Pre-heated dual-cured resin cements: analysis of the degree of conversion and ultimate tensile strength

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Abstract: This study evaluated the degree of conversion (DC) and ultimate tensile strength (UTS) of dual-cured resin cements heated to 50º C prior to and during polymerization. Disc- and hourglass-shaped specimens of Rely X ARC (RX) and Variolink II (VII) were obtained using addition silicon molds. The products were manipulated at 25º C or 50º C and were subjected to 3 curing conditions: light-activation through a glass slide or through a pre-cured 2-mm thick resin composite disc, or they were allowed to self-cure (SC). All specimens were dark-stored dry for 15 days. For DC analysis, the resin cements were placed into the mold located on the center of a horizontal diamond on the attenuated total reflectance element in the optical bench of a Fourier Transformed Infrared spectrometer. Infrared spectra (n = 6) were collected between 1680 and 1500 cm^{-1}, and DC was calculated by standard methods using changes in ratios of aliphatic-to-aromatic C=C absorption peaks from uncured and cured states. For UTS test, specimens (n = 10) were tested in tension in a universal testing machine (crosshead speed of 1 mm/min) until failure. DC and UTS data were submitted to 2-way ANOVA, followed by Tukey's test (α= 5%). Both products showed higher DC at 50º C than at 25º C in all curing conditions. No significant difference in UTS was noted between most light-activated groups at 25º C and those at 50º C. VII SC groups showed higher UTS at 50º C than at 25º C ($p < 0.05$). Increased temperature led to higher DC, but its effects on resin cement UTS depended on the curing condition.

Descriptors: Resin Cements; Temperature; Cure; Tensile Strength.

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Introduction

Dual-cure resin cements (RCs) were developed to establish a reliable bond between the prepared tooth and restorative materials.[1] These products were developed to polymerize properly even when a curing light is severely attenuated by the presence of an indirect restoration interposed between the curing unit tip and RC during light-activation.[2,3] However, it has been shown that the self-curing mode of RCs is less effective than the dual-curing mode.[4] Such evidence deserves some attention because only approximately 10% to 15% of the light intensity remains after the curing light passes through a 2-mm thick indirect restoration.[2,3,5] In such detrimental clinical conditions, most RCs present lower hardness, higher solubility, lower flexural and compressive strength values than properly cured RCs, resulting in lower bond strength values to dentin.[3,6-9]

Some studies have shown that pre-heating the resin composite to 50º C or 60º C increases its degree of conversion (DC).[10,11] As a result, increased hardness and fracture strength, increased flexural strength and modulus, and increased resistance to wear are expected.[12,13] Therefore, it is reasonable to assume that dual-cured RCs polymerized at increased temperature might show higher DC and improved mechanical properties than RCs polymerized at room temperature. However, only few studies have evaluated the effects of pre-heating on the DC and mechanical properties of dual-cured RCs.[14-16] Therefore, the aim of this study was to evaluate the effects of pre-heating on the DC and ultimate tensile strength (UTS) of dual-cured RCs subjected to different curing conditions. The research hypothesis was that dual-cured RCs heated to 50º C prior to and during polymerization exhibit higher DC and UTS than the RCs polymerized at 25º C when polymerization relied solely on the self-curing condition or after exposure to the severely attenuated curing light due to the presence of an indirect composite resin restoration.

Materials and methods

Specimen preparation

Two dual-cured RCs, Rely X ARC (RX, 3M ESPE, St. Paul, USA) and Variolink II (VII, Ivoclar Vivadent, Schaan, Liechtenstein) (Table 1), were evaluated. For the heated groups, base and catalyst pastes were equally dispensed on a glass plate resting on a heating stirrer surface (103, Cientec, Piracicaba, São Paulo, Brazil) set at 50±1º C. The mixed RCs were applied to an addition silicon mold (Panasil, Kettenbach GmbH & Co., Eschenburg, Germany), which was initially placed on the same heated glass plate where the resin cements were mixed, to create hourglass-shaped specimens (1-mm thick and 1-mm wide at the constriction region) for the UTS test. For the hourglass-shaped specimen, a Mylar strip was placed between the mold and the heated surface. The resin cements were mixed with a spatula heated to 50º C and applied into the mold. The mold allowed a direct contact between the heated RC and the Mylar strip in contact with the heated glass plate. As such, the specimen temperature was maintained not only during the mixing procedure but also during polymerization. For the other groups, the same procedures were performed at 25º C. All groups were subjected to three different curing conditions:

1. light activation through a glass slide (GS),
2. through a pre-cured 2-mm thick resin composite disc (A2 - A2 shade, TPH Spectrum, Dentsply Caulk, Milford, USA) to simulate the cementation of an indirect resin composite restoration, or
3. specimens were allowed to self-cure (SC).

In the GS and A2 groups, both the glass slide and the resin disc were left on the heated plate for 5 min prior to specimen fabrication to ensure that the specimen, glass slide, and indirect restoration all maintained the same temperatures during specimen fabrication. Each specimen was covered with another Mylar strip and was exposed to 40 s of curing light (power density: 600 mW/cm², Optilux 501, Demetron Kerr, Danbury, USA), which had its intensity continuously monitored with a radiometer (Cure Rite, Dentsply Caulk, Milford, USA). Specimen and glass plate temperatures were continuously measured with a thermocouple (SmartMether, Novus, Porto Alegre, Brazil) to ensure that the base and catalyst pastes reached 50º C and that the tem-

Table 1 - Brand, composition and batch number of the dual-cured RCs.

Product (Manufacturer)	Composition (Batch Number)
Variolink II (Ivoclar -Vivadent)	Paste of dimethacrylates, inorganic fillers, ytterbium trifluoride, initiators, stabilizers and pigments, Bis-GMA, TEGDMA, UDMA, and benzoyl peroxide (Base: L46354; Catalyst: L 36656)
RelyX ARC (3M ESPE)	• Paste A: Silane-treated ceramic, TEGDMA, Bis-GMA, silane-treated silica, and functionalized dimethacrylate polymer • Paste B: Silane-treated ceramic, TEGDMA, Bis-GMA, silane treated silica, and functionalized dimethacrylate polymer (GE9JG)

TEGDMA: triethylene glycol dimethacrylate; Bis-GMA: bisphenol A diglycidyl ether methacrylate; UDMA: urethane dimethacrylate peratures were constant during the entire specimen preparation. All heated specimens were left on the heated plate for 5 min after activation and were protected from light during this period. Specimens were dark-stored dry at 37º C for 15 days.

Degree of conversion

For the DC analysis, a disc-shaped mold was placed on the horizontal diamond attenuated total reflectance (ATR) element (Golden Gate, Specac, Woodstock, USA) in the optical bench of a Fourier Transformed Infrared spectrometer (Tensor 27, Bruker Optik GmbH, Ettlingen, Germany). As such, the mold allowed the ATR diamond surface to remain exposed. The RCs at 25º C were manipulated and applied into the mold to create 1-mm thick disc-shaped specimens (5 mm in diameter) with the bottoms in contact with the diamond surface. For the pre-heated groups, the RCs were heated to 50º C on the heated glass plate as previously described, were mixed with a heated spatula, and were applied to the diamond surface, which was also heated with a custom-made heater device to maintain the RC temperature at 50º C during the analysis. The infrared spectra from the uncured specimens at 25º C and 50º C were collected between 1680 and 1500 cm^{-1} at a 4 cm^{-1} resolution (16 scans per spectrum) before the RCs were subjected to the previously described curing conditions. All heated specimens were left on the heated ATR diamond surface for 5 min. All specimens were dark-stored dry at 37º C for 15 days. Afterwards, the cured specimens were placed on the ATR diamond surface and new infrared spectra were obtained. Monomer conversion was calculated by standard methods using changes in the ratios of the aliphatic-to-aromatic C=C absorption peaks in both the uncured and cured states obtained from the infrared spectra[17,18] according to the following equation, where abs is absorbance:

$$DC = 1 - \frac{[\text{abs } (C = C \text{ aliphatic}) / \text{abs } (C = C \text{ aromatic})] \text{ polymer}}{[\text{abs } (C = C \text{ aliphatic}) / \text{abs } (C = C \text{ aromatic})] \text{ monomer}} \times 100$$

Ultimate tensile strength test

For the UTS test, the hourglass-shaped specimen was attached to the grips of a microtensile testing jig with cyanoacrylate (Loctite Super Bonder Gel, Henkel, Düsseldorf, Germany) and tested in tension in a universal testing machine (EZ Test, Shimadzu Co, Kyoto, Japan) at a crosshead speed of 1 mm/min until failure. After testing, the specimens were carefully removed from the fixtures with a scalpel blade and the cross-sectional area at the site of fracture was measured to the nearest 0.01 mm with a digital micrometer (Series 406; Mitutoyo America Corp., Aurora, USA). The UTS data were expressed in units of stress, or MPa.

Statistical analysis

Ten specimens were prepared for each experimental group (n = 10) for the UTS test, while 6 specimens per group (n = 6) were required to perform the DC analysis. Because the aim of the current study was not to compare products, data were submitted to a 2-way ANOVA ("temperature" and "curing condition" factors) for each product followed by a *post hoc* Tukey's test at a pre-set alpha of 5%, using statistical software (SAS 8.0 for Windows; SAS Institute Inc., Cary, USA).

Results

Degree of conversion

The DC values are displayed in Table 2. Significant interaction was detected between "light-activa-

Table 2 - The mean DC values (standard deviation) for VII and RX according to the curing condition and temperature (%).

Product	Temperature	GS Group	A2 Group	SC Group
VII	25º C	63.5 (2.5) Ba	56.3 (3.2) Bb	45.3 (2.7) Bc
	50º C	68.8 (1.2) Aa	67.0 (1.6) Aa	60.4 (4.3) Ab
RX	25º C	68.2 (1.6) Ba	63.0 (3.5) Bb	44.5 (5.2) Bc
	50º C	76.4 (2.3) Aa	71.7 (3.1) Ab	61.8 (2.0) Ac

For each product, the means followed by different letters (upper case letters within the columns and lower case letters within the rows) are significantly different ($p < 0.05$). No comparisons were made between the products.

Table 3 - The mean UTS values (standard deviation) for VII and RX according to curing condition and temperature (MPa).

Product	Temperature	GS Group	A2 Group	SC Group
VII	25º C	75.5 (9.7) Aa	72.6 (10.3) Aa	16.8 (6.7) Bb
	50º C	62.4 (18.8) Aa	78.7 (13.5) Aa	35.6 (11.2) Ab
RX	25º C	77.3 (9.5) Aa	72.4 (7.1) Aa	35.7 (10.7) Ab
	50º C	68.5 (17.3) Aa	75.4 (8.9) Aa	45.7 (15.2) Ab

For each product, the means followed by different letters (upper case letters within the columns and lower case letters within the rows) are significantly different ($p < 0.05$). No comparisons were made between the products.

tion” and “temperature” for VII ($p = 0.001$). Both RCs showed higher DC values at 50º C than at 25º C ($p < 0.05$), regardless of the curing condition.

The GS groups exhibited higher DC than the A2 groups in both products at 25º C and in RX at 50º C ($p < 0.05$). No significant difference in DC was noted between the GS and A2 groups when VII was heated to 50º C. The SC groups showed the lowest DC regardless of the product or temperature ($p < 0.001$).

Ultimate tensile strength

The UTS values are shown in Table 3. Significant interaction was detected between “light-activation” and “temperature” for VII. The change in temperature had no significant effect in UTS for RX. No significant difference in UTS was noted between groups polymerized at 25º C and those polymerized at 50º C in either the GS or A2 groups for both products. The pre-heated SC groups of VII at 50º C exhibited higher UTS than the SC groups polymerized at 25º C ($p < 0.05$).

The comparison among the curing conditions demonstrated no significant differences in UTS between the GS and A2 groups for both RCs at either 25º C or 50º C. In both RCs at 25º C and 50º C, the SC groups showed lower UTS values than did the GS and A2 groups ($p < 0.05$).

Discussion

In this study, increased temperatures of RX and VII resulted in higher DC regardless of the curing condition. Such a finding corroborates previously reported results[10,11] and might be attributed to the increased radical mobility and collision frequency of the unreacted active groups and radicals resulting from the decrease in RC viscosity promoted by increased RC temperatures.

Despite the overall increase in the DC of RX, the values still depended on the curing condition. Therefore, the increased temperature did not compensate for the lower light intensity when an indirect restoration was used or for the lower effectiveness of self-curing components when polymerization relied solely on the self-curing mode. However, it should be emphasized that the DC in the A2 groups of RX cured at 50º C was apparently similar to that observed in the GS groups at 25º C. As higher DC decreases the material solubility,[19] one can expect an increase in the longevity of indirect restorations cemented with RCs at higher temperatures.

When VII was polymerized at 50º C, no significant difference in DC was noted between the GS and A2 groups, while the A2 group showed lower DC than the GS group at 25º C. Based on these results, the GS group at 50º C exhibited DC approximately 8.3% higher than at 25º C, while the A2 group at 50º C showed DC 19% higher than at 25º C. Therefore, as approximately only 10% of the light intensity reaches the RC after the curing light passes through a 2-mm thick indirect resin composite restoration,[4] the effects of increased temperature may be more evident when the curing light was severely attenuated by the resin disc.

Although the increased temperature resulted in significantly higher DC in both RCs, the 8% to 10% increase in the DC values had no influence on the UTS of cements light-activated at 50º C. According to Loza-Herrero *et al.*,[20] a parabolic relationship can be observed between DC and mechanical properties. In that study, as conversion increased, strength values tended to plateau or even decline. Based on those results, the authors implied that once a threshold conversion value was reached, the polymer network strength did not markedly increase with additional curing. The authors also emphasized that strength may even decline as a result of increasing brittleness. Furthermore, in comparison to resin composites, RCs usually have lower filler content and higher content of diluent monomers to ensure proper viscosity (as stated in the manufacturer's information). At increased temperatures, these materials may present fast cure rates when exposed to the curing light. As a consequence, the material develops high shrinkage strain and internal stress during polymerization.[20,21] Moreover, the required slow homogenization of the internal stress created in the polymers during polymerization may be compromised by such a fast cure rate as well.[20]

The SC groups of VII cured at 50° C exhibited higher UTS than at 25° C. It has been shown that the degradation rate of the self-curing component benzoyl peroxide to radicals increases with increased temperatures.[22] For this reason, more radicals are created more quickly, so the decrease in resin viscosity and increased radical mobility promoted by higher resin temperatures during polymerization most likely were not the only factors contributing to the higher DC and UTS values in the heated RCs when polymerization was initiated via this curing condition. Thus, while the research hypothesis was validated for the effects of increased temperature on the DC of RCs, the research hypothesis was partially validated regarding the effects of increased temperature on the UTS because the temperature improved the mechanical properties of only one product under one curing condition.

A temperature of 50° C was chosen based on other studies[10,11,23] and was maintained for 5 min during specimen polymerization. This methodology may differ from a clinical situation where a drastic drop in temperature of the heated resin composites is observed when they are placed in tooth cavities.[24,25] For this reason, a decrease in the cement temperature is expected even if the RC is coupled to a heated indirect restoration. Because of such a drop in resin temperature, Froes-Salgado *et al.*[25] found no significant differences in DC, flexural strength, and cross-linking estimated values between pre-heated composites and composites polymerized at room temperature. For this reason, further studies simulating this clinical condition are required to evaluate the effects of temperature drop on the mechanical properties and DC of RCs.

Although resin-based materials were heated to 50° C in most studies evaluating the effects of temperature,[10,11,14-16] one could state that such a high temperature could damage the pulp tissue. However, it has been demonstrated that an increase in the temperature of resin composites to temperatures ranging between 54° C and 60° C does not significantly change the intrapulpal temperature.[23] Based on the findings from the current study, the use of RCs heated to 50° C might be a reliable option regarding the DC and mechanical properties of dual-cured RCs when they depend on the self-curing mode to bond indirect restorations to teeth. The long-term evaluation of the bond strength of indirect restorations to teeth using heated RCs is required to confirm the effectiveness of this technique.

Conclusion

The increased temperature of RX and VII prior to polymerization promoted higher DC regardless of the curing condition. However, an increase in temperature to 50° C improved the UTS of only VII polymerized via the self-curing mode.

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References

1. Diaz-Arnold AM, Vargas MA, Haselton DR. Current status of luting agents for fixed prosthodontics. J Prosthet Dent. 1999 Feb;81(2):135-41.
2. Arrais CA, Rueggeberg FA, Waller JL, de Goes MF, Giannini M. Effect of curing mode on the polymerization characteristics of dual-cured resin cement systems. J Dent. 2008 Jun;36(6):418-26.
3. El-Mowafy OM, Rubo MH. Influence of composite inlay/onlay thickness on hardening of dual-cured resin cements. J Can Dent Assoc. 2000 Mar;66(3):147.

4. Arrais CA, Giannini M, Rueggeberg FA. Kinetic analysis of monomer conversion in auto- and dual-polymerizing modes of commercial resin luting cements. J Prosthet Dent. 2009 Feb;101(2):128-36.
5. el-Mowafy OM, Rubo MH, el-Badrawy WA. Hardening of new resin cements cured through a ceramic inlay. Oper Dent. 1999 Jan-Feb;24(1):38-44.
6. Arrais CA, Giannini M, Rueggeberg FA, Pashley DH. Microtensile bond strength of dual-polymerizing cementing systems to dentin using different polymerizing modes. J Prosthet Dent. 2007 Feb;97(2):99-106.
7. Arrais CA, Giannini M, Rueggeberg FA, Pashley DH. Effect of curing mode on microtensile bond strength to dentin of two dual-cured adhesive systems in combination with resin luting cements for indirect restorations. Oper Dent. 2007 Jan-Feb;32(1):37-44.
8. Braga RR, Cesar PF, Gonzaga CC. Mechanical properties of resin cements with different activation modes. J Oral Rehabil. 2002 Mar;29(3):257-62.
9. Meng X, Yoshida K, Atsuta M. Influence of ceramic thickness on mechanical properties and polymer structure of dual-cured resin luting agents. Dent Mater. 2008 May;24(5):594-9.
10. Daronch M, Rueggeberg FA, De Goes MF. Monomer conversion of pre-heated composite. J Dent Res. 2005 Jul;84(7):663-7.
11. Daronch M, Rueggeberg FA, De Goes MF, Giudici R. Polymerization kinetics of pre-heated composite. J Dent Res. 2006 Jan;85(1):38-43.
12. Ruyter IE. Methacrylate-based polymeric dental materials: conversion and related properties. Summary and review. Acta Odontol Scand. 1982;40(5):359-76.
13. Milleding P, Ortengren U, Karlsson S. Ceramic inlay systems: some clinical aspects. J Oral Rehabil. 1995 Aug;22(8):571-80.
14. Cantoro A, Goracci C, Papacchini F, Mazzitelli C, Fadda GM, Ferrari M. Effect of pre-cure temperature on the bonding potential of self-etch and self-adhesive resin cements. Dent Mater. 2008 May;24(5):577-83.
15. Cantoro A, Goracci C, Carvalho CA, Coniglio I, Ferrari M. Bonding potential of self-adhesive luting agents used at different temperatures to lute composite onlays. J Dent. 2009 Jun;37(6):454-61.
16. Blalock JS, Holmes RG, Rueggeberg FA. Effect of temperature on unpolymerized composite resin film thickness. J Prosthet Dent. 2006 Dec;96(6):424-32.
17. Rueggeberg FA, Hashinger DT, Fairhurst CW. Calibration of FTIR conversion analysis of contemporary dental resin composites. Dent Mater. 1990 Oct;6(4):241-9.
18. Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. J Dent Res. 1988 Jun;67(6):932-7.
19. Pearson GJ, Longman CM. Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. J Oral Rehabil. 1989 Jan;16(1):57-61.
20. Loza-Herrero MA, Rueggeberg FA, Caughman WF, Schuster GS, Lefebvre CA, Gardner FM. Effect of heating delay on conversion and strength of a post-cured resin composite. J Dent Res. 1998 Feb;77(2):426-31.
21. Spinell T, Schedle A, Watts DC. Polymerization shrinkage kinetics of dimethacrylate resin-cements. Dent Mater. 2009 Aug;25(8):1058-66.
22. Zaman F, Beezer AE, Mitchell JC, Clarkson Q, Elliot J, Davis AF, *et al*. The stability of benzoyl peroxide by isothermal microcalorimetry. Int J Pharm. 2001 Oct 4;227(1-2):133-7.
23. Daronch M, Rueggeberg FA, Hall G, De Goes MF. Effect of composite temperature on *in vitro* intrapulpal temperature rise. Dent Mater. 2007 Oct;23(10):1283-8.
24. Daronch M, Rueggeberg FA, Moss L, de Goes MF. Clinically relevant issues related to preheating composites. J Esthet Restor Dent. 2006 Nov;18(6):340-50.
25. Froes-Salgado NR, Silva LM, Kawano Y, Francci C, Reis A, Loguercio AD. Composite pre-heating: effects on marginal adaptation, degree of conversion and mechanical properties. Dent Mater. Sep;26(9):908-14.