Composite resin vs resin cement for luting of indirect restorations: Comparison of solubility and shrinkage behavior

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The aim of this study was to evaluate relationship between shrinkage development and early solubility of two commonly used luting materials, a self-adhesive cement (GCem chemical and light cured) and composite resin (Tetric). Linear displacement, shrinkage forces and leaching of UDMA from specimens immersed in 75% ethanol/25% water were measured. The least amount of linear shrinkage ($33.0 \pm 2.9 \mu\text{m}$) and polymerization force ($4.1 \pm 0.3 \text{ kg}$) was observed in Tetric. UDMA leaching ($\% \mu\text{g/mL}$) was the following: chemically cured GCem (4.2 ± 0.2) > light cured GCem (1.5 ± 0.1) > Tetric (0.1). Shrinkage development in the early stages of polymerization was much slower in the self-cured specimens in respect to light cured ones. With the chemically cured self-adhesive cement, incomplete materials' setting during the initial stages after polymerization favored monomer leaching from the cements' mass.

Keywords: Solubility, Shrinkage, Self-adhesive, Resin composite, Luting

INTRODUCTION

Composite resin is a widely used material for the direct restoration of anterior and posterior teeth. Due to their advantages in terms of mechanical properties and extended handling time, in early days Besek *et al.*¹⁾ were the first to recommend composite resin for the luting of CEREC ceramic inlays as well. At that time, this CAD/CAD system was rather inaccurate so the use of a resin composite as a luting agent was an efficient solution to protect restoration margins from micro leakage, esthetic defects, and caries.

With self-adhesive cements the luting procedure has been simplified, as no adhesive system is necessary prior to the application of the cement. Several studies have shown promising results when used for the luting of inlays and onlays. However, marginal degradation of the cement interface has been reported after 1 year of clinical service²⁾.

One reason for the degradation of the cement layer is polymerization contraction of the luting agent. Even if it is present in a thin layer³⁾ shrinkage has been reported to cause early marginal gap formation between luting agent and tooth substrate. Shrinkage is directly related to the degree of conversion of the monomer systems present in composites. This is why shrinkage profiles of a given material can be considered as indicators of the degree of polymerization the material can attain through a certain period of time. An incompletely polymerized material may experience less polymerization shrinkage. In this respect, evaluations of shrinkage kinetics of luting agents have shown higher contraction stresses some hours after polymerization⁴⁾.

Another reason for the degradation of the cement layer has been attributed to liquid inward flow into the cement with the subsequent out-ward flow of free monomers and fillers into the oral environment^{5,6)}. This

may result in an increased release of monomers^{7,8)} since in the clinical practice the luting interface is directly in contact with the oral environment shortly after polymerization. As a result, mechanical properties of the luting agent can be adversely affected, in addition to biocompatibility problems due to the release of unreacted monomers to the oral environment or, through dentin, to the dental pulp⁹⁾.

The risk of debonding for indirect restorations has been found to be higher immediately after placement because the cement would not have reached the highest degree of monomer conversion¹⁰⁾. This is why the evaluation of a materials' performance early after polymerization may be of clinical relevance. Therefore, the aim of the present study was to evaluate the leaching potential and shrinkage development of two representative materials commonly used as luting agents: a self-adhesive cement and a hybrid composite. The first null hypothesis was that the self-curing cement would not release more residual monomers than the light cured cement during the same interval of time. The second null hypothesis was that during the 1st hour following polymerization there would be no differences in the elution of residual monomers from the self-adhesive cement compared to the hybrid composite. The third null hypothesis was that no differences in linear shrinkage development and polymerization force would be observed between the self-adhesive cement and the hybrid composite.

MATERIALS AND METHODS

Two UDMA-based representative materials used for luting purpose, a hybrid restorative composite (Tetric, Ivoclar Vivadent, Schaan, Liechtenstein) and a self-adhesive cement (GCem, GC Corporation, Tokyo, Japan) were evaluated. The composition of the materials and

application protocols are detailed in Table 1. For sample preparation, a standardized amount (150 mg) of test material was compressed between two 1-mm-thick glass plates. A transparent plastic matrix strip (Odus Universal Strips, 0.05 mm thickness, Odus Dental, Vevey, Switzerland) was placed between the materials and the glass plates to avoid sticking of the material to the glass, especially when GCem was used. For GCem chemically cured, the material was dispensed and left undisturbed for 7 min. For Tetric and GCem in its light-cured version, 40 s polymerization was performed at a standardized distance of 1 mm from the test material by placing the tip of the light-curing unit (Bluephase, Ivoclar Vivadent AG) in contact with the glass plate covering the top surface of the specimen. The light intensity was controlled periodically using a radiometer (Optilux, Model 100; SDS Kerr, Danbury, CT, USA), ensuring a constant output intensity of 950 mW/cm². To evaluate the early solubility of both materials, after polymerization the specimens ($n=5$) were immersed in a storage medium (75% ethanol and 25% distilled water) for 60 min. Specimens were then removed and the storage liquid was used for chromatographic measurements.

Detection and quantification of monomer elution

The amount of monomer elution (urethane dimethacrylate: UDMA) was calculated by high-performance liquid chromatography (HPLC), following the protocol of Nguyen *et al.*¹¹⁾. In brief, separation of UDMA from the other constituents was obtained from the two materials, Tetric and GCem. Pure UDMA, molecular formula: C₂₃H₃₈N₂O₈, molecular weight: 470.5 g/mol was graciously provided by a dental manufacturer (IvoclarVivadent) and this molecule was used as a standard for the analysis. A stock solution at 10 mg/mL in ethanol was prepared and appropriately diluted to attain final concentrations ranging around 1 mg/mL. This allowed for the construction of the calibration curves. Methanol (MeOH) for HPLC grade was obtained from a chemical provider (Panreac Quimica, Barcelona, Spain). Water was obtained from a Milli-Q Water

Purification System (Millipore, Bedford, MA, USA). The chromatographic separations were performed with an appropriate system (Merck LaChrom, Merck, Darmstadt, Germany) constituted of L-7100 programmable pumps, a L-7200 autosampler with a 100 µL loop (20 µL injected in the partial loop mode), a L-7614 on-line degasser, a L-7400 UV-VIS programmable detector and a Jetstream 2 plus column oven set at 30°C. The UV-VIS detector contained a 14 µL standard flow cell, the time constant was set at 0.1 s (lowest value) and data sampling rate was 5 Hz. Data acquisition, data handling and instrument control were performed with the D-7000 HPLC System Manager Software. A gradient from 60% to 98% MeOH in 10 min was implemented, followed by a 15 min reequilibrating time in the initial gradient conditions (*i.e.* 60% MeOH). The column used throughout this study was a GraceSmart RP18 of 150×4.6 mm, 5 µm from Grace Davison (Reinach, Switzerland) operating at a flow rate of 1 mL/min. A wavelength of 235 nm was found suitable to quantify UDMA in the ethanol solution. To determine the concentration of UDMA released from the specimens stored in ethanol, calibration standards, at a concentration of 3, 10, 100 and 1000 µg/mL were prepared by an appropriate dilution of the stock standard solution with ethanol.

Measurement of shrinkage development

Linear displacement measurements (expressed in µm) induced by polymerization shrinkage were carried out with a custom made measuring device, described in detail by Stavridakis *et al.*¹²⁾. In brief, it consisted of a stable metal frame, upon which a thin aluminium platelet with a perpendicular diaphragm was loosely placed. A standardized amount (150 mg) of material was placed on the aluminium platelet of the device. Then the material was flattened with a glass plate to a test height of 1.5 mm. For shrinkage measurements of GCem chemically cured, the cement was placed on the aluminum platelet and self-curing was monitored during 3,600 s (1 h). Polymerization in Tetric and in GCem light activated

Table 1 List of materials

Materials name	Batch number	Composition Application procedure according to manufacturer recommendations
Tetric IvoclarVivadent, Schaan, Liechtenstein	L43164	UDMA, dimethacrylate, bariumglass filler, Ba-Al-Fluorosilicate-glass, Ytterbiumtrifluoride, mixed oxide, high dispersed silica, additives, catalysts and stabilizers, pigments. Filler weight: 78.6 wt% Apply and light-cure each 2 mm layer for 40 s.
GCem Automix GC Corp, Tokyo, Japan	0811201	Liquid: UDMA, dimethacrylate, 4-MET, phosphoric ester monomer, distilled water, initiator. Powder: fluoro-alumino-silicate glass particles, initiator. Filler weight: 65–70 wt% The working time is 3 min 30 s from start of mix. Light-cure each restoration surface for 20 s. Or allow the cement to self-cure for 4 min.

was carried out for 40 s at a standardized distance of 1 mm from the test material. The light intensity and device were the same as previously mentioned. The light intensity was controlled periodically using a radiometer (Optilux, Model 100; SDS Kerr, Danbury, CT, USA), ensuring a constant output intensity of 950 mW/cm². The vertical movement of the diaphragm caused by polymerization shrinkage of the materials was detected from the start of polymerization and up to 3,600 s (1 h) by an infrared sensor with an accuracy of 100 nm and a sampling frequency of 5 Hz.

Measurements for polymerization shrinkage force (expressed in Kilograms) were carried out with a custom made measuring device that was also described in detail by Stavridakis *et al.*¹²⁾. In brief, the upper part consisted of a semi-rigid load cell to which a metal cylinder of 8 mm diameter was screwed. The cylinder was coated with a standardized amount (150 mg) of test material, which was compressed at a distance of 1.5 mm on to a glass plate attached to the base of the device. To improve adhesion, the surfaces of the metal cylinder and of the glass plate were sandblasted with 50 µm aluminium oxide particles at 2 bars pressure and silanised. No light activation was used in GCem chemically cured. Polymerization in Tetric and in GCem light activated was carried out for 40 s. Light curing was performed with the same device and under the same conditions as above mentioned for linear shrinkage measurements. Forces generated during polymerization shrinkage were detected for up to 1 h by means of the load cell at a sampling frequency of 5 Hz. The data were fed on-line by means of an A/D converter using custom made software to a personal computer and stored on its hard disc. Eight measurements for linear displacement and eight for polymerization shrinkage force were performed on each group and their mean values were reported.

Statistical analysis

Analysis of data was performed with SPSS 14.0 software for Windows. Each test parameter (% of monomer leaching, linear shrinkage and polymerization force) was analyzed using one-way ANOVA and Duncan *post-hoc* test with a level of significance set at 0.05.

RESULTS

Linear shrinkage and polymerization force

Table 2, Fig. 1 and Fig. 2 represent scores and time-dependent mean curves of linear shrinkage and polymerization force registered during the 1st hour (3,600 s) following polymerization. Tetric was the material that developed the least linear shrinkage (33.0±2.9 µm) and polymerization force (4.1±0.3 kg). The shrinkage curves of Tetric (green curve) showed that the time delay before reaching the near-linear horizontal growth pattern was almost non-existent, as with light activated polymerization strain and stress are generated immediately after light curing starts. GCem light cured presented the highest values of linear shrinkage (58.2±3.9 µm) and polymerization force (6.1±0.3 kg) after 1 h of polymerization. Similar values were obtained with GCem chemically cured (linear shrinkage 57.3±3.2 µm and polymerization force 5.8±0.3 kg). Statistical analysis showed significant less shrinkage with composite resin (Tetric) when compared to GCem Light cured and GCem chemically cured. No significant differences after 1 h polymerization could be detected between these two groups.

In GCem light cured, the shrinkage curves (in red) followed a similar pattern in respect to Tetric. Already after 120 s, the curve had reached an almost linear growth pattern. However, the shrinkage profile of GCem chemically cured (in blue) was delayed in time; even after 15 min (900 s) the linear growth pattern was still not attained, indicating that this material had just started to react.

Determination of leached monomer

UDMA that eluted from the specimens stored in ethanol are shown in Table 2. Data is reported as relative percentages (% µg/mL). Micro hybrid composite resin (Tetric) was the most stable material, with the smallest quantity of UDMA leaching (0.1 % µg/mL). When GCem was light cured for 40 s, the concentration of residual UDMA in ethanol was around 10 times higher (1.5±0.1 % µg/mL) in comparison to Tetric. The highest monomer leaching was observed when GCem was chemically cured. UDMA presence in ethanol was around 30 times higher (4.2±0.2 % µg/mL) in comparison to Tetric. The shrinkage profile of GCem chemically cured (Figs. 1 and 2) together with the high amount of elution showed that

Table 2 Results of monomer elution, linear shrinkage and polymerization force measured from the interval immediately after polymerization up to 1 h after (3,600 s).
Levels connected by different letters are significantly different at the $p=0.05$ level and apply to each column

Materials	Linear shrinkage after 1 h (µm)	Polymerization force after 1 h (kg)	Amount of UDMA elution after 1 h (% µg/mL)
Composite resin (Tetric)	33.0±2.9 A	4.1±0.3 A	0.1 A
Self-adhesive cement light-cured (GC)	58.2±3.9 B	6.1±0.3 B	1.5±0.1 B
Self-adhesive cement chemically-cured (GC)	57.3±3.2 B	5.8±0.3 B	4.2±0.2 C

Fig. 1 Curve profile of linear shrinkage for the three materials tested up to 1 h (3,600 s) following polymerisation.

CC: chemical curing, LC: light curing.

Fig. 2 Curve profile of polymerization force for the three materials tested up to 1 h (3,600 s) following polymerization.

CC: chemical curing, LC: light curing.

leaching occurred while the material was chemically polymerizing.

DISCUSSION

For this study, two representative materials commonly used for luting of adhesive indirect restorations, a self-adhesive luting cement and a micro hybrid composite, were chosen¹³. The experimental methodologies, *i.e.* High Performance Liquid Chromatography (HPLC), linear shrinkage and polymerization force, have been used in previous studies^{8,14-17} to detect differences within materials in respect to their response to contraction forces and to leaching of chemical components from the materials' mass.

An interval of 1 h after polymerization was chosen because it corresponds approximately to the time frame of a luting appointment for an indirect restoration. In addition to time saving, a recent study showed no significant differences between UDMA leaching after storage periods of 10 min, 1 h, 24 h, 3 days and 7 days⁶. Immediately after seating of the restoration and

polymerization, the clinician proceeds with the removal of cement excess and occlusal adjustment; the luting material is particularly stressed during this period¹⁰. In terms of leaching potential, this time frame can be also considered of clinical importance since in the daily practice an indirect restoration is luted, adjusted and polished immediately after polymerization and shortly after the patient leaves the dental office. This means that during the first hour after polymerization, the restoration has already been in contact with the humid oral environment for about 45 min. A solution of 75% ethanol/25% water was used following a published protocol⁸. This solution is recommended as a food simulator according to the guidelines of the US Food and Drug Administration⁷. To standardize testing conditions, sample's immersion for elution tests and shrinkage measurements were done at room temperature. Expectedly, under clinical conditions (increased temperature in the mouth) monomer elution and shrinkage would possibly be even higher than the results obtained in the present study.

Our results could show that the self-adhesive cement was significantly more prone to monomer leaching compared to the hybrid composite. Significantly higher amounts of UDMA were released from the chemically cured cement in respect to the light cured one (Table 2), validating the first research hypothesis. This was probably due to the fact that during the first hour after polymerization the cement was still hardening and therefore, more prone to chemical attack. This may explain why in the clinic, the integrity of the luting interface can be compromised if polishing is performed immediately after cementing¹⁸. However, no significant differences were observed between the chemically cured and light cured self-adhesive cement after 1-h polymerization (Figs. 1 and 2). This indicates that, provided that the cement is protected with some varnish during the early stages of polymerization, the chemical reaction will be effective in its ability to increase the materials' degree of conversion through time, confirming the result of a recent study¹⁹. It has been advocated that the curing reaction of dual-cure cements has a marked effect during the initial 30 min after polymerization. But after this period, the curing process initiated chemically or by light advances at very similar rates²⁰. Graphs in Figs. 1 and 2 are confirmatory of the precedent statement as after 1,800 s (30 min), the curve profiles were very similar for the chemically and light cured self-adhesive cement. Reporting this finding to the clinic means that protection of the luting cement from the oral environment during the first hour following polymerization may be convenient, especially when using the self-adhesive tested in this study. Although one self-adhesive cement was tested, it is known from previous studies that solubility of self-adhesive cements is material dependent²¹. In respect to the materials composition, the performance of self-adhesive cements seems to depend also on the amount of resinous component present within the cement, information that is not, unfortunately, clearly provided

by the manufacturers. In the case of GCem, a recent study reported that its composition is very similar to a glass-ionomer and that it should be classified as a resin-modified glass-ionomer²². If this would be the case, our results could be explained by a high initial solubility and therefore monomer leaching, like occurs with glass-ionomers immediately after placement. Shrinkage values of this cement were significantly higher than the ones attained by the hybrid composite. A lower filler weight in the self-adhesive cement in respect to composite (Table 1) could have contributed to the higher shrinkage values. This observation is in agreement with the one of a recent study¹⁷ in which shrinkage stresses of resin-cements have been found to be relatively high. Therefore, the second and third research hypotheses can be validated.

The least amount of residual UDMA monomer was observed in the micro hybrid composite resin. Due to an increased filler level in composite resin, early solubility is not as important as for cements with more resinous content²³. In terms of shrinkage development, significantly lower scores of linear displacement and of polymerization force were recorded in respect to the chemical and light activated versions of the self-adhesive cement. Similar results were observed in a recent study that compared the shrinkage kinetics of several restorative composites¹². Clinically, less shrinkage may contribute to reduce gap formation at the margins of the restoration and eliminate or limit adjacent penetration of micro-organisms¹⁷.

The present findings have some clinical implications. Luting of full non-opaque crowns with resin composite should be avoided as its high viscosity may compromise the seating of the restoration. However, using composite resin as luting agent for inlays and onlays has some handling advantages in respect to excesses removal and unlimited handling time, as demonstrated in a recent clinical study^{13,24}. In cases of wide luting spaces where the luting layer is more exposed to oral environment, a stable material like resin composite may be preferable.

CONCLUSION

Hybrid composite showed the best results in terms of shrinkage development and stability against leaching. Shrinkage values of the self-adhesive cement tested (self-cured or light cured) were significantly higher than those observed for the hybrid composite. For the chemically cured self-adhesive cement, incomplete materials' hardening during the initial stages after polymerization favoured monomer leaching from the cements mass.

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