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Degree of conversion of three composite materials employed in the adhesive cementation of indirect restorations: A micro-Raman analysis

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ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form
24 March 2009
Accepted 3 April 2009

Keywords:
Adhesive cementation
Degree of monomer conversion
Indirect restorations
Micro-Raman analysis
Polymerisation

ABSTRACT

Objectives: Adhesive luting of indirect restorations can be carried out employing dual- or light-curing materials. This *in vitro* study evaluated the degree of conversion (DC) of the materials employed in this procedure, seeking how the combination of time and power of curing applied during polymerisation, as well as the temperature of the light-curing composite, influenced the DC.

Materials and methods: One hundred and eighty onlays of different thicknesses (2 mm, 3 mm, 4 mm) were luted with three different composites: two dual-curing cements (Variolink® II and Calibra®) and a light-curing composite (Venus®). The same halogen lamp was used with three different modalities selected to provide a constant quantity of energy. The time/power combinations tested were 400 mW/cm^2 for 120 s, 800 mW/cm^2 for 60 s and 1200 mW/cm^2 for 40 s. The light-curing composite was employed at room temperature and after preheating at 54 °C. Each sample was examined in three positions using the Micro-Raman Dilor HR LabRam spectrometer to evaluate the polymer conversion degree. The data were analysed using analysis of variance and the Student–Newman–Keuls test ($p = 0.05$).

Results: The dual-curing materials showed average conversion percentages close to 64%, although onlays thickness clearly influence the degree of conversion, the light-curing composite showed satisfactory results only when onlays thickness was thin, however preheating significantly improved the performance of the light-curing composite under onlays of great thickness.

Conclusions: Optimal luting of indirect restorations is clearly dependent from light source power, irradiation time and dual-cure luting cement or light-curing composite chosen. It should be calibrated for each material to acquire high DCs. Preheating of light-curing only composites allows for the materials to reach optimal conversion degrees.

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0300-5712/$ – see front matter
doi:10.1016/j.jdent.2009.04.001

1. Introduction

Morphological and functional restoration of compromised teeth can be achieved by means of a direct or indirect restoration.

The need for amalgam alternatives and the demand for aesthetic restorations have led to increased popularity of resin composite restorations for posterior teeth, but the main shortcoming of the composites – the polymerisation shrinkage of the resin – still presents a problem.[1–3] In posterior cavities, especially with the cervical margin situated in dentin, the mass to be polymerised is so large that the shrinkage forces prevail, thereby producing marginal gaps and defects.[4,5] This promotes micro-leakage, which can lead to secondary caries, pulp irritation, postoperative sensitivity and marginal discolouration.[6–8]

A promising method to reduce the shrinkage problem is the resin composite inlay/onlay technique[9–11] in which the shrinkage amount is limited to the thin luting resin composite layer. Improved marginal adaptation and seal of the inlays have been reported,[12–14] and Peutzfeldt and Asmussen[15] showed that contraction gap formation around resin composite inlays could be prevented. Excellent marginal quality has been reported initially and after *in vivo* aging,[13,16,17] and the clinical potential of the inlay/onlay technique has been described in several short-term studies.[16,18–22] Moreover, van Dijken reported on an 11-year follow up of direct composite inlays and onlays[23] in which good durability, excellent marginal adaptation and low frequency of secondary caries were observed.

Criteria that must be considered while cementing a restoration follow:

- Mechanical: for a micro-mechanical and chemical adhesion.
- Structural: for an increase in the restoration resistance.
- Biological: to hermetically seal the space between tooth and restoration.
- Aesthetic: to guarantee chromatic integration between tooth and restoration.

Indirect restorations adhesive luting is performed employing both dual-curing and light-curing cements.[24–27] A literature analysis describes how each material presents advantages and disadvantages in this clinical procedure.

Dual-curing materials are advantaged by their self-curing component, which favours the conversion even in presence of scarce radiant energy, but have the disadvantage of being considerably fluid and requiring the mixture of two elements (responsible for the formation of porosities or voids and for the incorporation of bubbles). Light-curing composites are easily handled and are characterised by controllable hardening times that create high quality margins, but their light only activation constitutes a disadvantage.

The cement properties are determined by the degree of monomer conversion. The non-reacted double-bonds provide the parameter used to assess the materials degree of conversion (DC). For the composites currently used in commerce, the DC ranges from 35 to 67%, and with light-activated systems, the DC decreases as the distance from the surface increases due to the attenuation of the radiant energy as it passes through the thickness of the material.[28,29] The DC of composite resins can be different from the surface to the inner part because of the diffusion of oxygen in the superficial layer of material (5–100 μm), which partially or totally inhibits polymerisation.

Preheating the light-curing composites has been widely shown to increase the composite DC, which improves the properties of the luting agent and results in a more easily handleable and homogenous material.[30–44] A precise method for assessing the DC of cement is Raman spectroscopy,[45–47] which allows for detailed measurement of the non-reacted methacrylate groups.

This experimental study analysed the DC of composite materials employed in the adhesive luting of indirect restorations, and evaluated the incidence on the polymerisation rate of the following variables: restoration thickness, polymerising method applied and temperature of the composite material. The null hypothesis was that there would be a difference in the DC among the various materials and curing methods used.

2. Materials and methods

2.1. Preparation of onlays

One hundred and eighty onlays of different thickness were realised employing a metal custom template. In the template, three holes (6 mm diameter and 2, 3 and 4 mm depth) were prepared. Inside of each hole a standard quantity of Signum® composite shade A2 (Heraeus, Hanau, Germany) was cured for 180 s in the dedicated oven.

2.2. Tested composites

The luting materials considered were Calibra® (Dentsply, Woodbridge, Ontario, Canada), Variolink® II (Ivoclar-Vivadent, Schaan, Liechtenstein) and Venus® (Heraeus). The latter, a micro-hybrid composite material, was employed at two different temperatures: first at room temperature and then at 54 °C after preheating in a Calset® oven (AdDent, Danbury, CT, USA). The heated composite temperature was verified by means of a thermometer.

2.3. Luting procedure

Three different curing modalities were chosen to provide the same quantity of energy (48 J) to the material: 1200 mW/cm^2 for 40 s, 800 mW/cm^2 for 60 s and 400 mW/cm^2 for 120 s.

Before luting, the composite material was put onto a glass slide, then quickly measured by a precision balance in order to standardise the quantity of material employed for luting.

The onlays were then put onto the slide carrying the cement, and light-curing was subsequently carried out by the halogen lamp Swiss Master Light® (EMS, Neun, Switzerland), which was screened to make the light reach the cement obligatorily passing through the onlay.

2.4. Micro-Raman analysis

Twenty-four hours after the polymerisation procedure, the onlays were detached from the slide and the superficial

cement DC was quantified using a micro-Raman spectrometer Dilor HR LabRam (laser, He:Ne; wavelength, 632.8 nm; numerical aperture, 0.7) at 50× magnification with an exposure time of 60 s. Each spectrum was calibrated relative to the main Si peak (521 cm^{-1}). All Raman measurements were made with a single acquisition of 60 s, in order to decrease the background noise, then a baseline correction was applied.

Micro-Raman spectroscopy assesses the luting material DC based on the intensity variation at 1638 cm^{-1} (C=C in methacrylate) relative to the peak corresponding to the C=C bond in the aromatic ring (1608 cm^{-1}), which remains stable during the conversion from monomer to polymer. For each tested material, the reference monomer and polymer spectra were realised.

Each sample was investigated in three positions: centre (0), periphery (2) and at the average distance between these two points (1). A fitting procedure was used to evaluate the signal intensity of the aliphatic C=C bond and to obtain the intensity values of the Raman signals corresponding to 1638 and 1608 cm^{-1}. The ratio between the two peaks was then calculated as previously described,[48,49] and the DC was determined using the following formula:

$$DC\,(\%) = 100 - \frac{\left[\mathrm{abs(C{=}C)_{1638}/abs(C{=}C)_{1608}}\right]_{\mathrm{polymerised}}}{\left[\mathrm{abs(C{=}C)_{1638}/abs(C{=}C)_{1608}}\right]_{\mathrm{monomer}}} \times 100$$

DC was calculated by subtracting the % C=C from 100%.

The three collections taken for each sample at the points 0, 1 and 2 provided superimposable values, that differed from one another by less than 1%. For this reason, the median data was considered.

2.5. *Statistical analysis*

The data were statistically analysed with analysis of variance (ANOVA) and the Student–Newman–Keuls tests ($p = 0.05$) to test the null hypothesis, which stated that the result would not vary according to the treatments performed.

3. Results

As shown in Table 1, onlays thickness strongly affected the degree of conversion in almost all samples: the values collected underneath 4 mm thick restorations were lower than those relative to 2 mm thick ones, although the difference was only weakly significant ($p = 0.05$). This observation was valid for all materials tested, particularly for the light-curing composite employed at room temperature.

Based on the mean DC of the materials tested (64%), dual-curing materials gave acceptable degrees of polymerisation. Nevertheless, each material tested gave different results underneath onlays whose thickness ranged from 2 to 4 mm. For Calibra®, the average difference in the percent conversion was 10.9%, whereas this value was greater for Variolink® II (11.6%).

Calibra® maintained an acceptable DC at greater depths, showing homogeneous polymerisation, independent of the test variables. However, Variolink® II exhibited good behaviour with the lamp set on a power of 800 mW/cm^2 for 60 s; this data differs in a statistically significant way ($p = 0.05$) from the others referring to this time/power combination.

Room temperature Venus® micro-hybrid composite (Normal) had good performances only with the interposition of a 2-mm thick onlay; as thickness increased, the degree of conversion decreased considerably decreased.

The application of heat (54 °C) to the micro-hybrid composite Venus® contributed to the achievement of a higher monomer DC throughout the samples of varying thickness.

Summing up the results and making a post-hoc comparison between the tested materials divided according to the time/power combination tested, it can be inferred that:

- At the curing mode of 1200 mW/cm^2 for 40 s (Fig. 1): (a) with the interposition of a 2-mm thick composite onlay, the micro-hybrid composite at room temperature reached significantly lower ($p = 0.05$) degrees of conversion than the other tested composites. (b) Increasing the restoration

Table 1 – Mean degree of conversion (in percentage) and standard deviation of the tested materials polymerised according to three different time/power combinations.

Material	Curing mode	Onlay thickness		
		2 mm	3 mm	4 mm
Variolink II	40 s × 1200 mW/cm^2	72 (1,2) (±8.6)	51 (2) (±9.8)	45 (1) (±10.5)
	60 s × 800 mW/cm^2	73 (±6.1)	66 (±11.6)	64 (±7.5)
	120 s × 400 mW/cm^2	77 (3,4) (±2.8)	52 (3) (±9.9)	51 (4) (±12.3)
Calibra	40 s × 1200 mW/cm^2	73 (5) (±4.6)	69 (6) (±9.1)	60 (5,6) (±8.1)
	60 s × 800 mW/cm^2	74 (7,8) (±3)	64 (7) (±12.5)	61 (8) (±13.7)
	120 s × 400 mW/cm^2	71 (±6.1)	68 (±9.7)	65 (1 ± 2.4)
Venus (normal)	40 s × 1200 mW/cm^2	65 (9,10) (±6.1)	40 (9) (±4.4)	34 (10) (±5)
	60 s × 800 mW/cm^2	68 (11,12) (±2.6)	39 (11) (±7)	36 (12) (±7.6)
	120 s × 400 mW/cm^2	68 (13,14) (±2)	40 (13) (±8.2)	31 (14) (±6.1)
Venus (54 °C)	40 s × 1200 mW/cm^2	72(15,16) (±7)	64 (15) (±6.1)	60 (16) (±7)
	60 s × 800 mW/cm^2	70 (17,18) (±2.6)	67 (17) (±4.1)	59 (18) (±6.4)
	120 s × 400 mW/cm^2	68 (19,20) (±3.3)	65 (19) (±5.3)	59 (20) (±6.9)

Equal numbers show statistically significant differences among group of the same material ($p = 0.05$).

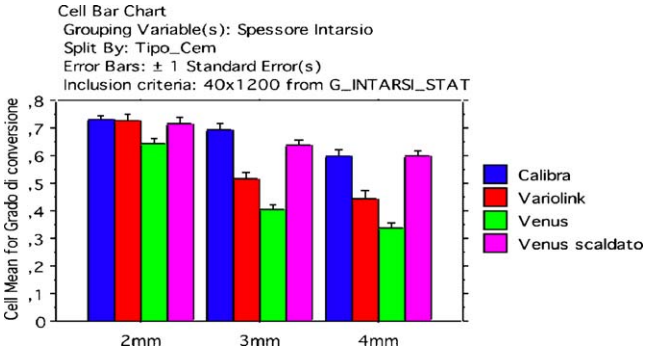

Fig. 1 – The percentage degree of conversion reached by the tested materials when cured at 1200 mW/cm^2 for 40 s. Relevant differences in DC can be evidenced as long as the thickness of the interposed onlay increases, both intra- and inter-material, setting the significance level at 5%.

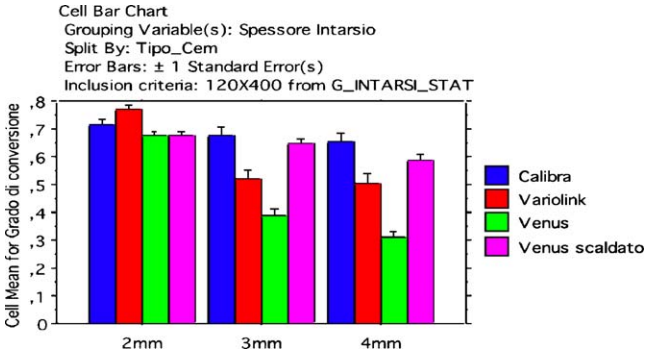

Fig. 3 – The percentage degree of conversion reached by the tested materials when cured at 400 mW/cm^2 for 120 s. The significant ($p = 0.05$) drawback in the performances of Variolink II and Venus is clearly displayed.

thickness to 3 and 4 mm, Calibra® and the pre-heated micro-hybrid composites had significantly higher results ($p = 0.05$) than the other two composites. In particular, the room temperature micro-hybrid composite reached the worst degree of conversion ($p = 0.05$). Surprisingly, the DC of the dual-curing composite Variolink II shows a relevant decrease underneath 2 and 4 mm thick onlays: this can be due to the relatively short irradiation time, unable to fully activate the light-curing component (that probably is strongly represented in this material).

- Curing at 800 mW/cm^2 for 60 s (Fig. 2): (a) under 2 mm thick onlays, the micro-hybrid composite (normal and pre-heated) had significantly lower DCs ($p = 0.05$) than the two dual-curing materials, while (b) under 3 and 4 mm thick onlays, the room temperature micro-hybrid material had significantly lower performances than the other composites ($p = 0.05$).
- Applying 400 mW/cm^2 for 120 s (Fig. 3): (a) under 2 mm thick onlays, the two dual-curing materials reached significantly higher degrees of conversion ($p = 0.05$) if compared to the room-temperature and the pre-heated micro-hybrid composites. (b) Under 3 and 4 mm thick onlays Calibra and the pre-heated micro-hybrid composite worked significantly better than the other materials ($p = 0.05$).

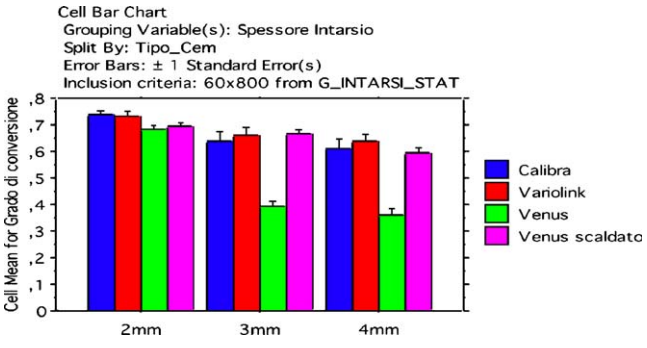

Fig. 2 – The percentage degree of conversion reached by the tested materials when cured at 800 mW/cm^2 for 60 s. Relevant differences in DC can be evidenced as long as the thickness of the interposed onlay increases setting the significance level at 5%. It is therefore evident the increase in the degree of conversion of Variolink II.

4. Discussion

This study measured the DC of different cements polymerised beneath 2, 3 and 4 mm thick onlays. Our results may be explained according to previous literature[1] reports regarding the decrease in light intensity with increasing distance from the composite surface.

The difference in the DC of the materials underneath onlays of different thickness can be explained considering their composition, as reported by Ogunyinka et al.[50] According to their research, the disparities in bulk conversion of the light-activated resin composite materials containing different photoinitiator chemistries were correlated with changes in light transmission measured in real time throughout polymerisation. The polymerisation efficiency was reliant upon the spectral distribution of the light-curing unit, absorption spectra of the photoinitiator and co-initiator type.

The influence of the restoration thickness on the material DC was also investigated by Musanje and Darvell.[51] Their data showed that the dramatic attenuation in irradiance with increasing specimen thickness is in accord with previous reports,[52,21] even though little consideration seems to have been given to the essential physics. Although this attenuation is expected to be in part dependent on filler volume fraction, particle size distribution, particle shape (roughness) and refractive index difference (compared with the matrix), making direct comparisons is difficult due to the lack of adequate data on the fillers.

Note that using a dual-curing material or a pre-heated micro-hybrid composite reduced the influence of the restoration thickness on the DC. While this outcome was predictable for the dual-curing composites, data referring to the heat application to micro-hybrid composite were extremely interesting.

In 1996, Park[53] compared the DC of light-cured and additionally heat-cured composites using the Fourier trans-

form infrared (FT-IR) technique. In all tested composites, significant differences in the DC were observed for both distance from the light source and the different curing methods by two-way ANOVA. When the samples were light-cured only, the DC decreased as the distance from the light source increased in all types of composites ($p < 0.05$). The degree of increase in DC after heat-curing differed among the composites. Moreover, the physical properties of composites can be increased significantly through the heat-curing process, and they are related to the overall increase in DC. From this study, the following conclusions were drawn. First, when the composites were light-cured, the degree of conversion diminished as the distance from the light source increased, especially when it exceeded 2 mm from the light source. Second, significant increases were observed in the degree of conversion after heat-curing, and the amount of increase differed among materials. Third, in heat-cured composites, the degree of conversion for the outer parts of the samples was greater than for the inner portion. Our study fully confirms Park's[53] findings, even if the evaluation method was different (micro-Raman spectroscopy vs. FT-IR) and the heat-curing times applied by Park[53] were much longer.

Our study was designed to reproduce the clinical conditions of cementation, and thus our results are clinically applicable. To perform this study we used Micro-Raman spectrometry: several studies reported that this is a precise, non-destructive and able to evaluate small sections of a sample[45,54] technique to determine the DC in methacrylate-based materials. The data show that a dual-cure material is necessary in thick onlays cementation because the self-curing component ensures adequate monomer conversion underneath restorations of great thickness. The distance from the light source is a variable that cannot be disregarded independently of the nature of the composite cement used. If a micro-hybrid composite is used as a luting material, employing it after heating would be advisable. From a clinical perspective, we obtained the highest conversion rate using Variolink® II cured at 800 mW/cm^2 for 60 s. Future studies will compare these results, which were obtained by curing the samples with a halogen lamp, to those obtained using the same protocol and employing a LED curing device.

During the measurements, no relevant differences were found between the three collections performed for each sample at the points 0, 1 and 2 (centre, average point between periphery and centre, and periphery, respectively): this is probably due to the fact that the samples and the light tip had the same diameter, so the light distribution was uniform on the specimens. Basing on this outcome, since the difference between the data was less than 1%, it was chosen to compute the median of the previously mentioned three values before performing the statistical analysis. The same procedure is reported in a study by Vieno et al.[55]: three measurements were performed for each sample, then the median value was considered.

Some clinically relevant outcomes should be underlined: first of all, the decrease in the degree of conversion of the dual-curing luting composites shows that the light-curing component of these materials has an important role in the polymerisation. Another interesting finding is that the results reached by micro-hybrid composite tested confirm that the lack of a self-curing component negatively affects the results, and that the light-curing component is not able to guarantee an acceptable degree of conversion underneath onlays of greater thickness (note, however, that this composite is mainly utilised in direct restorations). It is then clear that the application of heat to the above mentioned material guarantees good results even in the cementation of thick onlays.

Basing on the obtained data and on the statistical analysis performed, the null hypothesis, which stated that a difference was expected among the tested materials cured according to different modalities, is then accepted.

5. Conclusions

Onlays thickness affect the degree of conversion of both dual-curing cements and light-curing composite; no ideal curing time and power combination could be suggested, although the differences were pointed out only under 3 or 4 mm thick onlays. All these parameters must be optimised for each material. An optimal conversion degrees was reached with preheating light-curing only composites.

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