A Study of the Physical and Chemical Properties of Four Resin Composite Luting Cements

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Purpose: This study evaluated the surface microhardness and flexural and compressive strengths of five luting cements and compared the degree of conversion of dual and autopolymerized forms of four resin-based luting cements. ***Materials and Methods:*** Four resin composite luting cements—Panavia F, Variolink 2, RelyX Unicem Applicap, and RelyX ARC—and a polycarboxylate cement (Durelon, control group) were used in three-point bending, compression, and Vickers hardness tests following water storage for 1 week. Resin composite cements were additionally investigated with both dual and autopolymerization techniques under Fourier transformed infrared spectroscopy. Differences were analyzed using one-way ANOVA. ***Results:*** The highest flexural strengths were obtained with Variolink 2 (90 MPa, SD 22), whereas the lowest were observed with Durelon (28 MPa, SD 4). RelyX Unicem showed the highest hardness values (44 HV, SD 5), whereas Variolink 2 gave the lowest (32 HV, SD 6). The highest compressive strengths were obtained with RelyX Unicem (145 MPa, SD 32), whereas the lowest were observed with Durelon (41 MPa, SD 17). For both dual and autopolymerized groups, RelyX ARC showed the highest degrees of conversion (81% and 61%, respectively) and RelyX Unicem had the lowest (56% and 26%, respectively). ***Conclusion:*** Resin composite luting cements of similar chemical characterizations differed in their physical properties, and polymerization method influenced their degree of conversion. *Int J Prosthodont 2004;17:357–363.*

Properties of the luting cement and cementation procedure are essential in the clinical success of crowns and fixed partial dentures (FPD) because marginal discrepancies and leakage, which might lead to periodontal disease, secondary dental caries, pulp sensitivity, and necrosis, and esthetic problems such as staining or marginal discoloration, are as closely related to the longevity of FPDs as their fracture resistance.[1]

The choice of a luting agent is dependent on the clinical situation combined with its physical, biologic, and handling properties.[2–7] The luting cement must provide a durable bond between the tooth and restoration surfaces, together with adequate hardness values, compressive and tensile strengths, and appropriate elastic modulus and fracture toughness to prevent dislodgment as a result of interfacial or cohesive failures. It must have an acceptable film thickness and viscosity to ensure complete seating, be resistant to disintegration in the oral cavity, be tissue compatible, and demonstrate adequate working and setting times.[8–12] In addition to these requirements, resin composite luting cements have to provide an adequate degree of conversion (DC%) through their monomer and initiator system compositions. Incomplete polymerization of resin composite cements is a possible cause of postoperative sensitivity.[13–15] Some modern resin composite luting cements can be cured by means of autopolymerization (self-curing) or by dual curing.

There are an inadequate number of systematic investigations regarding the mechanical characterization of recently developed resin composite luting cements commonly used with FPDs. Furthermore, significant

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Table 1 Materials Used in the Study

Material	Type*
Durelon, 3M/ESPE	Carboxylate cement; contains powder (zinc oxide) and liquid (polyacrylic acid)
RelyX ARC, 3M/ESPE	Dual-curing or autopolymerizing resin composite cement; contains adhesive resin cement (bis-GMA and TEGDMA)
Panavia F, Kuraray	Dual-curing or autopolymerizing resin composite cement; contains adhesive resin cement (paste A: silanized and colloidal silica, dimethacrylate; paste B: silanized barium glass, titanium oxide, dimethacrylate, and sodium fluoride)
Variolink 2, Ivoclar Vivadent	Dual-curing or autopolymerizing resin composite cement; contains adhesive resin cement (bis-GMA, UDMA, and TEGDMA)
RelyX Unicem Applicap, 3M/ESPE	Dual-curing or autopolymerizing resin composite cement; contains adhesive resin cement (powder: glass powder, initiator, silica, substituted pyrimidine, calcium hydroxide, peroxy compound, and pigment; liquid: methacrylated phosphoric ester, dimethacrylate, acetate, stabilizer, and initiator)

*Compositions from manufacturer information.
bis-GMA = bisphenol-A-glycidyldimethacrylate; TEGDMA = triethylene glycol dimethacrylate; UDMA = urethane dimethacrylate.

differences among the mechanical properties of tested materials have been reported.[11,16–18] Thus, the aim of the present study was to evaluate the surface microhardness and flexural and compressive strengths of five luting cements and to compare DC% of the dual and autopolymerized forms. The hypotheses to be tested were: *(1)* whether resin composite luting cements of similar chemical characterizations would differ in physical properties; and *(2)* whether DC% of dual-curing resin composite luting cements would be influenced by the method of polymerization.

Materials and Methods

The materials used in this investigation are listed in Table 1. Materials were prepared and handled in accordance with the manufacturers' instructions. For Panavia F, Variolink 2, and RelyX ARC, equal amounts of base and catalyst pastes were mixed, whereas RelyX Unicem Applicap capsules were inserted into the activator and activated by pressing down and holding the handle for 4 seconds. The capsules were then inserted into the mixing device (Silamat Plus, Ivoclar Vivadent) and mixed for 15 seconds on the highest speed. Specimens were inserted into appropriate molds, followed by light polymerization with a light-curing unit (Optilux 501, SDS, Kerr/Demetron) for 40 seconds from each aspect. Irradiation intensity was 800 mW/cm^2, and it was verified with the hand-curing unit's internal radiometer. Durelon specimens, which were included as a control group of conventional-type luting cements, were prepared in a ratio of one dose of powder to two scale units of liquid for the normal setting time. All specimens were stored in distilled water at 37 ± 1°C for 1 week and subjected to the tests described below.

Flexural Strength (Three-Point Bending Test)

Six rhombic test specimens of each cement group (2 mm × 2 mm × 25 mm) were prepared in accordance with the recommendation of ISO 4049.[19] The same recommendations were followed for the three-point bending test used. The cross-head speed of the testing machine (Lloyds LRX, Lloyds Instruments) was 1 mm/min. Flexural strength was calculated with NEXYGEN 4.0 software (Lloyds LRX).

Compressive Strength

Twelve cylindric specimens of each cement group (6-mm height and 4-mm diameter) were prepared in accordance with the recommendation of ISO 9917.[20] The same recommendations were followed for the compression test used. The cross-head speed of the testing machine (Lloyds LRX) was 1 mm/min. Compressive strength was calculated with NEXYGEN 4.0 software.

Weibull analysis proceeded using Excel 2002 software (Microsoft) and the following formulas. Experimental values for fracture probability P_{fe} from the Weibull formula[21] were:

$$P_{fe} = n/(N + 1)$$

where N = total number of specimens; and n = rank number of specimens.

$$P_f = 1 - \exp - \left(\left[\frac{S - S_u}{S_o} \right]^m \right)$$

where P_f = failure probability; S = failure strength; S_u = theoretic failure stress (0); m = Weibull modulus, a constant, which determines the slope of the distribution function; and S_o = characteristic load (ie, the load level at which 63% of

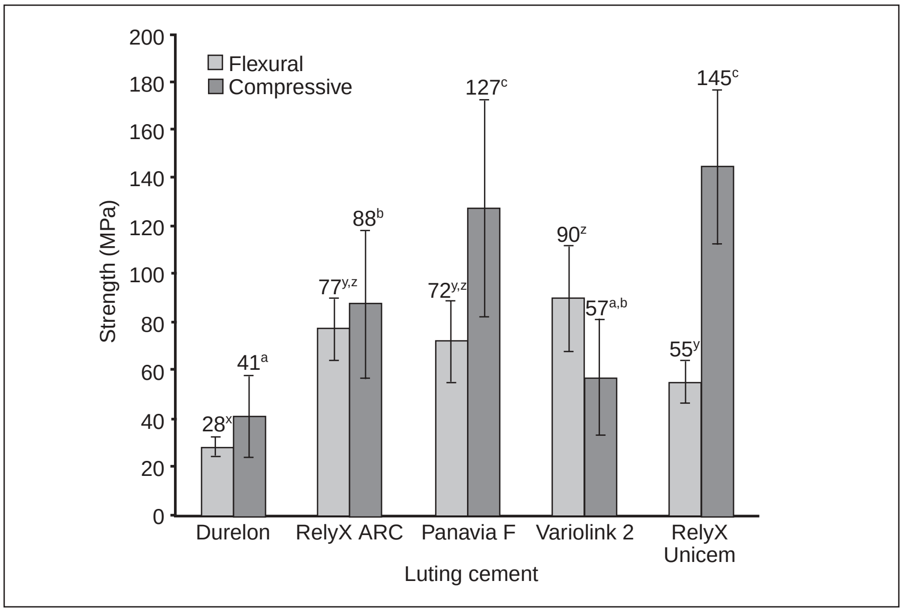

Fig 1 Means and standard deviations of flexural and compressive strengths after 1-week water storage. (Groups with the same letters did not differ statistically.)

the specimens have failed). R^2 was the correlation coefficient that tells how well data fit the model.

Surface Microhardness (Vickers Hardness Test)

Three rhombic test specimens of each cement group (2 mm × 2 mm × 25 mm) were prepared. The surface hardness of the cements was measured using a Vickers microhardness indenting and measuring microscope (Duramin-10, Struers). A diamond pyramid indenter made five indentations at different sites on the surface for 10 seconds, with a load of 0.1 N. Vickers hardness numbers were calculated as a mean of 15 indentations with the Duramin Video Measurement System, version 2.0.3.0 (Struers).

Degree of Conversion (Fourier Transformed Infrared Spectroscopy)

Six cylindric specimens of each resin-based luting cement group (1.8-mm height and 3.6-mm diameter) were prepared. Cements were mixed according to the manufacturers' recommendations. The mixed material was covered with a glass slide. Half of the materials of each cement group were separated to be autopolymerized. Light-polymerized materials were polymerized with Optilux 501 for 40 seconds (irradiation intensity 800 mW/cm^2). Autopolymerized specimens were not photopolymerized. DC% was measured by Fourier transformed infrared spectroscopy (FTIR) (Spectrum One, Perkin Elmer) on the attenuated total reflectance sampling accessory. DC% was calculated from the aliphatic C=C peak at 1,638 cm^{-1}, normalized against the aromatic C=C peak at 1,608 cm^{-1}, according to the following formula:

$$DC\% = 1 - \left(\frac{C_{aliphatic}/C_{aromatic}}{U_{aliphatic}/U_{aromatic}}\right)100\%$$

where $C_{aliphatic}$ = absorption peak of the cured specimen at 1,638 cm^{-1}; $C_{aromatic}$ = absorption peak of the cured specimen at 1,608 cm^{-1}; $U_{aliphatic}$ = absorption peak of the uncured specimen at 1,638 cm^{-1}; and $U_{aromatic}$ = absorption peak of the uncured specimen at 1,608 cm^{-1}.

Spectra were recorded immediately after mixing (autopolymerized) or after 40-second light polymerization (dual-cured) and repeated every 2.5 minutes up to 15 minutes. Each spectrum was recorded with eight scans using a resolution of 4 cm^{-1}. DC% was calculated as a mean of eight observations.

Statistical analysis was performed using SPSS for Windows, release 10.0.5/1999 (SPSS). One-way analysis of variance (ANOVA) was used for each test group. *P* values less than .05 were considered to be statistically significant in all tests. Multiple comparisons were made by means of the Dunnett T3 post hoc test.

Results

The highest flexural strengths were obtained with Variolink 2 resin composite cement (90 MPa), whereas the lowest were observed with the Durelon polycarboxylate cement (28 MPa) (Fig 1). RelyX Unicem self-adhesive resin composite cement showed the highest hardness values (44 HV), whereas Variolink 2 gave the lowest (32 HV) (Fig 2). The highest compressive strengths were obtained with RelyX Unicem (145 MPa), whereas the lowest were observed with Durelon (41 MPa) (Fig 1). Weibull analysis is summarized in Fig 3 and Table 2.

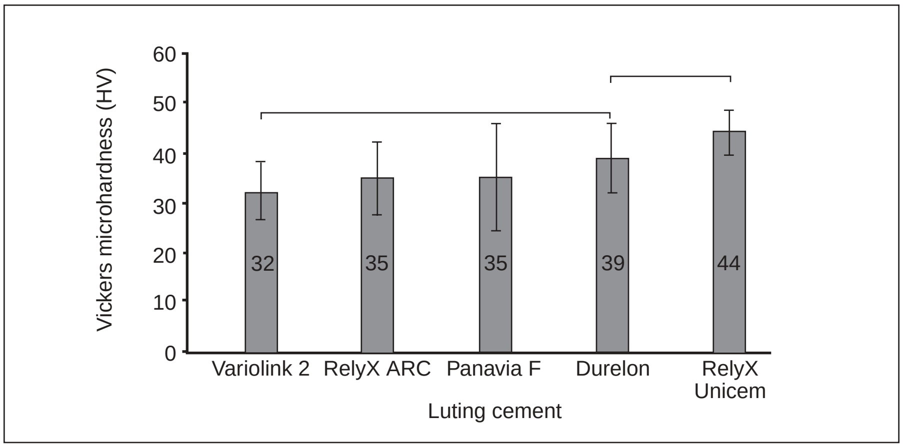

Fig 2 Means and standard deviations of microhardness values after 1-week water storage. (Groups connected with horizontal lines did not differ statistically.)

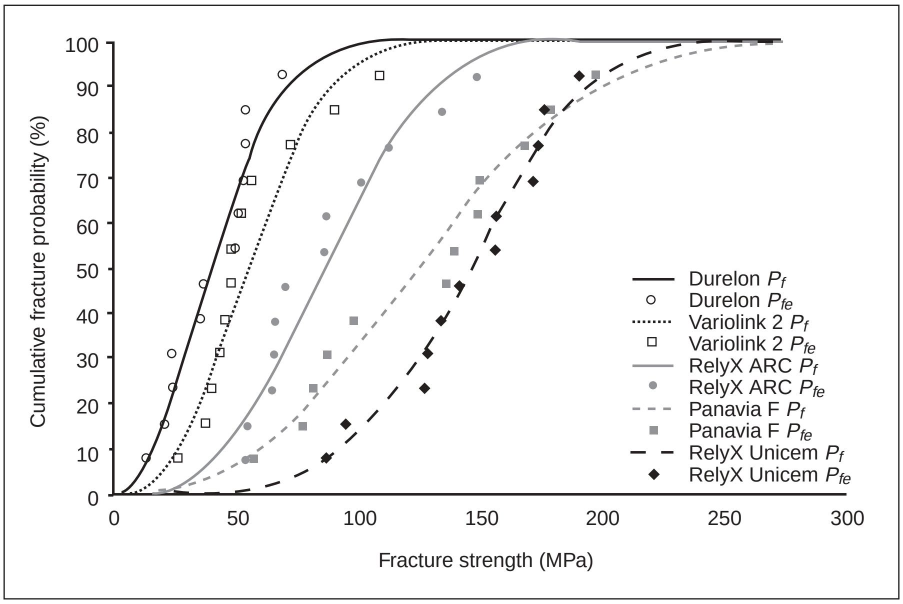

Fig 3 Cumulative fracture probability of various cements loaded in compression.

Table 2 Weibull Analysis of Cement Compression Strength

Group	Weibull modulus *(m)*	Characteristic strength (S_o; in MPa)	R^2	10% failure probability (MPa)
Durelon	2.1	48	.96	45
Variolink 2	2.5	64	.89	26
RelyX ARC	2.9	99	.90	45
Panavia F	2.6	144	.96	60
RelyX Unicem	4.1	159	.96	93

When characteristic strength values are compared, the two highest values were achieved with RelyX Unicem (159 MPa) and Panavia F (144 MPa); however, the mean values were not statistically significantly different. When 10% failure strength values were compared (Panavia F = 60 MPa; RelyX Unicem = 93 MPa), RelyX Unicem revealed better reliability.

For both dual-cured and autopolymerized groups, RelyX ARC resin composite cement showed the highest DC% (81% and 61%, respectively; Fig 4). RelyX Unicem had the lowest DC% (56% and 26%, respectively), measured 15 minutes after mixing (Fig 5). For all resin cements, the dual-cured material showed the highest degree of conversion.

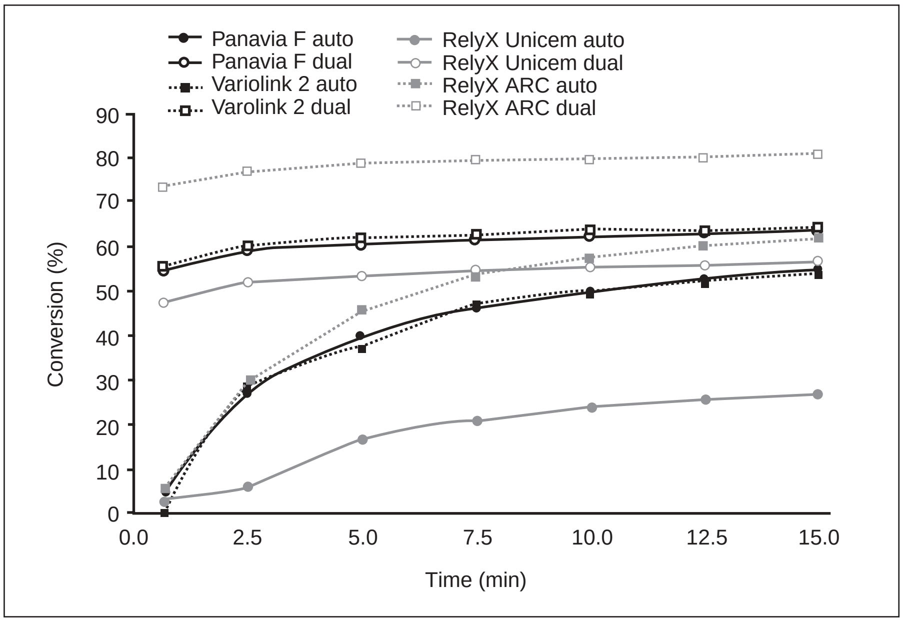

Fig 4 Degree of conversion of resin composite luting cements after 40-second light polymerization of dual-curing cements *(dual)*, or after mixing of autopolymerized cements *(auto)*.

Discussion

The properties of resin composites are influenced by the nature of the matrix, type of filler, filler volume, filler-matrix interfacial bond, filler load, and polymerization mode.[7,22]

Compressive strength of dental materials has been used as a predictor of their clinical performance.[23–27] In some studies evaluating compressive strength of luting cements, resin composite cements had significantly higher compressive strengths than polycarboxylate cements.[23–25,27] Because of their thixotropic nature, polycarboxylate cements exhibit different behaviors from resin-based cements under pressure.[18] Similarly, the compressive strength of Durelon polycarboxylate cement, which was included in the present study as a control group, was significantly lower than that of the resin-based composite cements investigated.[11] RelyX Unicem, which exhibited the highest compressive strength among the tested materials, had the highest microhardness value as well. Surface hardness of materials characterizes their outer surface properties and is an important parameter in determining their capacity to be polished and their abrasive wear rate.[28–30] In addition, a hard and rough material may scratch, groove, and abrade the opposing dentition.[31] As a general requirement, the surface characteristics of dental restorative materials should approximate those of the natural dentition.[30]

Water that has entered the polymer through sorption can also hydrolyze covalent bonds in the resin matrix, filler-matrix interface, or filler.[32,33] The effects of hydrolysis may include loss of mass, filler debonding, and degradation of mechanical properties such as strength and modulus.[33,34] Knobloch et al[35] report no significant difference in resin cement fracture toughness after 24 hours and 7 days of storage in distilled water, whereas others[11] report a statistically insignificant increase in flexural modulus measured over 1 hour, 1 day, 1 week, 1 month, and 1 year of storage in distilled water. In the present study, all specimens were stored in distilled water for 1 week prior to compression, Vickers hardness, and flexural strength tests.

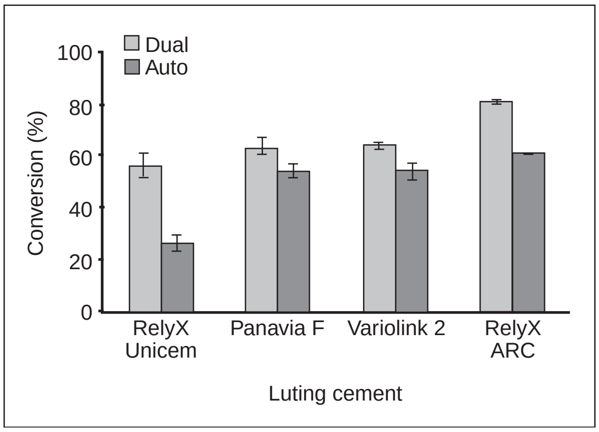

Fig 5 Degree of conversion of resin composite luting cements measured 15 minutes after light curing (dual-cured cements) or mixing (autopolymerized).

Some researchers report that DC% of resin composite materials is not necessarily positively correlated with their mechanical properties.[36] The type and content of the fillers in resin composites also influence their mechanical properties. Taking this into consideration, it is interesting to note the high flexural strength of Variolink 2 in both dual and autopolymerized versions, even considering the light intensity that decreases in the deeper parts of the cement and the small amount of chemical activators verified in the hardness test. Besides the high filler content compared with the other materials tested, another possible explanation for the behavior of Variolink 2 is the presence of urethane dimethacrylate (UDMA) in its monomer composition. UDMA monomer is more flexible than commonly used bisphenol-A-glycidyldimethacrylate (bis-GMA) because of the urethane linkages and lower viscosity of monomers, which facilitate the migration of free radicals and increase the cross-linking density. In addition, the filler content of the resin composite is also responsible for its hardness.[36,37] The compressive strength and microhardness of Variolink 2 were, however, not as high as could be expected from its flexural strength. A correlation between filler content and hardness has been demonstrated.[37] In the present study, the Vickers hardness values for Panavia F, Variolink 2, and RelyX ARC, with similar filler weight percentages (≈ 78 wt%, ≈ 73 wt%, and ≈ 68 wt%, respectively),[5,16] were also similar. Consistent with the results of another study,[16] the differences between Vickers hardness values of the materials tested were not in accordance with the differences in their flexural strengths.

Dual curing was more effective than autopolymerization alone. This finding is supported by the results of some other researchers.[15] It should be noted that the differences in DC% between dual-cured and autopolymerized forms of both Variolink 2 and Panavia F specimens 15 minutes after mixing were relatively small. Harashima et al[38] reported a maximum of about 80% conversion for dual curing and 75% for autopolymerization alone. The results of the present study (81%) were in accordance with the maximum DC% reported in that study,[38] 61% in autopolymerized forms. In the present study, DC% was measured at room temperature, which can cause a slower reaction compared to the reaction at mouth temperature. The mean DC% of autopolymerized RelyX Unicem was significantly lower (26%) than those of the other groups. Such a low value can be considered unacceptable from a clinical perspective. However, it should be remembered that DC% values in the present study were compared 15 minutes after light polymerization, and RelyX Unicem is a resin cement that also includes a glass-ionomer cement component. Phosphorulated methacrylates have acid-base reactions with glass particles, which can eventually produce a matrix with a high degree of monomer conversion. This might have influenced the highest compression strength and hardness among the cements studied. However, the phosphoric acid neutralization reaction was not analyzed in the present study.

Adequate polymerization of the resin-based cement is an important prerequisite for the stability and biocompatibility of the restoration.[22] Adhesive resin composite luting systems are furthermore recommended for the cementation of many all-ceramic systems,[1] not metal-based FPDs, because of the possible risk of inadequate polymerization.

Within the limitations of the present study, it can be concluded that: *(1)* there was a difference in the physical properties of different resin composite luting cements of similar chemical characterization; and *(2)* the method of polymerization influenced the degree of conversion of dual-curing resin composite luting cements. To increase the clinical relevance of studies in which mechanical, chemical, and physical properties of luting cements are evaluated, further tests must be performed under clinical conditions.

Acknowledgments

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