Degree of Conversion and Mechanical Properties of Modern Self-Adhesive Luting Agents

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Abstract: New self-adhesive resin composite luting agents have currently been developed, claiming improved properties. The study aimed to evaluate the composition, degree of conversion, and mechanical properties of Panavia SA Plus (PSP), Panavia SA Universal (PSU), SpeedCem Plus (SPC) and TheraCem Ca (THC), with the resin luting agent Panavia V5 (PV5) serving as a control. The structure of the materials was studied by FTIR spectroscopy and SEM/EDX spectrometry. Disk-shaped specimens were prepared from each material under dual- and self-curing modes (n = 5/mode and material). After a 3-week storage period (dark/37 °C/80%RH) the Martens hardness, indentation modulus, elastic index, and creep were determined by instrumented indentation testing (IIT), while the degree of conversion was assessed by FTIR spectroscopy. Statistical analysis was performed by 2-way ANOVA and post-hoc testing (α = 0.05). All materials were based on aromatic monomers, except for SPC. Fillers with potentially bioactive Ca-glasses were identified in SPC and THC, which showed the highest P/Si ratio. The dual-curing mode demonstrated superior performance in all properties. Differences between materials within each curing mode were limited to SPC, THC (highest conversion) and PSA, PSU, SPC (highest elastic index) for dual-curing, and THC (lowest hardness and elastic index). The results confirmed a lower self-curing conversion in these materials, which may affect some of the mechanical properties tested.

Keywords: self-adhesive luting agents; composition; degree of cure; mechanical properties; X-ray microanalysis; infrared spectroscopy; instrumented indentation testing

1. Introduction

Self-adhesive luting agents, the latest development in the field of adhesive luting materials, have become popular in contemporary clinical practice. The main reason was that their mechanical properties, solubility, adhesive strength with dentine, and various substrates (alloys, polymers, ceramics) were considered comparable with the multi-step adhesive resin composite luting agents, but attainable within a single application step. These materials are composed of (a) crosslinking aromatic and aliphatic dimethacrylate monomers, (b) acidic methacrylate adhesive monomers (phosphate, carboxylic), (c) ion-leachable glass filler particles or basic compounds, to neutralize bulk residual acidic monomers, (d) silanated reinforcing filler particles, (e) acid-compatible dual-cure catalysts and stabilizers, and (f) pigments [1,2]. Most products also contain sources of fluoride release (fluorosilicate glass fillers, YbF₃, NaF, etc.).

The curing capacity of the self-adhesive luting agents has been assessed in several studies, leading to the conclusion that it is lower than the conventional resin luting agents [3] with the self-curing mode, providing a significantly lower degree of conversion than dual-curing [3–6], regardless of the differences in monomer composition. The delayed onset and slower rate of conversion were attributed to the presence and neutralization...
rate of the acidic monomers [2,7]. It has been shown that the extent of acid-neutralization varies between materials and curing modes [6–9], with the dual-curing mode demonstrating prolonged neutralization time [6]. The mechanical properties have been tested by a variety of methods, such as uniaxial [8–11] and biaxial testing for flexural strength and modulus [5], compressive strength, diametral tensile strength, hardness and sliding wear testing [7,11–14] and instrumented indentation testing (IIT), the latter determining an array of properties (i.e., hardness, modulus, elastic work, recovery, creep, etc.) by a single indentation [6,15]. In most of these studies, the self-adhesive luting agents were found to be slightly or significantly inferior to composite resin luting agents when tested under the same curing modes. Moreover, the improved conversion documented in dual-cured materials had a positive impact on the mechanical properties of the same materials over the self-curing mode.

Recently, new materials have been introduced to improve the performance of the self-curing component, providing enhanced buffering capacity to the demineralization by Ca-release and expanding the clinical applications to luting of etchable glass ceramics through the incorporation of a silane.

The aim of the study was to comparatively evaluate the composition, curing capacity, and the IIT-derived mechanical properties of the new materials vs. a typical self-adhesive luting agent and an adhesive monomer-free luting agent. The null hypothesis was that there are no statistically significant differences among the materials tested and the controls.

2. Materials and Methods

The dual-cured resin composite luting agents tested are presented in Table 1. Four materials (PSP, PSU, SPC, THC) are MDP-based self-adhesive luting agents and one (PV5) is an adhesive monomer-free resin composite luting agent to be combined with adhesive primers. From the self-adhesive agents tested, PSU contains a silane coupling agent (methacryloxydecyl trimethoxysilane or “long-chain” silane) for universal use, including etchable ceramics, whereas THC contains a bioactive filler based on Portland cement.

Table 1. The materials tested.

| Product/(Code)          | Composition *                                                                 | Manufacturer                      |
|------------------------|-------------------------------------------------------------------------------|-----------------------------------|
| Panavia SA Plus Automix (PSP) | BisGMA, TEGDMA, HEMA, MDP, hydrophobic aliphatic dimethacrylate, hydrophobic aromatic dimethacrylate, silanated Ba–glass filler, silanated colloidal SiO₂, surface treated NaF, CQ, peroxide, catalysts, accelerators, pigments. (Filler: 66%w/46%v, 0.02–20 µm), Shade: Universal (A2) | Kuraray Noritake Dental Inc., Okayama, Japan |
| Panavia SA Universal Automix (PSU) | BisGMA, TEGDMA, HEMA, MDP, hydrophobic aliphatic dimethacrylate, hydrophobic aromatic dimethacrylate, silane coupling agent, silanated Ba–glass filler, silanated colloidal SiO₂, Al₂O₃ filler, surface treated NaF (<1%), CQ, peroxide, catalysts, accelerators, pigments. (Filler: 62%w/40%v, 0.02–20 µm), Shade: Universal (A2) | Kuraray Noritake Dental Inc., Okayama, Japan |
| Panavia V5 (PV5)  | Bis-GMA, TEGDMA, hydrophobic aromatic dimethacrylate, hydrophilic aliphatic dimethacrylate, silanated Ba–glass filler, silanated FAISO₄-glass filler, silanated Al₂O₃ filler, colloidal SiO₂, CQ, initiators, accelerators, pigments. (Filler: 61%w/38%v, 0.01–12 µm), Shade: Universal (A2) | Kuraray Noritake Dental Inc., Okayama, Japan |
| Speedcem Plus (SPC) | UDMA, TEGDMA, PEGDMA, DDDMA, MDP, Ba–glass, YbF₃, Co-polymer and highly dispersed colloidal SiO₂, initiators, stabilizers, pigments. (Filler: 45%v, 0.1–7 µm, mean size: 5 µm), Shade: Yellow | Ivoclar Vivadent, Schaan, Liechtenstein |
| TheraCem Ca (THC)  | BisGMA, MDP; HEMA, Ba–glass with Yb, YbF₃, Portland cement, Tert-butyl perbenzoate, Brombenzene sulfonic acid-sodium dihydrate, catalysts, pigments. (Filler: 45%v, 0.1–7 µm, mean size: 5 µm), Shade: Yellow | Bisco Inc., Schaumburg, IL, USA |

* According to the manufacturers’ information. BisGMA: Bisphenol glycidyl dimethacrylate; TEGDMA: Triethylene glycol dimethacrylate; HEMA: 2-Hydroxyethyl methacrylate; MDP: Methacryloyloxydecyl dihydrogen phosphate; CQ: dl-Camphorquinone; UDMA: urethane dimethacrylate; PEGDMA: polyethylene glycol dimethacrylate; DDDMA: 1,10-decadiol dimethacrylate.

2.1. Specimen Preparation

Two groups of resin composite luting agents’ core specimens were prepared (n = 5 × 2/product). The first group comprised of dual-cured specimens (DC) and the sec-
ond of self-cured (SC). The mixed pastes were inserted in polyacetal molds (Ø = 10 mm, h = 4 mm) and placed on microscopic glass slides covered with transparent cellulose matrix strips and pressed with another set of strip and slide to remove material excess. The specimens of the DC group were light-cured immediately after mixing for 60 s (2 × 30 s, top/bottom surfaces) with a LED curing unit (Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein) operated in the standard exposure mode (1200 mW/cm² light intensity), as measured with a curing radiometer (Bluephase meter, Ivoclar Vivadent, Schaan, Liechtenstein). The specimens of the SC group were not irradiated. All specimen groups were stored in dark conditions at 37 °C and 80%RH for 3 weeks. Then, they were removed from the molds, the top surfaces were wet-ground with 600–1000 grit-size SiC papers, rinsed with water, air-dried with a strong stream of air (20 s), and used for testing.

2.2. Determination of Mechanical Properties by Instrumented Indentation Testing (IIT)

Measurements were performed with a universal hardness testing machine (ZHU0.2/Z2.5, Zwick Roell, Ulm, Germany). Force-indentation depth curves were recorded employing a Vickers indenter under 9.81 N load, 0.5 mm/s (loading) and 0.1 mm/s (contact point and unloading) speed, 2 s dwell time, and 2nd order polynomial zero-point determination. From these graphs, the following properties were determined according to the ISO 14577-1 specification [16]: (a) Martens Hardness (HM), (b) Indentation Modulus (EIT), and (c) Elastic Index (nIT—the elastic to total work ratio). For EIT calculation, a 0.35 value of Poisson’s ratio was used, which corresponds to a volume filler loading of 40–50% [17]. For Indentation Creep (CIT—the percentage increase in indentation depth under constant loading over a given period), the force of 9.81 N was applied for 120 s employing a tetragonal pulse mode (Figure 1) and the CIT was automatically determined based on the following formula:

\[
C_{IT} (%) = \frac{(h_2 - h_1)}{h_1} \times 100
\]

where h2 and h1 are the indentation depths at time constants t2 and t1. Three indentation depth-time curves were obtained from each specimen and the mean values were used as representatives.

![Figure 1](image)

**Figure 1.** A tetragonal pulse where a standard force (F = 9.81 N) was applied for 120 s.

2.3. Molecular Composition and Degree of Conversion

The specimens used for IIT measurements were employed for the assessment of the percentage of the degree of conversion (DC%). The margins of the top flat surfaces were pressed against the diamond reflective crystal (type III, 2 × 2 mm) of an attenuated total reflection (ATR) accessory (Golden Gate, Specac, Orpington, Kent, UK) of an FTIR spectrometer (Spectrum GX, PerkinElmer, Buckinghamshire, Bacon, UK). Spectra were acquired under the following conditions: 4000–650 cm⁻¹ wavenumber range, 4 cm⁻¹ resolution, 20 scans co-addition, ~2 μm depth of analysis at 1000 cm⁻¹. Spectra of uncured paste specimens recorded immediately after mixing (within 30 s at 23 °C) were used as...
unset controls and for assessment of molecular composition. For the degree of conversion measurements, the aliphatic C=C stretching vibrations at 1635 cm\(^{-1}\) were chosen as analytical bands (AN), whereas the aromatic C=C stretching vibrations at 1605 cm\(^{-1}\) (PSP, PSU, PV5, THC) and the N–H vibrations at 1545 cm\(^{-1}\) (SPC) were selected as reference bands (RF). Quantification was performed according to the equation:

\[
\text{DC} \% = 100 \times \left[ 1 - \frac{(\text{ApAN} \times \text{AmRF})}{(\text{AmAN} \times \text{ApRF})} \right] \tag{2}
\]

where, A is the net peak absorbance height of set (p) and unset (m) materials at the analytical (AN) and reference (RF) bands, respectively.

2.4. Microstructure and Elemental Composition

Representative specimens of the DC group were coated with a conductive carbon layer in a sputter-coater unit (SCD 004 with OCD 30 attachment, Bal-Tec, Vaduz, Liechtenstein) and examined in a scanning electron microscope (Quanta 200 SEM, FEI, Hillsboro, ON, USA) operating under high vacuum chamber conditions (4.9 × 10\(^{-6}\) Torr pressure), 20 kV acceleration voltage, and 95 µA beam current. The specimen microstructure was assessed by atomic number contrast backscattered electron images (BE) at 2000 × nominal magnification. The elemental composition of the specimens was determined by X-ray energy dispersive spectrometry (EDX), employing a spectrometer (Quantax, Bruker, Berlin, Germany) attached to the SEM, equipped with a slew-window silicon drift detector (X Flash 610, Bruker, Berlin, Germany) under 20 kV accelerating voltage, 105 µA beam current, 632 s acquisition time, 1% detector dead time and 64 µm × 64 µm collecting window. Quantitative analysis was performed employing ZAF (atomic number, absorbance, fluorescence) and carbon coating-correction routines with the dedicated software (ESPRIT ver. 1.9, Bruker, Berlin, Germany).

2.5. Statistical Analysis

Normality and equal variance of the values registered for IIT and DC% measurements were assessed by Shapiro-Wilk and Brown-Forsythe tests. Statistical analysis was performed by two-way ANOVA (independent parameters: material type and curing mode) and Holm-Sidak post-hoc tests. Spearman correlation analysis was used to evaluate the relationship between the properties tested per curing mode and the nominal filler volume content. For the statistical analysis, the Sigma Plot v.14 software (Systat Software Inc., San Jose, CA, USA) was used at a 95% confidence level (\(\alpha = 0.05\)).

3. Results

Representative force-indentation depth graphs for the dual- and self-curing modes of the materials tested are illustrated in Figure 2. The left curve peak shifting in the dual-cured materials indicates increased HM hardness, whereas the steeper the unloading curve the higher the indentation modulus (\(E_{IT}\)). The results for HM, \(E_{IT}\), and \(n_{IT}\) are summarized in Table 2.

| Product | HM (N/mm\(^2\)) | \(E_{IT}\) (GPa) | \(n_{IT}\) (%) |
|---------|------------------|-----------------|---------------|
|         | DC (N/mm\(^2\)) | SC (N/mm\(^2\)) | DC (GPa)     | SC (GPa)     | SC (% ) |
| PSP     | 329 (39)a,A     | 239 (23)a,B     | 7.6 (0.8)a,A | 6.1 (0.5)a,B | 42.7 (2.9)a,b,A |
| PSU     | 276 (16)a,A     | 235 (14)a,B     | 6.4 (0.5)a,A | 5.3 (0.4)a,B | 43.4 (1.4)a,A |
| PV5     | 325 (29)a,A     | 257 (15)a,B     | 7.5 (0.9)a,A | 6.3 (0.4)a,B | 39.5 (0.6)a,b,A |
| SPC     | 306 (40)a,A     | 290 (17)a,A     | 7.2 (1.3)a,A | 6.5 (1.3)a,B | 40.7 (1.2)a,b,A |
| THC     | 274 (23)a,A     | 164 (8)b,B      | 6.6 (0.4)a,A | 5.1 (0.2)a,B | 39.8 (1.4)b,A |

* Means and standard deviations (in parentheses). Same low-case letters show mean values with insignificant differences between the products within the same curing mode, whereas same upper-case letters show mean values with insignificant differences for the same product between the two curing modes (\(p > 0.05\)).
left peak shifting in dual-cured materials denotes increased HM hardness, whereas the steeper the unloading curve, the higher the indentation modulus (E\text{IT}).

Representative force-indentation depth IIT curves for the dual-cured (a) and self-cured (b) materials tested. The left peak shifting in dual-cured materials denotes increased HM hardness, whereas the steeper the unloading curve, the higher the indentation modulus (E\text{IT}). 1: PSP, 2: PSU, 3: PV5, 4: SPC, 5: THC.

For HM, data distributions passed normality (p = 0.385, >0.05) and equal variance tests (p = 0.268, >0.05). Two-way ANOVA demonstrated a significant interaction between the independent parameters (p = 0.02), therefore the main effects of the parameters could not be properly interpreted. There was no statistically significant difference between the materials within the DC and SC groups, except for the significantly lower values of TCH in the SC group (p < 0.001). Comparison between the two curing modes demonstrated statistically higher HM values in the DC mode in all materials, with the only exemption being the SPC, where insignificant differences were registered (p = 0.425).

The results of E\text{IT} passed normality and equal variance tests (p = 0.627 and 0.247 respectively, p > 0.05). The two-way ANOVA manifested a statistically significant difference only in the curing mode (p < 0.001), with no interaction with the material type (p = 0.056). In all materials, the dual-curing mode showed higher values from the self-curing mode (p < 0.001), without significant differences between the products within each curing mode. For n\text{IT}, although the results passed normality and equal variance tests (p = 0.931 and 0.223 respectively, p > 0.05), there was a significant interaction between the parameters (p = 0.006). Within the dual-curing group, the significant differences were limited between PSU-THC (p = 0.024) and PSU-PV5 (p = 0.045). Within the self-curing group, insignificant differences were found between PSP, PSU, PV5, and SPC (p > 0.05). Between the curing modes per material, all differences were significant.

Representative indentation depth-time graphs used for the assessment of the C\text{IT} are presented in Figure 3. The creep curves comprised of a steep initial part and a main horizontal part related to creep deformation. The dual-cured products exhibited lower indentation depth values at the testing period than the self-cured. The results of C\text{IT} passed normality and equal variance tests (p = 0.918 and 0.651 respectively, p > 0.05). Two-way ANOVA showed an insignificant difference in the material type (p = 0.478, >0.05), and a significant difference in the curing mode (p < 0.001), with no interaction (p = 0.805, >0.05).

Full range ATR-FTIR spectra of the auto-mixed pastes of the luting agents are presented in Figure 4. The major resin peak assignments are as follows (cm\textsuperscript{-1}): O–H (3442, 1140–1110), N–H (3371), aromatic C–C (3010, 1608, 1595, 1510, 830, 801), CH\textsubscript{3}/CH\textsubscript{2}/CH (2920–2880, 1465–1430, 1370–1360, 720–700), C=O (1715, 1320, 1290), C=C (1634, 1500, 895), CON–H (1540), C–O–C (1260, 1105–1000) and Si–O (1150–1000). The phosphate peaks of MDP appear at 1247 (P=O) and at 1040 (P–O–C), 1111, 1014 (P–O) overlapping with the Si–O vibrations. However, the absence of the 1111 cm\textsuperscript{-1} peak (P–O of MDP) from the PV5 spectrum is a characteristic finding.
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Table 2. The results of HM, EIT and nIT for the materials tested in dual-curing (DC) and self-curing (SC) modes.*

| Product | DC            | SC            |
|---------|---------------|---------------|
| PSP     | 5.5 (1.8)a, A | 7.3 (1.5)a, B |
| PSU     | 6.2 (0.7)a, A | 10.1 (1.2)a, B |
| PV5     | 3.9 (1.3)a, A | 8.6 (0.7)a, B |
| SPC     | 5.5 (1.2)a, A | 10.1 (1.5)a, B |
| THC     | 5.1 (2.8)a, A | 9.1 (1.7)a, B |

* Means and standard deviations (in parentheses). Same low-case letters show mean values with insignificant differences for the same product between the two curing modes (p > 0.05).

Figure 3. Indentation depth-time IIT curves for the dual-cured (a) and self-cured (b) products tested based on the tetragonal pulse loading (Figure 1). All the products, exempt for SPC, demonstrated lower curve profiles in dual- than light-curing modes. 1: PSP, 2: PSU, 3: PV5, 4: SPC, 5: THC.

Figure 4. ATR-FTIR spectra of unset auto-mixed pastes of the materials tested. Arrow shows the absence of the P–O peak from the PV5 spectrum (4000–650 cm⁻¹ wavenumber range, A: Absorbance scale).

Representative expanded ATR-FTIR spectra used for calculation of the degree of conversion (DC%) are illustrated in Figure 5. All materials contained aromatic group peaks,
which were used as reference bands, except for SPC, where the N–H vibrations were used as reference. The results of the degree of conversion (DC%) are presented in Table 4. The results passed normality and equal variance tests ($p = 0.051$). Between the curing modes per material, all differences were significant ($p < 0.001$).

Table 4. The results of DC% for the products tested in dual-curing (DC) and self-curing (SC) modes *.

| Product | DC (%) | SC (%) |
|---------|--------|--------|
| PSP     | 55.3 (1.6)a,A | 39.6 (1.9)a,B |
| PSU     | 55.1 (1.3)a,A | 50.7 (1.2)b,B |
| PV5     | 66.6 (1.7)b,A | 53.3 (3.2)b,B |
| SPC     | 69.9 (1.5)c,A | 62.3 (1.7)c,B |
| THC     | 72.3 (1.4)c,A | 56.9 (2.5)d,B |

* Means and standard deviations (in parentheses). Same low-case letters show mean values with insignificant differences between the products within the same curing mode, whereas same upper-case letters show mean values with insignificant differences for the same product between the two curing modes ($p > 0.05$).

The only statistically significant correlation found was between HM and E\textsubscript{IT} for the self-curing mode ($\rho = 1, p = 0.0165$).

The microstructure and the EDX spectra of the products tested are presented in Figure 6. The quantitative results of the EDX elemental analysis are presented in Table 5. The BE images demonstrated the typical structure of particle-filled composites. The filler particles in PSP and PSU were greater than in PV5. Some particles in PSP manifested increased greyscale contrast. SPC and THC exhibited a diffuse distribution of ultrafine high-contrast particles with a greater surface area occupied in SPC. The latter demonstrated some randomly distributed bigger size particles of medium contrast. The elemental analysis showed that all products contained O, Na, Al, Si, P, Cl, and Ba. PSP, PSU, SPC, and THC additionally contained K, SPC and THC, Ca and Yb and PV5, SPC and THC, F. PSP contained the highest amount of Ba and Al, SPC of Ca, Yb and F and THC of O and P. The atomic ratios of the major material elements are presented in Table 6. The highest Al/Si ratios were found in SPC, PSP and the lowest in THC. From the Ca-containing materials, SPC showed the highest Ca/Si and P/Si ratios from THC. SPC and THC demonstrated higher P/Si ratios from PSP, PSU, and PV5.
Figure 6. BE images and the corresponding EDX spectra of the products tested. (a) PSP, (b) PSU, (c) PV5, (d) SPC and (e) THC. (BE images: 2000 × magnification, scale bar: 20 µm; EDS spectra 64 µm × 64 µm area scan analysis).
Table 5. The results of the elemental analysis by EDX (atomic %).

| Product | O    | F    | Na   | Al   | Si   | P    | S    | Cl   | K    | Ca   | Ba   | Yb   |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|
| PSP     | 54.99| -    | 1.19 | 11.09| 24.65| 0.78 | 0.39 | 0.30 | 0.20 | -    | 6.41 | -    |
| PSU     | 56.11| -    | 1.06 | 9.18 | 25.87| 0.83 | 0.19 | 0.25 | 0.29 | -    | 6.21 | -    |
| PV5     | 58.62| 0.44 | 1.14 | 9.13 | 23.34| 0.12 | 0.42 | 0.30 | -    | -    | 6.21 | -    |
| SPC     | 45.00| 20.5 | 1.42 | 6.60 | 12.61| 2.46 | -    | 0.14 | 0.13 | 5.57 | 1.28 | 4.28 |
| THC     | 59.40| 0.89 | 1.98 | 5.88 | 24.91| 2.60 | 0.76 | 0.49 | 0.23 | 1.35 | 0.63 | 0.87 |

Table 6. Atomic ratios of the major elements in the products tested.

| Product | Al/Si | Ca/Si | P/Si | Ba/Si | Yb/Si |
|---------|-------|-------|------|-------|-------|
| PSP     | 0.49  | -     | 0.03 | 0.26  | -     |
| PSU     | 0.35  | -     | 0.03 | 0.24  | -     |
| PV5     | 0.35  | -     | 0.005| 0.27  | -     |
| SPC     | 0.52  | 0.84  | 0.2  | 0.48  | 0.34  |
| THC     | 0.24  | 0.23  | 0.1  | 0.03  | 0.04  |

4. Discussion

The results of the present study showed that the dual-curing mode demonstrated superior results in comparison with the self-curing mode in all the material properties tested. Significant differences were found between materials within the same curing mode for HM (SC), C\textsubscript{IT} (DC), n\textsubscript{IT}, DC\% (DC and SC). Moreover, differences were registered between the structure and elemental composition of the materials tested. Therefore, the null hypothesis should be rejected for these properties.

The self-adhesive luting agents tested were representative of the most current commercially available types based on the characteristics stated by their manufacturers. PSP is a typical dual-cured material, PSU is the only material of this category incorporating a silane, SPC is marketed as a self-curing material with a light-curing option and THC as a Ca-releasing material. A composite luting agent, without adhesive monomers (PV5) was used as a control in all experiments.

All materials demonstrated a typical structure of particle-filled composites, with differences in particle size and mean atomic number (greyscale level of BE images). The greatest particles were found in SPC with a maximum size of approximately 10 µm, which may correspond to pre-polymerized particles, based on their greyscale level. The high-contrast (bright) submicron size particle phase found mainly in SPC and THC is attributed to Yb (salts or glasses), which enhance radiopacity and in the case of Yb\textsubscript{3}F\textsubscript{3} may serve as a source of slow fluoride release \[18\]. From the series of Panavia products, PSP showed the highest Al content, although no information for the presence of Al is given in the manufacturer’s files.

The P/Si ratios of PSP and PSU were six times greater than PV5, which is an adhesive-free monomer composite. This difference may be assigned to the presence of MDP or/and P\textsubscript{2}O\textsubscript{5} in the glass fillers of the former. SPC and THC resulted in the highest Ca/Si and P/Si ratios, suggesting that these materials may exert a bioactive effect. Their P/Si ratios were 6.6 and 3.3 times greater than PSP and PSU respectively, implying that P should be also part of the filler fraction. The composition of THC includes Portland cement powder, with major constituents Ca- and Al-silicates. This has been considered by the manufacturer as a major Ca-source for two important reactions: First, the fast neutralization of unreacted acidic phosphate monomers upon setting, and second, the Ca-releasing capacity at the vicinity, which may reduce or inhibit dental hard tissue demineralization after exposure to acidic challenges, assisted by the synergistic effect of F\textsuperscript{-} released from Yb\textsubscript{3}F\textsubscript{3} particles. However, surprisingly, SPC exhibited a 3.7 times greater Ca/Si ratio than THC, anticipating a stronger inhibitory effect, which is further assisted by the 20 times greater F content of...
the former. Although no further information is given by the manufacturer for the filler content, it seems that SPC may demonstrate increased bioactivity.

The ATR-FTIR spectra recorded confirmed the absence of aromatic monomers in SPC. The dual-curing irradiation mode provided higher conversion in all materials, including SPC, which showed the highest self-curing conversion. Despite the developments in the self-curing catalysis, the materials tested failed to reach the levels of dual-curing, a finding already documented in previous studies for most dual-cured luting agents [3–6]. Although quantitative data for the monomer content is missing, some assumptions for the effects of specific monomers can be made. PSP and PSU showed lower conversion from PV5 in the dual-curing mode; the latter, though, was used without the dedicated tooth-primer which facilitates conversion via a touch-cure mechanism [19]. A possible explanation may be given based on the acidic nature of the mixed PSP and PSU pastes, due to the presence of acidic monomers (such as MDP), known to interfere with conversion [2]. An interesting finding was that PSU, processing the same chemistry with PSP with the exemption of the long-chain silane, demonstrated better self-curing conversion from PSP, reaching the levels of the control (PV5). This might be explained by the presence of the long CH₂ chain hydrophobic silane. The flexible chain may increase the segmental mobility of terminal methacrylate groups and enhance slow-setting conversion via copolymerization. It should be noted that it was not possible to identify characteristic peaks of the long-chain silane in the spectra of PSU (presence of methoxy at 2835 cm⁻¹ or silanol groups at 904 cm⁻¹) to assess the silane status in the material (unset, dual- or self-cured state), possibly due to the low silane content. The high conversion values manifested by SPC in both curing modes should be assigned to the presence of fast-reacting aliphatic dimethacrylate monomers, which show less residual unsaturation than stiff dimethacrylate aromatic monomers, such as BisGMA, due to steric hindrance phenomena [20]. On the other hand, the presence of Ca-containing fillers may neutralize the acidic monomers upon mixing, creating more favorable conditions for enhanced C=C conversion, due to pH balance and molecular orientation effects [21]. This is especially important for the slow-setting self-curing mode [7]. The same mechanism may explain the curing performance of the BisGMA-containing THC. The high THC conversion in the dual-curing mode should be additionally ascribed to the presence of the fast-reacting hydrophilic mono-methacrylate HEMA, known to improve conversion when used as a BisGMA comonomer [22]. Nevertheless, the self-curing conversion, of THC was significantly lower than SPC, reflecting a lower self-curing activation capacity of the material.

The IIT-derived mechanical properties tested may have a significant clinical impact on the performance of the luting agents. Hardness is associated with wear resistance and may affect the marginally exposed part of the luting agent [23]. The elastic modulus is strongly implicated in the fracture strength of glass-ceramics [24]; a material with low modulus may elastically deform at a lower load increasing the propensity of ceramic fracture. The elastic index, a measure of material brittleness, expresses the elastic to total (plastic and elastic) ratio after fracture. Finally, creep, defined as a time-dependent material permanent deformation under a constant load, is related to bulk material phenomena such as particle flow, atomic diffusion, micro-cracking, sliding, stick-slipping, etc [25,26]. High creep has been linked to the poor clinical performance of composites [27].

From the mechanical properties assessed, HM, Eₘ, and nₘ were higher in the dual-curing mode, whereas Cₘ was greater in the self-curing mode. The increased conversion in dual-curing mode, possibly associated with the greater crosslinking capacity of dimethacrylate monomers, resulted in materials with improved mechanical properties. The characteristics of the reinforcing fillers (loading fraction, shape, size distribution) have a determinant factor in the mechanical performance of the materials. In HM, Eₘ, and Cₘ measurements the filler content diminished the material differences as originally encountered in DC% within each mode, resulting in insignificant differences between them, except for THC in HM and Eₘ in the self-curing mode. The results for nₘ were more complex in interpretation. Although in the self-curing mode THC showed the lowest values from
all materials which comprised a statistically homogeneous group, photopolymerization changed the statistical ranking revealing a significant contribution of conversion to this property. The higher creep values of self-curing cements indicate that the non-irradiated materials are more vulnerable to plastic deformation under constant loading.

The results of the present study showed inferior HM and E\textsubscript{IT} results in both curing modes in comparison with previously studied materials with the same methodology, possibly attributed to the higher filler content of the latter [6]. The differences between the dual- and self-curing modes were less than those already registered for the same IIT parameters range employing nano-hardness testing, apparently due to the surface sensitivity of the technique [15]. Hardness measurements may better characterize the material performance including bulk response, rather than limiting the measurements to superficial layers, as in cases of nano-hardness [28]. The E\textsubscript{IT} was calculated based on a Poisson’s ratio given for composite materials with similar filler volume loading, which may not correspond exactly to the specific materials’ values. Nevertheless, the sensitivity of modulus to Poisson’s ratio is low, since only a 5% error on modulus estimation has been found at 40% uncertainty in the ratio values [29]. The testing conditions involved prolonged specimen storage (3 weeks, dark conditions at 37 \degree C/80%RH), to include the contribution of delayed post-curing effects [30], which are important for slow-setting materials, as in the case of self-curing mode. The humidity was used to accelerate the acid-base reaction. No water immersion was used during storage to avoid the dissolution of immature materials, as in the case of self-curing or the slow acid-neutralization reaction.

The results of the present study show that the latest versions of self-adhesive cements, although improved, they still demonstrate reduced conversion in the self-curing mode. Considering that the vast number of applications of self-adhesive luting agents involves opaque restorations or restorations with minimal light-transmission characteristics, it can be concluded that there is a need for further enhancement of the self-curing conversion, since each of the materials tested has potential for additional conversion, as documented from dual-curing data. This would improve their mechanical properties and biocompatibility. To avoid stability problems, the addition of a touch-cure primer could be a valuable contribution to these materials. Such primers have been already introduced by the manufacturers of several self-adhesive luting agents. The issue of bioactivity, determined by the Ca-releasing capacity, merits further investigation. The principle of “smart” response to pH reduction by Ca and OH\textsuperscript{-} release from resin composite filler particles has been first introduced in light-curing restorative materials two decades ago [31] and after certain developments is still available in two-phase (self- or dual-cured) restoratives [32]. The rate of Ca-release after an acidic stimulus, the buffering capacity of the released species and the associated inhibition of hard dental tissue demineralization, the material degradation rate, and the Ca-recharging capacity from saliva are some topics that need to be addressed in future research, to establish the clinical efficacy of Ca-releasing luting agents.

5. Conclusions

Under the limitations of the current study, the following conclusions can be reached:

(a) The self-adhesive luting agents tested demonstrated important structural differences mainly associated with the filler content. Two materials (SPC, THC) contained Ca-glasses, Yb, F with the highest P/Si ratio.

(b) In all materials, the dual-curing mode demonstrated higher conversion, hardness, elastic modulus, elastic index, and lower creep than the self-curing mode.

(c) Within the dual-curing mode, significant differences were found in favor of SPC, THC in conversion and PSA, PSU, and SPC in elastic index.

(d) Within the self-curing mode, THC demonstrated the lowest hardness and elastic index.

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**References**

1. Radovic, I.; Monticelli, F.; Goracci, C.; Vulicevic, Z.R.; Ferrari, M. Self-adhesive resin cements: A literature review. *J. Adhes. Dent.* 2008, 10, 251–258.
2. Manso, A.; Carvalho, R.M. Dental cements for luting and bonding restorations. Self-adhesive cements. *Dent. Clin. N. Am.* 2017, 61, 821–834. [CrossRef] [PubMed]
3. Vrochari, A.D.; Eliades, G.; Hellwig, E.; Wrbas, K.T. Curing efficiency of four self-etching, self-adhesive resin cements. *Dent. Mater.* 2009, 25, 1104–1108. [CrossRef]
4. Aguiar, T.R.; de Oliveira, M.; Arrais, C.A.G.; Ambrosano, G.M.B.; Rueggeberg, F.; Giannini, M. The effect of photopolymerization on the degree of conversion, polymerization kinetic, biaxial flexure strength, and modulus of self-adhesive resin cements. *J. Prosthodont. Dent.* 2015, 113, 128–134. [CrossRef]
5. Aguiar, T.R.; de Oliveira, M.; Arrais, C.A.G.; Ambrosano, G.M.B.; Rueggeberg, F.; Giannini, M. The effect of photopolymerization on the degree of conversion, polymerization kinetic, biaxial flexure strength, and modulus of self-adhesive resin cements. *J. Prosthodont. Dent.* 2015, 113, 128–134. [CrossRef]
6. Pilo, R.; Papadogiannis, D.; Zinelis, S.; Eliades, G. Setting characteristics and mechanical properties of self-adhesive resin luting agents. *Dent. Mater.* 2017, 33, 344–357. [CrossRef]
7. Baena, E.; Fuentes, M.V.; Garrido, M.A.; Rodriguez, J.; Ceballos, L. Influence of post-cure time on the microhardness of self-adhesive resin cements inside the root canal. *Oper. Dent.* 2012, 37, 548–556. [CrossRef]
8. Sasalkauskaitė, E.; Tam, L.E.; McComb, D. Flexural strength, elastic modulus, and pH profile of self-etch resin luting cements. *J. Prosthet. Dent.* 2008, 10, 262–268. [CrossRef]
9. Zorzin, J.; Petschelt, A.; Ebert, J.; Lohbauer, U. pH neutralization and influence on mechanical strength in self-adhesive resin luting agents. *Dent. Mater.* 2012, 28, 672–679. [CrossRef]
10. Roedel, L.; Bednarzig, V.; Beller, R.; Petschelt, A.; Lohbauer, U.; Zorzin, J. Self-adhesive resin cements: pH-neutralization, hydrophilicity, and hygroscopic expansion stress. *Clin. Oral Invest.* 2017, 21, 1735–1741. [CrossRef] [PubMed]
11. Nakamura, T.; Wakabayashi, K.; Kinuta, S.; Nishida, H.; Miyamae, M.; Yatani, H. Mechanical properties of new self-adhesive resin-based cement. *J. Prosthodont. Res.* 2010, 54, 59–64. [CrossRef] [PubMed]
12. Kim, A.-R.; Jeon, Y.-C.; Jeon, C.-M.; Yun, M.-J.; Choi, J.-W.; Kwon, Y.H.; Huh, J.B. Effect of activation modes on the compressive strength, diametral tensile strength and microhardness of dual-cured self-adhesive resin cements. *Dent. Mater.* 2016, 35, 298–308. [CrossRef] [PubMed]
13. Furuichi, T.; Takamizawa, T.; Tsujimoto, A.; Miyazaki, M.; Barkmeier, W.W.; Latta, M.A. Mechanical properties and sliding-impact wear resistance of self-adhesive resin cements. *Oper. Dent.* 2016, 41, E83–E92. [CrossRef] [PubMed]
14. Takamizawa, T.; Barkmeier, W.W.; Latta, M.A.; Berry, T.P.; Tsujimoto, A.; Miyazaki, M. Simulated wear of self-adhesive resin cements. *Oper. Dent.* 2016, 41, 327–338. [CrossRef]
15. Ilie, N.; Simon, A. Effect of curing mode on the micro-mechanical properties of dual-cured self-adhesive resin cements. *Clin. Oral Investig.* 2012, 16, 505–512. [CrossRef] [PubMed]
16. ISO 14577–1:2002. *Metallic Materials-Instrumented Indentation Test for Hardness and Materials Parameters*; International Organization for Standardization: Geneva, Switzerland, 2002.
17. Chunga, S.M.; Yapa, A.U.J.; Kohb, W.K.; Tsai, K.T.; Lin, C.T. Measurement of Poisson’s ratio of dental composite restorative materials. *Biomaterials* 2004, 25, 2455–2460. [CrossRef]
18. Arends, J.; Dijkman, G.E.H.M.; Dijkman, A.G. Review of fluoride release and secondary caries reduction by fluoridating composites. *Adv. Dent. Res.* 1995, 9, 367–376. [CrossRef]
19. Yoshihara, K.; Nagaoka, N.; Benino, Y.; Nakamura, A.; Hara, T.; Maruo, Y.; Yoshida, Y.; Van Meerbeek, B. Touch-cure polymerization at the composite cement-dentin interface. *J. Dent. Res.* 2021, 100, 935–942. [CrossRef] [PubMed]
20. Ruyter, I.E. Methacrylate-based polymeric dental materials: Conversion and related properties. Summary and Review. *Acta Odontol. Scand.* 1982, 40, 359–376. [CrossRef] [PubMed]
21. Mitra, S.B.; Li, M.Y.; Culler, S.R. Setting reaction of Vitrebond light cure glass ionomer liner/base. *Trans. Acad. Dent. Mater.* **1992**, *5*, 130–152.

22. Eliades, G. Clinical relevance of the formulation and testing of dentine bonding systems. *J. Dent.* **1994**, *22*, 73–81. [CrossRef]

23. Mandikos, M.N.; McGivney, G.P.; Davis, E.; Bush, P.J.; Carter, J.M. A comparison of the wear resistance and hardness of indi-rect composite resins. *J. Prosthet. Dent.* **2001**, *85*, 386–395. [CrossRef]

24. Shahrbaf, S.; van Noort, R.; Mirzakouchaki, B.; Chassemieh, E.; Martin, N. Fracture strength of machined ceramic crowns as a function of tooth preparation design and the elastic modulus of the cement. *Dent. Mater.* **2014**, *30*, 234–241. [CrossRef] [PubMed]

25. Cao, P.; Short, M.P.; Yip, S. Understanding the mechanisms of amorphous creep through molecular simulation. *Proceed. Natl. Acad. Sci. USA* **2017**, *114*, 13631–13636. [CrossRef] [PubMed]

26. Yang, J.; Zhang, Z.; Friedrich, K.; Schlarb, A.K. Creep resistant polymer nanocomposites reinforced with multi walled carbon nanotubes. *Macromol. Rapid Commun.* **2007**, *28*, 955–961. [CrossRef]

27. Baroudi, K.; Silkas, N.; Watts, D.C. Time-dependent visco-elastic creep and recovery of flowable composites. *Eur. J. Oral Sci.* **2007**, *115*, 517–521. [CrossRef]

28. Alcock, J.P.; Barbour, M.E.; Sandy, J.R.; Ireland, A.J. Nanoindentation of orthodontic archwires: The effect of decontamination and clinical use on hardness, elastic modulus and surface roughness. *Dent. Mater.* **2009**, *25*, 1039–1043. [CrossRef] [PubMed]

29. Hay, J. Introduction to instrumented indentation testing. *Exp. Tech.* **2009**, *33*, 66–72. [CrossRef]

30. Watts, D.C.; Amer, O.M.; Combe, E.C. Surface hardness development in light-cured composites. *Dent. Mater.* **1987**, *3*, 265–269. [CrossRef]

31. Kukletova, M.; Kuklova, J.; Christofordis, G. Ariston pHc restorative material. Clinical and morphological study. *Scr. Med. (BRNO)* **2003**, *76*, 39–48.

32. Ruengrungsom, C.; Burrow, M.F.; Parashos, P.; Palamara, J.E.A. Evaluation of F, Ca, and P release and microhardness of eleven ion-leaching restorative materials and the recharge efficacy using a new Ca/P containing fluoride varnish. *J. Dent.* **2020**, *102*, 103474. [CrossRef] [PubMed]