Influence of ceramic thickness on mechanical properties

and polymer structure of dual-cured resin luting agents

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Short Title: Properties and structure of dual-cured luting resins

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ABSTRACT

Objective. To investigate the influence of ceramic thickness on the mechanical properties and polymer structure (degree conversion and cross-linking density) of three dual-cured resin luting agents

Methods. Three dual-cured resin luting agents {Linkmax HV (GC), Nexus 2 (Kerr), and Variolink IIHV (Ivoclar-Vivadent)} were polymerized with or without 800 mW/cm^2 irradiation through 0- to 3-mm-thick GN-I (GC) machinable ceramic. Bar-shape specimens were subjected to three-point bending to determine flexural strength (FS) and elastic modulus (EM) after dry storage at 37°C for 24 h. Knoop hardness was measured on the irradiated surface of disk-shaped specimens before (KHN1) and after (KHN2) storage of 100% ethanol solution at 37°C for 24 h. KHN1 and KHN2 were estimated as indirect indicators of degree of conversion (DC) and cross-linking density, respectively. Data were analyzed by one-way ANOVA and Student-Newman-Keuls test for each luting agent, and four mechanical properties were subjected to regression analysis.

Results. For three resin luting agents with dual-cured mode, FS, EM, KHN1 and KHN2 decreased with the increase of ceramic thickness. FS except for Nexus 2 and EM for three resin luting agents had a positive linear relationship with both KHN1 and KHN2.

Significance. The variables tested behaved differently. When the ceramic thickness increased, the chemical cured components of dual-cured resin luting agents did not produce significant compensation for all variables. Mechanical properties and polymer structure of dual-cured resin luting agents was dependent on the intensity of light irradiation.

1.   Introduction

Adequate polymerization is a crucial factor for obtaining optimal mechanical properties and satisfactory clinical performance of dental resin material. For light-cured resin materials, the reduction of energy density of light irradiation can decrease the degree of conversion (DC) and mechanical properties [1-4], which limits the application of light-cured resin luting agents in the bonding of thicker esthetic restorative materials.

Dual-cured resin luting agents were developed in an attempt to combine the desirable properties of chemically polymerizing and light polymerizing materials, and were expected to provide further polymerization by chemical catalysts in deeper areas or under thicker restoratives. However many studies have suggested that, even if under dual-curing mode, DC and final hardness of most dual-cured resin luting agents were reduced when the thickness of restorative materials is increased [5-8]. This may be attributed to the fact that fast light polymerization prevents any significant contribution from the chemical polymerization to DC of dual-cured resin luting agents [9].

Apart from thickness of restorations, the three curing modes (dual, light, and chemical) used for dual-cured resin luting agents may affect the mechanical properties [10-13]. It was believed that different brands of dual-cured resin luting

agent had different ratios of light/chemical catalysts. However Feng *et al.* [14] found that dual-cured composites could produce a similar DC polymerized by dual-cured and chemical-cured mode, but chemical-cured specimens showed a lower elastic modulus than dual-cured specimens. This suggests that dual-cured resin luting agents with different cure modes produce different polymer structures. Other studies showed that flexural properties of composite resin were not completely dependent upon DC [15,16]. Therefore, DC, despite being an important factor, does not give a complete characterization of polymer structures. Polymerization of the methacrylate monomers in dental resin can form a highly cross-linking matrix, in which a large number of strong covalent linkages between different kinetic chains may transform the molecules into a rigid, very high-molecular-weight material. The cross-linking density could affect the mechanical properties of dental resin material. Hardness of resin composite was shown to be a good predictor of DC [17]. The cross-linking density could be estimated indirectly by measuring the hardness of the polymer after ethanol softening [18-20]. With this method, it is inevitable that a certain amount of the polymeric material (unreacted monomer, oligomers, and linear polymer) is extracted into the ethanol.

Establishing the mechanical properties of ceramics is a matter of utmost importance in cementation of esthetic restorations involving dual-cured resin luting agents. Therefore, the purpose of the present study was to verify the influence of

increasing ceramic thickness on mechanical properties (flexural strength, elastic modulus, and Knoop hardness before and after ethanol softening) of three dual-cured resin luting agents.

## 2.	Materials and methods

2.1.	Ceramic and dual-cured resin luting agents

Three thick of ceramic plates (10 X 8 mm squares with 1.05, 2.05, and 3.05 mm thick) were prepared from machinable blocks (GN-I, shade A3, GC Corp., Tokyo, Japan) using a low-speed cutting saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA). Prefabricated ceramic material is mainly composed of SiO_2, K_2O, and Al_2O_3 and the main precipitated crystal is leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$. The ceramic plates were sanded to a flat surface by hand-grinding on wet 320-, 400-, 600-, and 800-grit silicon carbide paper and cleaned ultrasonically in distilled water for 5 min. The final thickness of each ceramic plate was 1.0, 2.0, and 3.0 mm. Three dual-cured resin luting agents (Linkmax HV, Nexus 2, and Variolink IIHV) were also prepared. Descriptions of these materials are summarized in Table 1.

2.2.	Specimens preparation for flexural strength and elastic modulus

Flexural strength and elastic modulus were evaluated according to ISO 4049 [21].

The apparatus as shown in Fig 1 were prefabricated with non-transparent self-cured pattern resin (GC Corp., Tokyo, Japan). The center of apparatus was a cylinder slot with 2.6 mm in height, 2.6 mm width, and 25 mm length to hold the resin specimens. There was a spaces above the cylinder slot, whose dimensions were 10 X 32 mm square with about 1, 2, and 3 mm in height respectively, in order to hold four pieces same thick ceramics aligned tightly to cover completely the resin specimens. When direct irradiation, there was no space above the cylinder slot in the apparatus. Equal amounts of base and catalyst pastes of dual-cured resin luting agents were mixed with a plastic spatula on a mixing pad for 10 s according to the manufacturers' directions, and put into a 2 X 2 X 25 cylinder glass tube template (cross-section square of inside 2 X 2 mm, outside 2.6 X 2.6 mm, VitroCom Inc., Mountain Lakes, NJ, USA) to fabricate 2 X 2 X 25 mm beam specimens. Specimens were put into the prefabricated apparatus as shown in Fig. 1, and polymerized by five different irradiation conditions: (1) direct irradiation, (2) irradiation through the overlays of different thickness (1, 2, and 3 mm) ceramics, in which four pieces same thick ceramics were aligned tightly above the specimens, (3) without irradiation. First the center of the specimen, and then the two ends were irradiated, respectively, by a halogen-visible-light-curing unit (Candelux VL-5, J Morita Mfg., Corp., Kyoto, Japan) with an 11-mm tip of light guide at an 800 mW/cm^2 light intensity for 3 X 40 seconds overlapping exposures. The output intensity of the light unit was assessed by

its own radiometer to ensure a constant output. Other specimens were polymerized directly without ceramic or without irradiation. After removed from the glass tube template, the specimens were transferred to a light-proof container maintained at 37 ± 1°C for 24 h. Seven specimens were prepared for each group. The irradiated side of specimens was used as the compressive side to receive a 3-point bending flexural test, which performed with a span length of 20 mm and a cross-head speed of 1 mm/min using a universal testing machine (model 5566S, Instron Corp, Canton, MA, USA). Flexural strength (FS) was calculated using $\sigma = 3Fl/2bh^2$; elastic modulus (EM) was calculated using $E = F_1l^3/4bh^3d$. Where σ is the flexural strength (in MPa), E is the elastic modulus (in GPa), F is the maximum load, in Newtons, exerted on the specimen, F_1 is the load, in Newtons, at a convenient point in the straight line portion of the trace; l is the distance between supports, b is the width and h is the height of the specimen (all in mm).

2.3.   Specimens preparation for Knoop hardness

Resin paste was placed in a non-transparent cylindrical acrylic mold (h=2 mm, d=4.5 mm), and covered by a clear micro-cover glass (thickness 0.15 mm, Matsunami Glass Ind., Ltd., Tokyo, Japan) to form a flat surface. Irradiation conditions were performed corresponding to procedures described above for specimens preparation of flexural strength. After the micro-cover glass was removed, specimens were stored in dry

conditions at 37°C for 24 h. A Knoop diamond indenter was applied under a load of 25 g for 30 s and the length of the indentation's long diagonal was measured using a digital microhardness tester (MVK-E, Akashi Co., Ltd., Tokyo, Japan) after the applied load was removed. The Knoop Hardness Number (KHN) is inversely proportional to the square of the long diagonal of the indentation and used for DC assessment. Subsequently, specimens were stored in 100% ethanol solution at 37°C for 24 h and Knoop hardness number was measured again for assessment of cross-linking density. Five specimens were prepared for each group. Each specimen had five readings averaged to form a single value.

2.4.   Statistical analysis

Data were analyzed by one-way analysis of variance (ANOVA), separately for each of the dual-cured resin luting agents tested, for all mechanical properties. Student-Newman-Keuls post hoc test was used for multiple comparisons, with global significance level at $p=0.05$. For four irradiation conditions except without irradiation, the Pearson's correlation coefficient and corresponding level of significance at $p=0.05$ were calculated to analyze a possible correlation between two mechanical properties.

3.   Results

FS and EM are shown in Table 2 for five different irradiation conditions. FS decreased with the increase of ceramic thickness for three resin luting agents. No significant differences in FS between irradiation conditions were observed for LMHV. For NX2, there was no significant difference in FS between specimens without irradiation and other irradiation conditions. VLIIHV irradiated through 3-mm-thick ceramic showed lower FS than that irradiated through 0-2 mm thick ceramic, and higher FS than that without irradiation. For all dual-cured resin luting agents, specimens irradiated directly showed the highest EM, and those without irradiation showed significantly lower EM. Specimens irradiated through 1- to 3-mm-thick ceramic showed intermediate EM. Although EM decreased with the increase of ceramic thickness, for only LMHV, EM irradiated through 1-3 mm thick ceramic showed no significant differences.

KHNs for specimens stored in dry conditions for 24 h (KHN1) followed by storage in an ethanol solution for 24 h (KHN2) are shown in Table 3 for five different irradiation conditions. For LMHV and NX2, no significant difference in KHN1 was observed between specimens with direct irradiation and without irradiation. VLIIHV without irradiation showed lower KHN1 than that with direct irradiation. Three dual-cured resin luting agents showed significant decrease of KHN1 and KHN2 with

the increase of ceramic thickness. For all dual-cured resin luting agents, specimens with direct irradiation showed the highest KHN2. LMHV and VLIIHV without irradiation showed the lowest KHN2, while that of NX2 was higher than those irradiated through 3-mm-thick ceramic.

Pearson's correlation coefficient and respective p values are shown in Table 4 for each dual-cured resin luting agent. Statistically significant correlations could be detected between all properties for LMHV and VLIIHV, except between FS and EM. For NX2, significant correlation between two properties among three properties of EM, KHN1, and KHN2 were observed.

4. Discussion

Musanje *et al*. [22] found that even under 25 mW/cm^2 light intensity, the light curing reaction could be initiated in resin composites. Our previous study showed that 800 mW/cm^2 light intensity through 1-3 mm machinable ceramic was reduced to 310, 160 and 80 mW/cm^2, respectively [8]. Although these reduced light intensities were enough to initiate the light curing reaction, they produced a continuous reduction of KHN1 with increase of ceramic thickness, and the chemical component of dual-cured luting agents did not produce significant compensation for KHN1. Nevertheless, three dual-cured resin luting agents without irradiation produced rather high KHN1,

similar to those with direct irradiation. This result further support these previous viewpoint that fast light polymerization can prevent the role of chemical polymerization of dual-cured resin luting agents. Truffier-Boutry *et al*. [23] suggested that fast hardening of resin matrix monomers under light polymerization could trap a large excess of free radicals, and although these free radicals can come into "contact" with double bonds of the methacrylated groups, they could only increase the DC of resin slightly.

KHN2 (cross-linking density) had a positive linear relationship to KHN1 (DC) for three dual-cured resin luting agents, which indicated a relationship between cross-linking density and DC. As mentioned by other studies on light-cured resin composite under different curing modes, a rapid standard continuous polymerization will initiate a multitude of growth centers and a polymer with a higher cross-linking density, while relatively few centers of polymer growth may favor the formation a more linear polymer structure with relatively few cross-links [18-20]. When without irradiation, chemical polymerization of dual-cured resin luting agents had a lower initiation rate, and generated fewer radicals per unit time and less termination by radical termination, which may favor the formation of extended polymer chains and hence less cross-linking. However, dual-cured resin luting agents with dual-cured mode could produce higher KHN2 than those without irradiation, except for NX2 irradiated through 3 mm thick ceramic. Even under low light intensity irradiation,

dual-cured resin still has a large amount of free radicals, mostly from chemical catalysts trapped in the hardening resin matrix. Although these trapped free radicals did not contribute significantly to overall DC, they could improve the cross-linking density of dual-cured resin luting agents through combining with a double link of methacrylated groups in local resin matrix to finish termination. In this study, absolute hardness values should not be used to compare the DC and cross-linking density between three resin luting agents, because of effects arising from variation in monomer composition, filler content, and type.

Although FS showed a significant linear relationship with both KHN1 and KHN2 for LMHV and VLIIHV under dual-cured mode, the statistical result of FS for NX2 did not support completely this linear relationship. For brittle materials, FS may be more sensitive to surface imperfections such as cracks, voids, and related flaws. Dual-cured resin luting agents usually produce voids (porosity) more easily, which is a consequence of incorporating air while mixing the two pastes. These imperfections may have interfered with the result of FS for NX2 in this study.

EM had a strong linear relationship with both KHN2 and KHN1 for three dual-cured resin luting agents. According to correlation coefficient of KHN1 and KHN2, crosslink density (KHN2) had a stronger effect on EM for LMHV and NX2, while DC (KHN1) had stronger effect on EM for VIIHV. It suggested that EM was depended not only on DC but also on crosslink density. This might further explain the

phenomena that EM, KHN1, and KHN2 were reduced continuously with increase of ceramic thickness under dual-cured mode. In other words, the chemical cured components of dual-cured resin luting agents did not produce significant compensation for these properties.

An optimal dental polymeric material would have high both DC and cross-linking density, which may be advantageous not only from the point of view of certain mechanical properties, but also because of reduced susceptibility to the softening action of food substances and to enzymatic attack. In conclusion, within the limitations of this study, the results described above imply that dual-cured resin luting agents with direct irradiation produced the best mechanical properties and polymer structure, suggesting that improvement of light irradiation conditions, such as longer irradiation periods and multidirectional irradiation is still necessary in clinics to overcome the influence of ceramic thickness.

REFERENCES

[1] Nomoto R, Uchida K, Hirasawa T. Effect of light intensity on polymerization of light-cured composite resins. Dent Mater J 1994;13:198-205.

[2] Unterbrink GL, Muessner R. Influence of light intensity on two restorative systems. J Dent 1995;23:183-9.

[3] Emami N, Soderholm KJ. How light irradiance and curing time affect monomer conversion in light-cured resin composites. Eur J Oral Sci 2003;111:536-42.

[4] Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. J Dent Res 2005;84:659-62.

[5] Hasegawa EA, Boyer DB, Chan DC. Hardening of dual-cured luting agents under composite resin inlays. J Prosthet Dent 1991;66:187-92.

[6] El-Mowafy OM, Rubo MH. Influence of composite inlay/onlay thickness on hardening of dual-cured resin luting agents. J Can Dent Assoc 2000;66:147.

[7] Ozyesil AG, Usumez A, Gunduz B. The efficiency of different light sources to polymerize composite beneath a simulated ceramic restoration. J Prosthet Dent 2004;91:151-7.

[8] Meng X, Yoshida K, Atsuta M. Surface hardness development of dual-cured resin luting agents through different thickness of ceramics. Dent Mater J 2006;25:132-7.

[9] Lee IB, Um CM. Thermal analysis on the cure speed of dual cured resin cements under porcelain inlays. J Oral Rehabil 2001;28:186-97.

[10] Darr AH, Jacobsen PH. Conversion of dual luting cements. J Oral Rehabil 1995;22:43-7.

[11] Hofmann N, Papsthart G, Hugo B, Klaiber B. Comparison of photo-activation versus chemical or dual-curing of resin-based luting luting agents regarding flexural strength, modulus and surface hardness. J Oral Rehabil 2001;28:1022-8.

[12] Braga RR, Cesar PF, Gonzaqa CC. Mechanical properties of resin cements with different activation modes. J Oral Rehabil 2002;29:257-2.

[13] Lu H, Mehmood A, Chow A, Powers JM. Influence of polymerization mode on flexural properties of esthetic resin luting agents. J Prosthet Dent 2005;94:549-54.

[14] Feng L, Suh BI. The effect of curing modes on polymerization contraction stress of a dual cured composite. J Biomed Mater Res B Appl Biomater 2006;76B:196-202.

[15] Ferracane JL, Greener EH. The effect of resin formation on the degree of conversion and mechanical properties of dental restorative resins. J Biomed Mater Res 1986;20:121-31.

[16] Viljanen EK, Lassila LV, Skrifvars M, Vallittu PK. Degree of conversion and

flexural properties of a dendrimer/methyl methacrylate copolymer: design of experiments and statistical screening. Dent Mater 2005;21:172-7.

[17] Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. J Dent Res 1988;67:932-7.

[18] Asmussen E, Peutzfeldt A. Influence of pulse-delay curing on softening of polymer structures. J Dent Res 2001;80:1570-4.

[19] Asmussen E, Peutzfeldt A. Two-step curing: influence on conversion and softening of a dental polymer. Dent Mater 2003;19:466-70.

[20] Soh MS, Yap AU. Influence of curing modes on crosslink density in polymer structures. J Dent 2004;32:321-6.

[21] International Organization for Standardization. ISO4049:2000:Dentistry-Polymer-based filling, restorative and luting materials, Geneva, Switzerland.

[22] Musanje L, Darvell BW. Polymerization of resin composite restorative materials: exposure reciprocity. Dent Mater 2003;19:531-41.

[23] Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, Leloup G. A physico-chemical explanation of the post-polymerization shrinkage in dental resins. Dent Mater 2006;22:405-12.

Table 1-Dual-cured resin luting agents tested in this study (information provided by manufacturers)

Dual-cured resin luting agents	Batch	Manufacturer	Monomer	Filler			Initiator	
				Content (wt%)	Size (µm)	Component	Base	Catalyst
Linkmax HV (LMHV)	B:0601131 C:0601131	GC Corp. (Tokyo, Japan)	UDMA TEGDMA	70.0	0.8	F-Al-Si-glass	CQ, amine	BPO
Nexus 2 (NX2)	439766	Kerr Corp. (Orange, CA, USA)	Bis-GMA UDMA TEGDMA	68.0	0.6	Ba-Al-B-Si-glass SiO_2	CQ, amine	BPO
Variolink IIHV (VLIIHV)	B:H23580 C:H22074	Ivoclar-Vivadent (Schaan, Liechtenstein)	Bis-GMA UDMA TEGDMA	75.3	0.7	Ba-Al-F-Si-glass	CQ amine	BPO

UDMA: urethane dimethacrylate, TEGDMA: triethyleneglycol dimethacrylate, Bis-GMA: bis-phenol-A-diglycidylmethacrylate, Al: aluminium, B: boron, Ba: barium, F: fluorine, Si: silicon, BPO: benzoyl peroxide, CQ: camphorquinone

Table 2-Mean flexural strength (FS, MPa) and elastic modulus (EM, GPa) for three dual-cured resin luting agents at different irradiation conditions

Dual-cured resin luting agent	Linkmax HV (LMHV)		Nexus 2 (NX2)		Variolink IIHV (VLIIHV)	
Irradiation condition	FS (SD)*	EM (SD)*	FS (SD)*	EM (SD)*	FS (SD)*	EM (SD)*
Direct irradiation	132.1 (12.9)^A	11.2 (0.3)^A	137.2 (12.7)^A	8.4 (0.2)^A	130.1 (16.0)^A	10.4 (0.2)^A
Irradiation through 1 mm ceramic	123.9 (13.5)^A	10.5 (0.2)^B	134.0 (9.7)^{A,B}	7.8 (0.3)^B	128.5 (6.2)^A	10.1 (0.3)^{A,B}
Irradiation through 2 mm ceramic	118.1 (14.7)^A	10.1 (0.3)^B	116.0 (14.9)^{B,C}	7.5 (0.3)^C	123.9 (13.9)^A	9.9 (0.3)^{B,C}
Irradiation through 3 mm ceramic	114.0 (12.2)^A	10.0 (0.5)^B	112.9 (14.8)^C	6.7 (0.2)^D	110.3 (8.1)^B	9.7 (0.1)^C
Without irradiation	117.1 (10.4)^A	8.7 (0.8)^C	120.2 (17.7)^{A,B,C}	7.0 (0.2)^D	95.1 (10.9)^C	7.2 (0.6)^D

*Same superscript letters at each property for each dual-cured resin luting agent were not significantly different by Student-Newman-Keuls test ($p>0.05$).

Table 3-Mean Knoop hardness number before (KHN1) and after (KHN2) storage in ethanol for 24 h for three dual-cured resin luting agents at different irradiation conditions

Dual-cured resin luting agent	Linkmax HV (LMHV)		Nexus 2 (NX2)		Variolink IIHV (VLIIHV)	
Irradiation condition	KHN1 (SD)*	KHN2 (SD)*	KHN1 (SD)*	KHN2 (SD)*	KHN1 (SD)*	KHN2 (SD)*
Direct irradiation	44.8 (1.8)^A	18.3 (0.7)^A	33.8 (1.3)^A	15.5 (0.9)^A	40.9 (1.3)^A	19.1 (1.5)^A
Irradiation through 1 mm ceramic	42.5 (1.9)^B	17.4 (1.0)^B	30.0 (2.0)^B	14.1 (0.9)^B	37.5 (3.1)^B	18.5 (1.0)^A
Irradiation through 2 mm ceramic	37.9 (1.9)^C	16.0 (1.4)^C	26.6 (2.6)^C	13.5 (1.2)^{BC}	34.6 (2.4)^C	16.4 (1.1)^B
Irradiation through 3 mm ceramic	36.4 (1.9)^D	15.6 (1.2)^C	16.3 (2.4)^D	11.7 (1.2)^D	29.3 (2.7)^D	14.8 (1.3)^C
Without irradiation	44.0 (1.8)^A	13.3 (0.5)^D	34.8 (2.1)^A	13.3 (0.5)^C	38.4 (1.9)^B	13.2 (1.0)^D

*Same superscript letters at each property for each dual-cured resin luting agent were not significantly different by Student-Newman-Keuls test (p>0.05).

Table 4-Pearson's correlation coefficient and respective p value between two properties

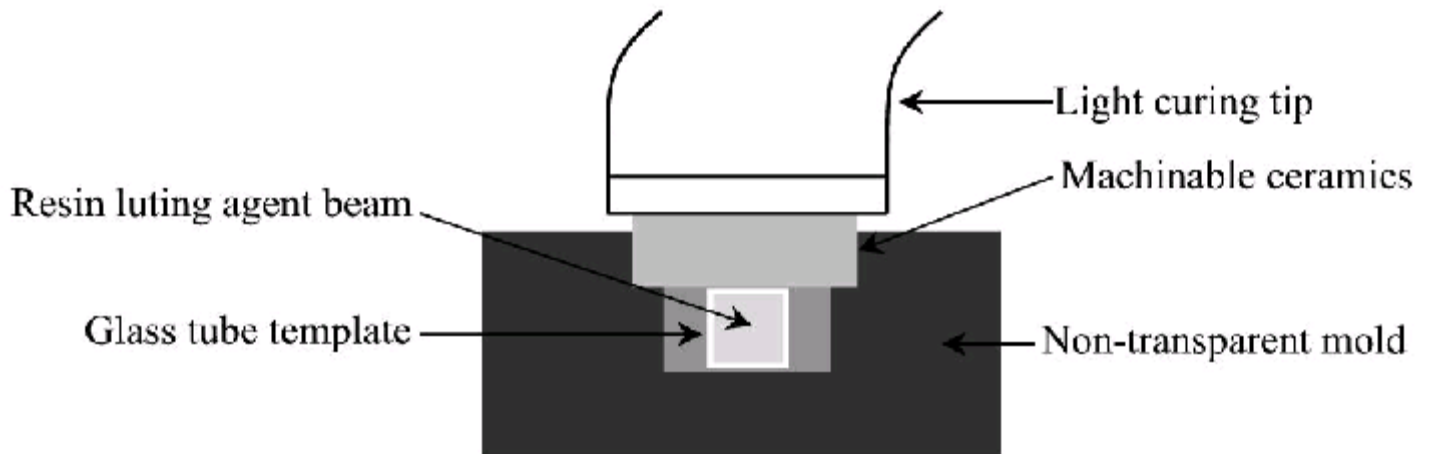| Dual-cured resin	Correlation between two properties					
luting agent	FS-EM	FS-KHN1	FS-KHN2	EM-KHN1	EM-KHN2	KHN1-KHN2
LMHV	0.985 (p=0.007)	0.978 (p=0.011)	0.985 (p=0.007)	0.950 (p=0.025)	0.967 (p=0.017)	0.998 (p=0.001)
NX2	0.892 (p=0.054)	0.873 (p=0.063)	0.884 (p=0.058)	0.985 (p=0.007)	1.000 (p<0.001)	0.983 (p=0.008)
VLIIHV	0.880 (p=0.060)	0.960 (p=0.020)	0.946 (p=0.027)	0.978 (p=0.011)	0.955 (p=0.022)	0.978 (p=0.011)

Fig. 1 Diagram of the experimental set-up to polymerize resin luting agent through different thick machinable ceramics using a halogen visible light curing unit.