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Effect of immediate and delayed light activation on the mechanical properties and degree of conversion in dual-cured resin cements

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Abstract: We evaluated the effect of activation mode (immediate or delayed light activation vs. no light activation) on diametral tensile strength (DTS), elastic modulus, ultimate tensile strength (UTS), and degree of conversion (DC) in dual-cured resin cements. Three resin cements were evaluated: Enforce, RelyX ARC, and Panavia F. The mixed cements were inserted into circular molds for the DTS test and into dumbbell-shaped molds for the UTS test. Inside the molds, the cements were light-activated either immediately or after 5 min (delayed light activation). If no light activation was performed, the materials were protected from light exposure (control). The DTS and UTS tests were performed until fracture. The elastic modulus was calculated using data from the DTS test, and DC was evaluated 24 h after manipulation using near-infrared spectroscopy. Data for each variable were individually analyzed by two-way ANOVA and the post-hoc Tukey test ($\alpha = 0.05$). Regarding DTS, activation mode influenced only Panavia F specimens, which had the lowest DTS values in the absence of light activation. Activation mode did not influence the elastic modulus or UTS of any resin cement evaluated. Immediate light activation yielded higher DC values as compared with the absence of light activation. (J Oral Sci 54, 261-266, 2012)

Keywords: resin cement; polymerization; dental cement.

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Introduction

Dual-cured resin cements were introduced to combine the favorable characteristics of self-cured and light-cured agents. The rationale was to develop a material that has an extended working time and is capable of reaching a high degree of conversion (DC) in the presence or absence of light. During cementation of posts and thick indirect restorations, exposed marginal areas can benefit greatly from photo activation, as they are readily accessible to the curing light; however, intensity may significantly decrease due to reflecting and scattering effects (1,2). Therefore, in some situations, the polymerization reaction is activated mainly by a chemical mechanism (self-cure).

Some studies suggest that dual-polymerized resin cements depend on light exposure to achieve better mechanical properties (3,4). However, other studies have

Table 1 Materials used in the present study

Material	Manufacturer	Composition*	Shade	Filler load (%) by volume
Enforce	Dentsply Petrópolis, RJ, Brazil	Base: Bis-GMA, TEGDMA, CQ, EDAB, BHT and DHEPT. Catalyst: Bis-GMA, BHT, EDAB, TEGDMA and BPO.	Translucent	66.0
RelyX ARC	3M ESPE St. Paul, MN, USA	Paste A: Bis-GMA, TEGDMA, dimethacrylate polymer, CQ, amine. Paste B: Bis-GMA, TEGDMA, dimethacrylate polymer, BPO	Transparent (A1)	67.5
Panavia F	Kuraray Co. Osaka, Japan	Paste A: 10-MDP, hydrophobic and hydrophilic dimethacrylate, CQ, BPO. Paste B: Hydrophobic and hydrophilic dimethacrylate, DHEPT, T-iso propylic benzenic sodium sulfinate	Light	78
ED Primer	Kuraray Co. Osaka, Japan	Primer A: HEMA, 10-MDP, NM-aminosalicylic acid, DHEPT, water Primer B: NM- aminosalicylic acid, T-isopropylic benzenic sodium sulfinate, DHEPT, water		—

*Information provided by the manufacturer

Bis-GMA: bisphenol-A glycidyl dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; CQ: camphorquinone; EDAB: ethyl 4-dimethylamine benzoate; BHT: butylhydroxytoluene; DHEPT: N,N-di-(2-hydroxyethyl)-4-toluidine; BPO: benzoyl peroxide; 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate; HEMA: hydroxyethyl methacrylate.

found similar properties in dual-cure resin cements tested after light activation and in self-cure mode (5,6). One hypothesis is that light activation negatively affects the self-curing mechanism (7), possibly because rapid formation of a cross-linked polymer upon exposure to light leads to entrapment of the reactive species, including the activators and initiators needed for the self-cure reaction. Thus, a delay between cement mixing and light activation might increase total free-radical concentration, which would lead to a higher overall DC, thereby ultimately improving the cement's mechanical properties (8-10).

The effect of delayed light activation on the DC of dual-cured resin cements seems to depend on the material and light intensity (10). However, no negative effect of delayed light activation on the DC has been demonstrated (9,10). Moreover, delayed light activation is effective in reducing stress shrinkage due to resin cement polymerization (10). Shrinkage stress is related mainly to the DC, rate of polymerization, and elastic modulus (11,12). A higher DC increases polymerization shrinkage and, consequently, the stress generated by shrinkage (13). A slower polymerization reaction (i.e., a low rate of polymerization) and lower elastic modulus reduce shrinkage stress (14,15).

In relation to dual-cured resin cements, it has been demonstrated that delayed light activation reduces shrinkage stress (10). Moreover, the DC was higher or similar to those obtained with immediate light activation. Interestingly, the rate of polymerization was not directly related to shrinkage stress, which suggests that the elastic modulus of resin cements was the main reason for the decrease in polymerization stress. In addition to reduced shrinkage stress, maintenance of the mechanical properties of resin cement is important in the clinical performance of indirect restorations. Thus, the purpose of this study was to investigate the effect of immediate and delayed light activation on the mechanical properties and DC of three commercially available dual-cured resin cements. As an experimental control, the cements were also tested in the absence of light. The hypothesis tested was that the point of light activation would not influence the mechanical properties or DC of the resin cements.

Materials and Methods

The name and composition of the investigated dual-cured resin cements are listed in Table 1. Panavia F was mixed with ED Primer before evaluation, as the manufacturer states that the primer is essential for proper cement polymerization. For this material, one drop each of primer liquids A and B were mixed for 10 s, after which the solution was gently air-dried for 5 s to allow the solvent to evaporate. Thereafter, 1 μL (1.4 mg) of this solution was dispensed onto a glass slab using a micropipette (model NPX2; Nichipet EX, Santa Clara, CA, USA) and mixed with the base and catalyst pastes (27 mg of each) of the dual-cure cement for 15 s. The volume of ED Primer added to the cement was based on information from a previous study (16).

The following polymerization scenarios were tested for all resin cements:

Immediate light activation: The resin cements were immediately light-activated in accordance with the manufacturers' recommended times, i.e., 20 s for Panavia F, 30 s for Enforce, and 40 s for RelyX ARC.

Table 2 Means (± SD) for diametral tensile strength (MPa)

	Activation mode		
Resin cement	Immediate light activation	Delayed light activation	Chemical activation
Enforce	33.7 (5.7) Aa	38.0 (6.5) Ba	30.8 (5.8) Aa
RelyX ARC	40.9 (6.4) Aa	52.2 (7.3) Aa	40.3 (9.3) Aa
Panavia F	35.3 (3.9) Aa	26.7 (4.6) Ba	17.0 (6.9) Bb

Values followed by the same letter are not statistically different ($P > 0.05$). Upper case letters refer to values in the same column; lower case letters refer to values in the same row.

Table 3 Means (± SD) for elastic modulus (MPa)

	Activation mode		
Resin cement	Immediate light activation	Delayed light activation	Chemical activation
Enforce	288.8 (49.6) ABa	327.6 (27.7) Aa	252.8 (28.1) Aa
RelyX ARC	335.4 (18.3) Aa	337.7 (43.2) Aa	324.5 (28.9) Aa
Panavia F	225.5 (46.4) Ba	259.7 (47.1) Aa	296.9 (68.8) Aa

Values followed by the same letter are not statistically different ($P > 0.05$). Upper case letters refer to values in the same column; lower case letters refer to values in the same row.

Delayed light activation: The luting agents were light-activated 5 min after beginning the mixing procedure for the same time durations described above.

Chemical activation: no light activation was performed, and polymerization was self-activated only.

All light activations were performed with a halogen-based light-curing unit (Optilux 501; Demetron Kerr, Orange, CA, USA). The output of the light-curing unit was periodically checked using a handheld radiometer (Model 100, Demetron Kerr) and was confirmed to be ≤ 800 mW/cm^2.

Diametral tensile strength and elastic modulus

Specimens were created using circular molds (5.0 mm in diameter and 2.5 mm in height). Mixed resin cements were inserted into the mold, and a Mylar strip was placed over the cement to avoid polymerization inhibition by oxygen. Five specimens were created per experimental condition and stored in a dark container at 37°C for 24 h before testing. Before the test, the dimensions of each specimen were input into TESC software (EMIC, São José dos Pinhais, PR, Brazil), which calculated the elastic modulus and DTS according to the dimensions and load. In a testing machine (EMIC DL-500, São José dos Pinhais, PR, Brazil) a compressive load was applied to the diametral surface of specimens at a cross-head speed of 1.0 mm/min until fracture. Data for the DTS and elastic modulus were analyzed individually by two-way ANOVA (with the cement and curing method as the main factors) using Sigmastat 3.5 statistical software (Systat Software Inc, San Jose, CA, USA). Multiple pair-wise comparisons were performed using the Tukey post-hoc test ($\alpha = 0.05$).

Ultimate tensile strength

Silicone dumbbell-shaped molds (13 mm long × 1 mm thick) with a gauge length of 5 mm and a cross-section of approximately 1 mm^2 were used to create the specimens for the UTS test. Mixed resin cements were inserted into the mold, and a Mylar strip was placed over the cement. Ten dumbbell-shaped specimens were created per experimental condition and stored in a dark container at 37°C for 24 h before testing. After storage, the specimens were attached to a testing machine (EMIC DL-500) with a cyanoacrylate adhesive and tested at a cross-head speed of 1 mm/min until fracture. The cross-sectional area of fractured specimens was measured with a digital caliper. UTS was calculated as UTS = F/A, where F is the tensile force at fracture (N) and A is the cross-sectional area of the specimen (mm^2). The data were analyzed by two-way ANOVA and the Tukey post-hoc test ($\alpha = 0.05$).

Degree of conversion

DC of the resin cements ($n = 3$) was determined using Fourier transform near-infrared spectroscopy (FTIR; Vertex 70, Bruker Optik, Germany). Disc-shaped specimens were made using a silicone mold (h = 1 mm, Ø = 7 mm) between two glass slides. FTIR spectra were recorded 24 h after manipulation in the absorbance mode; 32 scans were collected at a resolution of 6 cm^{-1}. The resin cements were light-cured or not, following the same procedures described previously. DC was determined by calculating the variation in intensity of the methacrylate peak (at 1665 cm^{-1}) as compared with the uncured mate-

Table 4 Means (± SD) for ultimate tensile strength (MPa)

Resin cement	Activation mode: Immediate light activation	Delayed light activation	Chemical activation	Pooled average
Enforce	65.6 (13.5)	64.3 (9.7)	67.4 (12.5)	65.6 (11.7) A
RelyX ARC	65.0 (9.8)	64.5 (17.7)	67.0 (9.0)	65.0 (12.4) A
Panavia F	47.6 (13.4)	51.7 (11.8)	41.5 (10.6)	47.6 (12.3) B

Different letters after mean pooled averages represent statistically significant differences between values ($P < 0.05$).

Table 5 Means (± SD) for degree of conversion (%)

Resin cement	Activation mode: Immediate light activation	Delayed light activation	Chemical activation	Pooled average
Enforce	81.5 (0.6)	79.8 (0.4)	75.3 (1.1)	78.9 (2.9) B
RelyX ARC	86.8 (0.9)	88.3 (0.9)	83.3 (0.9)	86.1 (2.4) A
Panavia F	79.7 (4.2)	74.5 (5.4)	78.0 (4.5)	77.4 (4.7) B
Pooled average	82.7 (3.9) a	80.9 (6.6) ab	78.9 (4.2) b	

Different letters in the same column, or different letters after means in the same row, represent statistically significant differences between the relevant values ($P < 0.05$).

rial. Data were analyzed by two-way ANOVA and the Tukey post-hoc test ($\alpha = 0.05$).

Results

Diametral tensile strength

ANOVA showed a significant effect for the resin cement ($P < 0.001$), activation mode ($P < 0.001$), and their interaction ($P = 0.009$). The results of the Tukey test are shown in Table 2. The absence of light activation resulted in a significantly lower DTS only for Panavia F specimens ($P < 0.05$), i.e., there was no significant difference in DTS with respect to activation mode for the other cements. All the cements had a similar DTS after immediate light activation. After delayed light activation, RelyX ARC had the highest DTS, but the other two cements did not significantly differ. In the absence of light activation, DTS was significantly lower for Panavia F than for the other cements ($P < 0.05$); Enforce and RelyX ARC had similar DTS means for this activation mode.

Elastic modulus

ANOVA showed a significant effect for the resin cement ($P < 0.001$) and the interaction between resin cement and activation mode ($P = 0.003$). Table 3 shows mean elastic modulus values, which were evaluated by using the Tukey test. Activation mode did not significantly alter mean elastic modulus values in any resin cement. A significant difference among cements was noted only after immediate light activation, namely, the mean elastic modulus was significantly higher for RelyX ARC than for Panavia F ($P < 0.05$). Enforce had intermediate values that did not significantly differ from those of the other cements.

Ultimate tensile strength

ANOVA showed a significant effect only for resin cement ($P < 0.001$). UTS values are shown in Table 4. The pooled mean UTS for Panavia F was significantly lower than those for the other cements. There was no difference between RelyX ARC and Enforce.

Degree of conversion

ANOVA showed a significant effect for the resin cement ($P < 0.001$) and activation mode ($P = 0.033$); however, the interaction between these factors was not significant ($P = 0.082$). The results for DC are shown in Table 5. RelyX ARC had the highest DC, while Panavia F and Enforce had significantly lower values. Immediate light activation resulted in a higher mean DC than did chemical activation. Delayed light activation resulted in an intermediate DC values, which did not significantly differ from those obtained with the other activation modes.

Discussion

Although the DC of resin-based materials can be used to estimate their mechanical properties, the development of these properties is both complex and related to the resulting polymeric structure (16,17). In the present study, the same test was used to evaluate two mechanical properties: DTS and elastic modulus. The latter is commonly calculated from data for a stress versus strain curve generated during flexural strength testing. However, the load applied on the specimen during the DTS test is more similar to those that occur from resin cement in clinical applications. Resin cement is confined between the indirect restoration and the tooth structure. Thus, it is compressed against the dental structure when an occlusal load is applied to the restoration, similar to the design of the DTS test. The DTS test was chosen in the present study due to this comparable load application. Clinically, cements with satisfactory DTS and elastic modulus may support higher occlusal loads, thereby potentially improving the longevity of restorations.

The main factors that determine the mechanical properties of resin-based material are DC (3,18), cross-linking density (19,20), and filler content (21,22). The first two factors are directly related to the polymerization process and can be influenced by the activation mode of the polymerization reaction and by the type and ratio of monomers (17). In the present study, the activation mode changed the DTS only in Panavia F specimens. This cement had the lowest values in the absence of light activation; immediate and delayed light activation yielded similar DTS values. As compared with DC values after immediate light activation, all the evaluated cements had lower values in the absence of light activation. These findings concord with those of previous studies (1-4). However, Panavia was the only cement that had a lower DTS in the absence of light activation, due to the polymeric structure that developed during polymerization. In the absence of light activation, slower polymerization reduces cross-linking density and results in a weaker polymer (16,19,20).

If slower polymerization affected the DTS of Panavia F, the same would be expected for the other cements. However, this expected reduction in DTS was not observed in Enforce or RelyX ARC specimens. Unlike Panavia F, the other two cements contain the resin monomer Bis-GMA. The use of this stiff monomer in resin-based cements reduces cyclization and thus increases the cross-linking density of the polymer (17). The mechanical properties of Bis-GMA are superior to those of more flexible monomers. Thus, the putative effect of slower polymerization on cross-linking density was more apparent for Panavia F, which contains a greater number of flexible monomers. Polymeric structure also explains why there was no difference in DTS between the resin cements only after immediate light activation. Polymerization rate is higher in this activation mode, which increases the density of cross-linking (16,19). The fact that DTS was higher for RelyX ARC than for Enforce after light activation is probably due to the fact that Enforce has the lowest rate of polymerization (10).

The polymerization process also seems to have a secondary effect on the elastic modulus, which was confirmed by the present results. Although activation mode did not alter the elastic modulus of any resin cement, there was a significant difference between RelyX ARC and Panavia F after immediate light activation. For this activation mode, RelyX ARC had a higher elastic modulus than Panavia F. Despite the fact that the filler content is higher for Panavia F than for RelyX ARC (78 and 67.5 v/v, respectively), the presence of the stiffer monomer Bis-GMA explains the superior elastic modulus of RelyX ARC (20,22).

Another mechanical property that was not influenced by activation mode was UTS. Unlike the DTS test, tensile stresses are predominantly generated in the specimen during UTS testing. When tensile stresses fracture the sample, UTS basically measures the cohesive strength of the material. Materials with high cohesive strength can withstand high loading stresses before fracture. Clinically, this property is relevant mainly when the cement film is thick. The present study showed differences in UTS only between resin cements. Panavia F had the lowest values, while Enforce and RelyX ARC had similar values. It might be assumed that Panavia F would have the highest UTS, due to its higher filler content (21). However, the opposite was true. The addition of fillers to resin-based materials increases fracture strength up to a filler percentage of around 55% (v/v) (23). Excessive filler content can make the material prone to fracture because fillers may act as areas of stress concentration in this condition, leading to failure propagation and reduced fracture strength (23). Since all the presently evaluated cements had a filler content greater than 55% v/v, the fracture strength of the material might have been reduced. RelyX ARC and Panavia had a similar filler content (66% and 67% v/v, respectively) and similar UTS values, while Panavia F (filler content, 78% v/v) had the lowest UTS.

In this study, the activation mode used for dual-cured resin cements had a limited effect on the evaluated mechanical properties, which seemed more influenced by monomeric composition and filler content. Thus, a delay of 5 min before light activation of the resin cements did not interfere with the mechanical properties of the evaluated luting agents. Thus, our experimental hypothesis was accepted. Because delayed light activation reduces shrinkage stress (10), it is likely to improve the clinical performance of indirect restorations.

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