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Influence of Curing Mode and Time on Degree of Conversion of One Conventional and Two Self-adhesive Resin Cements

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Clinical Relevance

Within the limited experimental conditions, self-adhesive cements provided a higher degree of conversion values when light-activated. In addition, the results showed that, after 15 minutes, the degree of conversion values increased for all materials in both activation modes.

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SUMMARY

This study evaluated the effect of curing mode (auto- and dual-polymerizing mode) and time interval (5, 10 and 15 minutes) on the degree of conversion of resin cements. One conventional dual-cured resin cement (Panavia F 2.0 [Kuraray Medical Inc]) and two self-adhesive cements (RelyX Unicem [3M ESPE] and BisCem [BISCO, Inc]) were evaluated. The products (n=5) were manipulated according to the manufacturer's instructions and applied to the surface of a horizontal attenuated reflectance unit attached to an infrared spectrometer. The materials were

either light-cured for 40 seconds (dual-polymerizing mode) or allowed to auto-polymerize. The degree of conversion was calculated according to changes in the aliphatic-to-aromatic peak ratios prior to and 5, 10 and 15 minutes after light-activation or after mixing when the specimens were allowed to auto-polymerize. Data (%) were analyzed by two-way repeated measure ANOVA (curing mode and time interval) and Tukey's post-hoc test (α=0.05%). The light-activating mode led to a higher degree of conversion values than the self-curing mode in self-adhesive cements (RelyX Unicem and BisCem), while there was no difference in the degree of conversion between the self- and light-cured groups of Panavia F 2.0 resin cement. All products showed a higher degree of conversion at 15 minutes post-curing than any other evaluation interval. The self-adhesive cements provide a higher degree of conversion values when light-activated. After 15 minutes of polymerization initiation, the degree of conversion was higher in all resin cements, regardless of the curing mode.

INTRODUCTION

Dual-polymerizing resin cements have been extensively used for the placement of indirect restorations and/or posts. The dual-polymerizing characteristic represents the combination of auto- and light-polymerizing components, which can promote their polymerization in the absence of light. In some clinical situations, such as in dark zones at the apical region and during the cementation of indirect restorations, severe light attenuation results in a low degree of conversion (DC) and compromised mechanical properties.[1-4]

Adhesive cementation techniques involve critical clinical procedures, including dentin hybridization, clinical protocols and an adequate polymerization of the resin luting agent.[5] Conventional dual-polymerizing resin cements are based on the use of a total-etch or self-etching adhesive system that involves three, two or only one application step prior to cementation. Such techniques are considered complex and more susceptible to operator error.[6] Recently, self-adhesive dual-polymerizing resin luting cements have been developed and do not require previous acid etching, priming or bonding resin applications, so that the number of clinical steps is reduced and the adhesive cementation procedures are simplified.[7]

Many researchers have evaluated polymerization effectiveness to determine the physical and mechanical properties of dental materials.[3,8-10] However, little information is known about the auto- and dual-polymerization behavior of new self-adhesive resin-luting agents. Thus, the purpose of the current study was to measure the DC of two commercially available self-adhesive cements and one conventional resin cement when they were light-activated or when the materials were allowed to self-cure alone. The DC was evaluated at 5, 10 and 15 minutes post light-curing. The first hypothesis of this experiment was that the dual-polymerizing mode of self-adhesive resin cements would result in significantly higher DC than the auto-polymerizing mode. The second hypothesis evaluated was that, after 15 minutes, the DC would be higher than that measured after 5 and 10 minutes from polymerization initiation for the self- and light-curing modes.

METHODS AND MATERIALS

Three commercial dual-cure resin cements were evaluated (Table 1). Two self-adhesive resin-luting agents (RelyX Unicem [3M ESPE, Seefeld, Germany] and BisCem [BISCO, Inc, Schuamburg, IL, USA]) and one conventional resin cement (Panavia F 2.0 [Kuraray Medical Inc, Kurashiki, Japan]) were chosen. Conventional cement consists of two paste components that were equally dispensed and mixed together with a specific primer (ED Primer, Kuraray Medical Inc). All the products were manipulated according to the manufacturers'] instructions.

Table 1: *Compositions of the Resin Luting Cements Used in This Study*

Resin Cement	Composition (Lot #)
Panavia F 2.0	ED Primer A: HEMA, 10-MDP, 5-NMSA, water, N,N-diethanol-p-toluidine (00237A); ED Primer B: 5-NMSA, N,N-diethanol-p-toluidine, water, sodium benzene sulphinate (00115A);
	Paste A: 10-MDP, silanated colloidal silica, bisphenol A polyethoxy dimethacrylate, hydrophobic and hydrophilic DMA, silanized silica filler, benzoyl peroxide, dl-Camphorquinone (00244A); Paste B: hydrophobic and hydrophilic DMA, sodium 2,4,6—triisopropyl benzene sulphinate, N,N-diethanol-p-toluidine, bisphenol A polyethoxy dimethacrylate, colloidal silica, sodium fluoride, silanized barium glass filler, silanized titanium oxide (00038B).
RelyX Unicem (clicker)	Base: glass powder, methacrylated phosphoric estersm TEGDMA, silane-treated silica, sodium persulfate. Catalyst: glass powder, dimethacrylate, silane-treated silica, sodium p-toluene sulfinate, calcium hydroxide (271448).
BisCem	Bis (hydroxyethyl methacrylate) phosphate (base); TEGDMA; dental glass (0600010619).

Abbreviations: HEMA: 2-hydroxyethyl methacrylate; 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate; 5-NMSA: N-methacryloyloxydecyl dihydrogen phosphate; DMA: dimethacrylates; TEGDMA: triethylene glycol dimethacrylate.

After mixing, the resin cements (n=5)[2-4] were applied to the horizontal attenuated total reflectance ZnSe crystal at 45° (Fourier Transform Infrared Spectrometer, FT-IR Spectrometer 520, Nicolet Instrument Corp, Madison, WI, USA) at room temperature. A Mylar strip (Quimidrol Com Ind Imp LTDA, Joinville, SC, Brazil) was placed over the cement and pressed flat to spread the material on the crystal surface. The spectrum of unpolymerized material was obtained and the cements were either light-cured (dual-polymerizing mode) or allowed to self-cure only (auto-polymerizing mode). Each specimen was left on the crystal surface and further spectra were obtained at 5, 10 and 15 minutes after post-mixing. For the light-cured groups, a halogen light-curing unit (XL 3000; 3M ESPE, St Paul, MN, USA) was used for 40 seconds (± 600 mW/cm^2). The light intensity was periodically checked with a radiometer (Curing Radiometer, Model 100, Kerr Corp Orange, CA, USA).

Spectra were obtained between 4000 cm^{-1} and 750 cm^{-1} at a resolution of 4 cm^{-1}. Monomer conversion was calculated (%) according to the changes in the ratio between the absorbance peaks corresponding to the aliphatic (C=C) (1638 cm^{-1}) and aromatic (1608 cm^{-1}) carbon double bonds prior to and 5, 10 and 15 minutes after polymerization.[11] The aromatic peak was used as an internal reference, because the intensity does not change during the polymerization reaction.[5,8]

The effects of curing mode and time intervals on DC were evaluated for each material. Two-way repeated measure analysis of variance (ANOVA) (curing mode and time intervals) was performed and the Tukey's post-hoc test was used to detect pairwise differences among the experimental groups. All statistical testing was performed at a preset alpha of 0.05.

RESULTS

The DC means for each product are described in Tables 2, 3 and 4. Figure 1 shows the DC of resin cements as a function of time. The auto-polymerizing groups showed lower DC values than the light-activating groups for RelyX Unicem and BisCem ($p<0.05$). Panavia F 2.0 was not affected by curing modes ($p>0.05$). All products exhibited higher DC values after 15 minutes post-mixing, and a significant difference was noted between 5- and 10-minute DC values, except when BisCem was allowed to auto-polymerize, which resulted in no significant difference in DC between the two time intervals.

DISCUSSION

The results of the current study showed that the effect of two curing modes (auto-polymerizing and dual-polymerizing) on DC depended on the product and the evaluation period. Thus, the first research hypothesis, which stated that the dual-polymerizing mode of the resin cements would result in a significantly higher DC than the auto-polymerizing mode, was partially accepted, since Panavia F 2.0 was not influenced by the curing mode. The second hypothesis was accepted, because all of the cements presented higher DC after 15 minutes than after 5 and 10 minutes.

The curing light passing through indirect ceramic and composite restorations has its intensity reduced considerably when reaching the resin cement.[2-3,12-13] Thus, the cementing system (bonding agent/resin cement) should develop a polymerization similar to that obtained with the direct exposure of curing light to ensure the same mechanical properties after curing. However, studies evaluating hardness, flexural strength and the DC of dual-cured resin

Table 2: *Degree of Conversion (%) (means [SD]) for Panavia F 2.0 Resin Cement*

Resin Cement	Time (minutes)	Curing Mode Autopolymerized	Curing Mode Dual-polymerized
Panavia F 2.0	5	53.6(4.4) Ac	58.5(4.8) Ac
	10	63.3(5.7) Ab	70.5(5.4) Ab
	15	71.6(4.5) Aa	78.0(4.5) Aa

Groups having similar letters (upper case–row, lower case–column) are not significantly different.

Table 3: *Degree of Conversion (%) (mean [sd]) for RelyX Unicem Self-adhesive Resin Cement*

Resin Cement	Time (minutes)	Curing Mode Autopolymerized	Curing Mode Dual-polymerized
RelyX Unicem	5	29.5(6.0) Bc	57.5(2.7) Ac
	10	39.3(4.1) Bb	66.9(7.2) Ab
	15	46.6(4.6) Ba	70.3(7.2) Aa

Groups having similar letters (upper case–row, lower case–column) are not significantly different.

Table 4: *Degree of Conversion (%) (mean [sd]) for RelyX Unicem Self-adhesive Resin Cement*

Resin Cement	Time (minutes)	Curing Mode Autopolymerized	Curing Mode Dual-polymerized
BisCem	5	50.0(8.5) Bb	66.3(8.6) Ac
	10	57.1(10.8) Bb	79.4(6.7) Ab
	15	67.1(6.8) Ba	86.2(3.4) Aa

Groups having similar letters (upper case–row, lower case–column) are not significantly different.

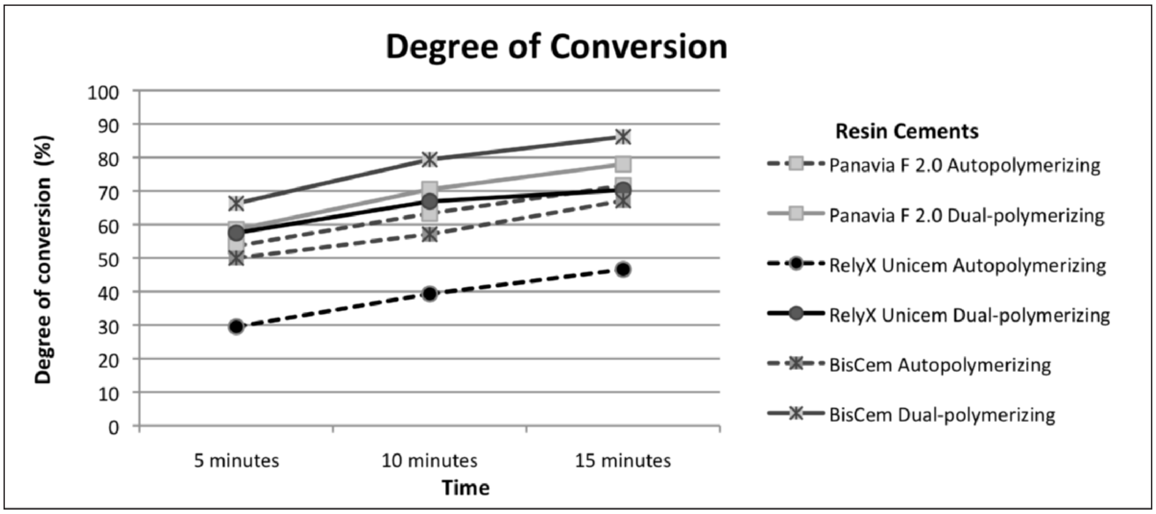

Figure 1: *Line graph of DC as a function of time post-mixing.*

cements have shown that self-curing components of most resin cements were not capable of compensating for the attenuation in light intensity or total absence of light, so the self-curing mode of resin cements is less effective when compared to the dual-cured or photo-cured cements.[2-3,13-16]

Similarly, without light-activation, the DC of RelyX Unicem and BisCem was lower than when the resin cements were light-cured. The changes in viscosity during the auto-polymerization reaction reduced the ability of radicals to migrate and continue the conversion reaction.[5] Moreover, the slow polymerization promoted by the self-curing mode might have been impaired by water produced during the neutralization reaction of phosphate monomers with basic filler within the self-adhesive resin cement.[17] Although water is supposed to be eliminated during set, it is not known how much water remains; therefore, further studies are required to evaluate the amount of water remaining in such cements after curing.

Panavia F 2.0 had a similar DC for the two curing modes. The contact between resin cement (Panavia F 2.0) and ED Primer starts polymerization via the self-curing mechanism. ED primer contains 5-NMSA, HEMA, MDP and only a self-curing catalyst system (chemical initiator). Aromatic sodium sulphinate salts, which are present in both resin cement and ED Primer, are effective reducing agents and allow for polymerization to occur without light exposure.[7,9,18-20]

Self-adhesive resin cements may have a disadvantage compared to conventional dual-cured cementing systems in that the main feature of conventional cementing systems is the presence of benzoyl peroxide, not only in resin cements, but also in dual-cured bonding agents. The mixture of resin cement and adhesive system has a higher content of self-curing components compared to self-adhesive cements and conventional cementing systems without co-initiator added to the bonding agent. Compared to self-adhesive resin cements, the higher content of self-curing components from the mixture of Panavia F and ED Primer compensated for light attenuation caused by the presence of an indirect restoration, so that the DC values in the self-cured groups were as high as those observed in the dual-cured groups.[2-3,21] Other cementing systems use only benzoyl peroxide in resin cements and they contain parabenzene sulfinic acid sodium salts in adhesive components. Similarly, RelyX Unicem contains sodium p-toluene sulphinate as the co-initiator, but it was not possible to identify the components responsible for the polymerization mechanism of BisCem in its MSDS (Material Safety Data Sheets).[17]

Except for BisCem, in which no significant difference in DC was observed between five and 10 minutes in the auto-polymerized group, the other resin cements exhibited lower DC after five minutes, compared to the values observed after 10 minutes. Regardless of the curing mode, the 15-minute DC values were significantly higher than those at five- or 10-minute intervals. Although changes in viscosity impair polymerization, the higher DC after 15 minutes indicates continuing polymerization.[2-4]

This *in vitro* study was based on well-controlled laboratory conditions. However, other variables, such as the presence of dentin humidity and the interaction between resin cement and dental tissues, could affect the DC, thus altering the mechanical properties of the resin cement polymer.[2-4]

CONCLUSIONS

Light-activation was important in providing higher DC in self-adhesive resin cements. After 15 minutes, the DC of all resin cements increased, regardless of the curing mode.

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