IPS Empress CAD 1.5 mm)	6.4 (0.5) cd	10.7 (0.2) a	6.9 (0.4) cde	7.2 (0.5) abcde	8.2 (0.4) ab
	Group VX3 (IPS Empress CAD 3 mm)	5.2 (0.3) e	10.2 (0.2) bc	6.8 (0.4) cdef	7.2 (0.4) abcd	6.4 (0.3) e
	Group VX4 (IPS e.max CAD 1.5 mm)	6.1 (0.4) d	10.2 (0.6) bc	6.7 (0.2) def	7.3 (0.6) abcd	8.0 (0.3) bc
	Group VX5 (IPS e.max CAD 3 mm)	4.2 (0.2) g	10.0 (0.5) bcd	6.6 (0.3) ef	6.9 (0.3) cde	5.8 (0.5) fg

n.a. not applicable

according to 16 curing modes. The microhardness indenter operated with a dynamic recording of test load and respective penetration depth of the indenter, allowing for simultaneous measurements of VH and Y_{HU}. With regard to VH, the surface microhardness of resin composite materials reflects mechanical properties such as resistance against wear/abrasion as a function of chemical composition, i.e. as a function of the organic as well as the inorganic/filler component [17]. Besides, surface microhardness has been shown to be a useful method to indirectly probe the DC of polymer networks within a given resin cement [12–14], and a previous study reported strong positive correlations between DC and surface microhardness or modulus of elasticity under experimental conditions comparable to the ones used in the present study [18]. With regard to Y_{HU}, the indentation modulus of a material reflects the readiness to elastically deform under functional stress. A strong positive correlation has previously been reported for different resin composite materials between the indentation modulus (measured under identical conditions as in the present study) and the flexural modulus as well as the flexural strength [19]. Measurement of VH and Y_{HU} of the five dual-curing resin cements showed significant differences between the resin cements as well as significant differences between the curing modes within one resin cement. Thus, the null hypothesis stating that all resin cements would yield similar VH and Y_{HU} was rejected. The 1-week storage in the present study was performed to investigate the effect of curing mode on the post-curing behaviour of the resin cements by means of VH and Y_{HU}. Clinically, glass ceramic restorations are loaded almost immediately after insertion, and in our previous study, we investigated the effect of curing mode on the immediate behaviour (i.e. during self-curing or shortly after light curing) of the resin cements by means of DC [4]. The positive correlations between DC of our previous study and the micromechanical properties VH and Y_{HU} of the present study varied in strength, which reflects a heterogeneous nature of the

Table 4 Spearman rank correlation coefficients between the degree of conversion (DC; previous study [4]) and Vickers hardness (VH) or indentation modulus (Y_{HU}) for each resin cement

Resin cement	Correlations	
	DC—VH	DC—Y_{HU}
Panavia F2.0	0.54	0.58
RelyX Unicem 2 Automix	0.61	0.42
SpeedCEM	0.42	0.36
BisCem	0.61	−0.06
BeautiCem SA	0.76	0.80

resin cements and suggests different effects of post-curing depending on the curing mode and the resin cement.

Generally, RelyX Unicem 2 Automix resulted in the highest VH and Y_{HU}, followed by BeautiCem SA, BisCem, SpeedCEM, and finally by Panavia F2.0. The high VH and Y_{HU} of RelyX Unicem 2 Automix are basically in accordance with another study comparing different dual-curing resin cements and in which the former RelyX Unicem also yielded the highest VH and Y_{HU} [2]. At the time of writing, BeautiCem SA had just been launched, and thus, no information about VH and Y_{HU} was available yet, and no information about VH and Y_{HU} could be found in literature for BisCem. With regard to SpeedCEM and Panavia F2.0, VH after 1 week of storage compared well with the VH determined in a previous study without storage [3].

When self-cured (groups SC), RelyX Unicem 2 Automix and SpeedCEM showed significantly lower VH and Y_{HU} compared to when light cured, BisCem and BeautiCem SA showed equal VH and Y_{HU}, and Panavia F2.0 showed significantly higher VH and Y_{HU}. When comparing VH (as an indirect determination of DC) obtained by RelyX Unicem 2 Automix and SpeedCEM with DC reported in our previous study [4], self-curing of both resin cements led to a significantly lower VH (measured after 1 week of storage) and a significantly lower DC (measured immediately) as when light curing was involved. In the previous study, BeautiCem SA was the only resin cement that showed an equal DC when self-cured as when light cured. A comparable result was found in the present study as BeautiCem SA yielded equal VH and Y_{HU} when self-cured compared to when light curing was involved. Whereas BisCem and Panavia F2.0 showed significantly lower DC when only self-cured, they now yielded equal (BisCem) or significantly higher (Panavia F2.0) VH and Y_{HU} as when light curing was involved. On the one hand, this suggests a marked post-curing effect of the two resin cements during the 1 week of storage. On the other hand, discrepancies between DC and micromechanical properties (such as VH and Y_{HU}) of the materials might be explained by a tendency to primary cyclization, a polymerization process that contributes to DC but not to overall network structure and (micro-) mechanical properties [20]. In the clinic, Panavia F2.0 is used after application of the ED Primer II. Thus, an additional self-curing mode was included (group SC*), and Panavia F2.0 was mixed with ED Primer II, which has been shown to accelerate curing [3, 21]. In the previous study and as expected, group SC* yielded significantly higher DC than all other curing modes of Panavia F2.0 [4], and in the present study, group SC* also showed significantly higher VH and Y_{HU} than the groups involving light curing. Interestingly, however, group SC* yielded significantly lower VH and Y_{HU} than group SC without ED Primer II. As measurements of DC in the previous study have shown, self-curing of Panavia F2.0 with ED Primer II yielded a DC of around 5 % as early as 1 min after the end of mixing and reached a DC of 60.1 % after 20 min. Self-curing of Panavia F2.0 without ED Primer II showed a rather slow increase in DC, reaching a DC of around 5 % only after 10 min and a DC of 29.4 % after 20 min [4]. This implies that ED Primer II accelerates curing of Panavia F2.0 and that curing of Panavia F2.0 without ED Primer II generally progresses slowly. However, based on VH and Y_{HU} of the present study, it may be that ED Primer II only accelerated curing of Panavia F2.0 at the very beginning and that this acceleration, at some point, hindered further curing and that Panavia F2.0 without the admixture of ED Primer II reached a more pronounced curing due to the 1-week storage. Moreover, storage in the present study was carried out at a temperature of 37 °C whereas measurement of DC in the previous study was carried out at room temperature (20 °C) [4]. It is likely that the higher temperature of the present study influenced curing of Panavia F2.0 to a higher extent than the admixture of ED Primer II whereas in the previous study and measured immediately at room temperature, the ED Primer II was required for Panavia F2.0 to cure.

When light cured (groups EF, VH, and VX), generally all five resin cements yielded similar or even higher VH and Y_{HU} when light cured through 1.5-mm-thick discs of IPS Empress CAD and IPS e.max CAD compared to when directly light cured through a Mylar strip (groups EF1, VH1, and VX1). It must be noted that when directly light cured, the resin cements were exposed to rather high irradiances (maximum irradiance: 1,545 mW/cm^2 for the second-generation and 1,869 or 3,505 mW/cm^2 for the third-generation LED curing unit), and there is a controversial discussion in literature whether high irradiances of light curing units negatively affect the curing of resin composite materials due to, e.g. higher concentrations of radicals resulting in a premature termination of curing or a lack of proper polymer network formation and structure [22–24]. It could be that the relatively high irradiances of the present study negatively affected VH and Y_{HU} of the resin cements when directly light cured and that the decrease in irradiance through 1.5-mm-thick discs of glass ceramic had a beneficial effect on the curing of the resin cements and the resulting micromechanical properties. However, it has previously been shown that the decrease in irradiance through 1.5-mm-thick ceramic discs was substantial, the decreases in irradiance ranging from 81.9 to 86.5 % depending on the glass ceramic material and the mode of the curing unit [4]. This suggests that not only the irradiance reaching the resin cements through the ceramic discs is of importance but also the light curing times. In order to have near identical radiant exposures for both LED curing units in the three modes used, light curing times were reduced with increasing irradiance of the mode (40 s for the Elipar FreeLight 2 in the Standard Mode, 32 s for the VALO in the High Power Mode, and 18 s for the VALO in the Xtra Power Mode).

It must be mentioned, though, that the light curing times used for the VALO were considerably longer than those recommended or stipulated by the manufacturer (i.e. 8 to 12 s for the High Power Mode and 3 to 6 s for the Xtra Power Mode) and that the decreased irradiance through 1.5-mm-thick ceramic discs in combination with the prolonged light curing times did not jeopardize the micromechanical properties of the present study. This is also in accordance with the previous study in which light curing of the resin cements through 1.5-mm-thick discs of the same ceramic materials led to a similar DC compared to direct light curing through a Mylar strip [4]. A similar DC when directly light cured compared to when light cured through a 1.5-mm-thick ceramic disc (IPS e.max) was also reported in a study by Oliveira et al. for two dual-curing resin cements when light curing was performed at room temperature (25 °C) [25]. In the present study and at a ceramic disc thickness of 3 mm, four of the five resin cements (Panavia F2.0, RelyX Unicem 2 Automix, BisCem, and BeautiCem SA) generally showed a significant reduction in VH and/or Y_{HU}. The decrease in irradiance through 3-mm-thick ceramic discs was ≥95 % compared to the maximum irradiance [4], and it is likely that even the prolonged light curing times could not compensate for this drastic decrease in irradiance. In corroboration with the results of the present study, Öztürk et al. also found that Vickers hardness and modulus of elasticity obtained following light curing of resin cements through thin (0.75 mm) ceramic discs were similar or significantly higher than these two micromechanical properties obtained following direct light curing through a Mylar strip and that, in contrast, Vickers hardness and modulus of elasticity obtained following light curing through thick (2 mm) ceramic discs were significantly lower [26]. The possible clinical implication may be to prolong the times even further when light curing resin cements through regions of glass ceramic restorations (e.g. of inlays/onlays or of partial crowns) of 3 mm thickness or more—despite the high irradiances of modern LED curing units. Prolonged light curing times at increased irradiances, however, may lead to a marked temperature rise at the tip end of the light curing unit with the temperature being e.g. >40 °C at the tip end of the VALO in the Xtra Power Mode after 6×3 s (curing mode of groups VX). Clinically, a marked temperature rise at the tip end of the light curing unit is not only a potential hazard for the pulp tissue (especially when light curing is performed directly or through thin glass ceramic restorations) but also for the surrounding soft tissues.

Finally, of the five resin cements investigated, SpeedCEM was the least affected by light curing through ceramic discs. This might be ascribed to a sensitive type or a high amount of photo-initiator used for the light curing part of the catalyst system. It must noted, however, that self-curing of SpeedCEM led to extremely low VH and Y_{HU}, and thus, this resin cement should only be recommended in clinical situations in which light curing is possible.

Comparing the micromechanical properties of the five resin cements, clinicians should keep in mind that the dual-curing resin cements performed very heterogeneously. Whereas self-curing alone seems inadequate for some dual-curing resin cements, other resin cements performed equally when either self- or light cured. Light curing through the glass ceramics of 1.5 mm thickness did not impair the micromechanical properties of the resin cements, most likely due to the higher irradiances (as provided particularly by the third-generation LED curing unit) in combination with the prolonged light curing times. However, when light cured through the glass ceramics of 3 mm thickness, most resin cements showed a significant reduction in the micromechanical properties investigated. Thus, clinicians should consider to prolong the light curing times (even with LED curing units providing high irradiances) when light curing resin cements through thick glass ceramic restorations.

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