Nanoindentation and Raman spectroscopy measurements on dual-cure luting cement for dental conservative restoration

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***Abstract*—The employment of innovative all-ceramic materials and adhesive cement, as well as the development of new bonding procedures, allow clinicians to use minimally invasive approaches in conservative restorations. In particular, dual-cure cement allows for obtaining higher aesthetic and functional results. However, the reduced light transmission through ceramic materials could prevent the proper curing and affect the adhesion of these materials to the tooth surface. In this context, the development of an accurate measurement methodology to assess the extent of polymerization of dental resin-based luting cement and to correlate the conversion degree with the mechanical properties is of particular importance from the clinical and scientific point of view. A measurement approach that exploits Raman Spectroscopy and nano-hardness measurements is hereby proposed. In particular, in this study, two different light-curing protocols are employed on a dual-cure luting cement, usually used for the full-crown restoration of single-rooted teeth. The effect of different times and tack-curing steps on the polymerization shrinkage of resin-based luting cement is investigated. The preliminary results allow concluding that both curing protocols lead to a good polymerization, without significant differences in the degree of conversion along the cement-tooth interfacial surface, as proved by the almost constant ratio of the Raman vibration characteristic peaks. However, the nanoindentation modulus was lower in the case of the tack-cured protocol.**

***Index Terms*—Raman Spectroscopy, Degree of Conversion, dual-cure luting cement, nanoindentation**

I. Introduction

In clinical situations involving esthetic restorations, ceramic materials have the capability to replicate the appearance and the optical properties of natural teeth. These ceramic materials are suitable for manufacturing several types of all-ceramic restorations, such as inlays, onlays, crowns, veneers, and bridges. Contemporary all-ceramic materials and adhesive types of cement allow clinicians to use a minimally invasive approach and make more conservative restorations obtaining superior aesthetic and functional results. Since the introduction of all-ceramic materials, the limitation in light transmission typical of metal-based restorations has been overcome. Furthermore, the introduction of CAD/CAM technology has facilitated the spread of these new materials providing the clinician with several opportunities to treat aesthetic challenging cases. In this field, the employment of resin-based cement is becoming more and more diffused in restorative and prosthetic dentistry. Thanks to the development and improvement of bonding procedures, it is nowadays possible to significantly promote the adhesion between tooth hard tissues and metal-free materials. However, due to the limitation of light transmission through ceramic materials and the consequent difficulties in reaching the cement layer with enough energy density to ensure a proper curing process, dual-curing resin-based types of cement were introduced [1], [2].

These kinds of resin-based cements were designed to embed the chemical and mechanical properties of both chemical curing mode and light-cure polymerization. Indeed, their composition includes both chemical and photoinitiator. Therefore, they are able to complete the entire curing process taking advantage of self-curing capability also when light is attenuated and can not reach the material directly [3], [4].

It is worth noticing, that the success of a clinical restorative process strongly depends on the adhesion properties of the

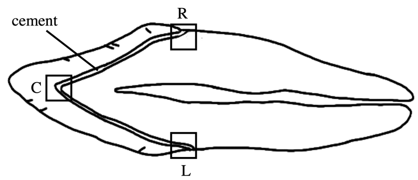

Fig. 1. Representative scheme of the Raman spectroscopy analyses position on surface sample: left (L), centre (C), and right (R).

restorative material towards the tooth surface. Optimal mechanical and adhesive properties are developed in the cement once the appropriate degree of conversion (DC) is reached [5].

It should be stressed that the degree of conversion is influenced not only by the chemical composition of the luting cement but also by the curing protocol employed. The difficulties in designing a well-defined protocol for dual-curing cements usage arise from the fact that the polymerization kinetic of these cements is influenced by time and irradiance [3], [6], [7].

For instance, when it is necessary to remove the excess luting cement in ceramic indirect restorations, the practice of "tack-cure' is often employed [8]. The procedure involves a short light curing of the cement to change its structure, to a gel phase that can be easily removed. Nevertheless, this step can have an impact on the polymerization, preventing the cement from reaching optimal conditions.

In this context, it is important to investigate the extent of the polymerization of dental resin-based materials and how it is affected by the curing approach. To this aim, vibrational techniques and, in particular, Raman Spectroscopy (RS) have proven to be useful tools [5], [9]–[14]. Indeed, through RS it is possible to calculate the degree of conversion of this kind of material on the basis of the peak height ratio change in intensity of the specific vibrational modes. In particular, different studies [9], [11], [14], successfully evaluated the percentage of vinyl functions converted to aliphatic functions, by comparing the methacrylate stretching vibration with the aromatic carbon-carbon double bonds.

The degree of conversion reached by self-adhesive resin cement has an impact also on their mechanical properties, and therefore must be investigated [15].

As a matter of fact, hardness measurements can be exploited in the determination of the mechanical properties of resin-based materials. Indeed, hardness values can be effectively correlated to the degree of conversion of polymeric materials [16]. Low values of the degree of conversion have an influence on several parameters, involving low values of hardness, flexural and compressive strengths, a high value of solubility, and low bond strength between the cement material and the dentin [17]. Dual-curing cements can be analyzed using several techniques. For instance, nanoindentation enables the analyses of the mechanical response of these materials and the quantification of their hardness and elastic modulus [18]–[20]. It is worth mentioning that testing the mechanical properties of the luting cement layer in a clinical scenario is difficult due to its reduced dimension and morphology of it. A critical aspect could be represented by the nanoindentation method that can be performed on single points or on wide areas along with the cement layer. Indeed, due to the resin cement composition, different results could be obtained by testing a wide area instead of a single point where a higher amount of fillers could be located.

In addition, to the best of our knowledge, there are no studies that evaluated a correlation between the degree of conversion and the nanoindentation modulus of a luting cement cured with different protocols.

Therefore, the principal aim of this study is to investigate the influence of the tack-curing process on the conversion degree of a dual-curing cement (G-Cem One) by evaluating the degree of conversion through Raman Spectroscopy. In addition, the hardness modulus of the cement is evaluated by nanoindentation, in order to correlate DC and hardness values. The preliminary results are then compared and presented in this paper.

II. Materials and Methods

A. Specimen Preparation

Ten intact human single-rooted teeth were extracted for periodontal reasons and then selected for the present in vitro study. All samples were collected with informed consent in the Department of Cariology and Operative Dentistry, University of Turin (Italy). The ethical committee of the University of Turin approved the study protocol. The samples were selected on the basis of specific criteria. In particular, the samples were chosen with the absence of radicular caries or fractures, with no cracks under transillumination at $6\times$ magnification, no endodontic, restorative, or prosthetic treatments. All specimens were stored in 0.5% chloramine-T solution at $4\ ^{\circ}\mathrm{C}$ and analyzed within one month after extraction.

Specimens have been prepared for a full-crown restoration by a single experienced operator. Then, an optical scan has been performed, and a full crown restoration with chamfer margin has been designed with CAD software (Cerec System 5.1). Adhesive full crowns have been milled using a lithium silicate material (Celtra Duo, Dentsply). Once completed

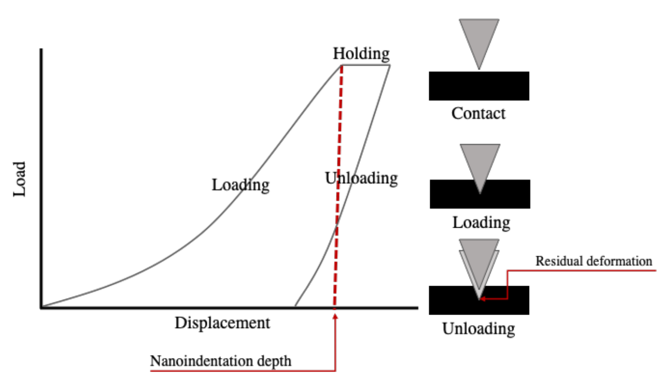

Fig. 2. Schematic representation of the principal phases of a nanoindentation test.

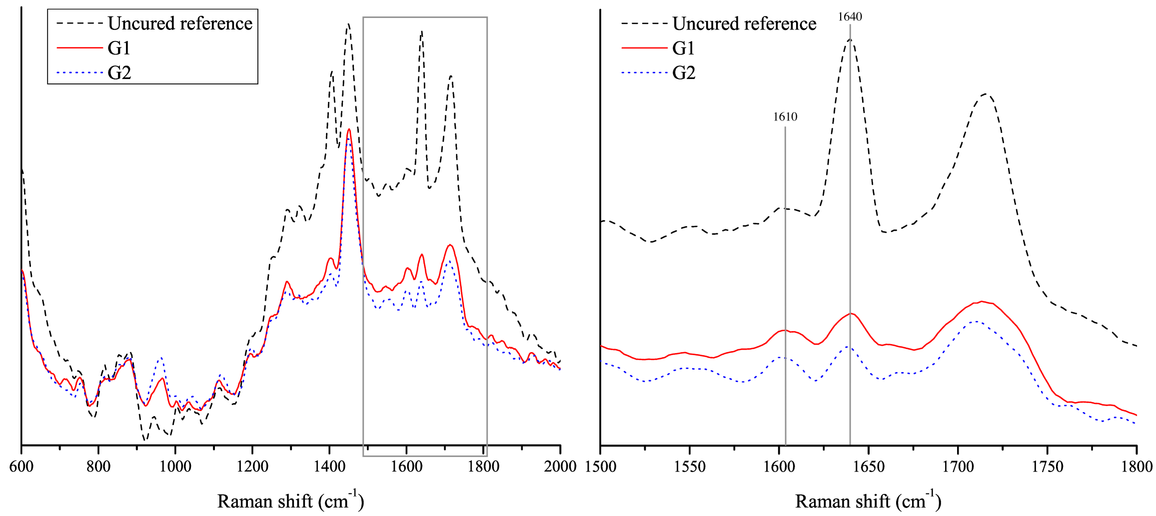

Fig. 3. Representative Raman spectra acquired on a polymerised and unpolymerised sample. On the right side it possible to observe the spectra in the range between $440 - 3000$ cm^{-1}, while on the bottom a magnified section is reported. Representative Raman spectra of the two typology of samples investigated, group 1 (G1) and group 2 (G2), together with the uncured reference sample.

the sintering and glazing/polishing procedures (10 minutes sintering, 10 minutes glazing), the crowns were luted over the prepared specimen using a universal dual-curing cement (G-Cem One, GC), which has been applied in self-adhesive mode, following the manufacturer instructions. In particular, the crown surface was etched with a solution of hydrofluoric acid (4%) for 20 s, then it was rinsed in alcohol for 10 min through an ultrasonic bath, and a G-Multi Primer was applied. On the other hand, the tooth surface did not undergo any pre-treatment and a self-adhesive approach was employed.

The samples were then divided into two subgroups, on the basis of the curing protocol employed:

- Group 1 (G1): the cement excess was removed with a brush and, after 1 min, the sample was light-cured for 20 s per side;
- Group 2 (G2): each side was tack-cured for 5 s, then the excess was removed with a scaler, and after 1 min, the sample was light-cured for 20 s per side.

During the luting and curing process, the samples have been set in a gypsum model, in order to simulate the clinical condition. The curing-light tip is positioned in contact with the buccal, incisal, and oral surfaces.

Finally, samples have been sectioned in two halves by means of a diamond saw along the vertical axis in the tooth midline in order to expose a cement layer. The so-obtained flat surface was then finished and polished with ascending grit papers (320 grit, 600 grit, 800 grit, and 1200 grit) and samples were stored in distilled water at 37 $^{\circ}C$.

B. Raman Spectroscopy and Data Acquisition

The cement layer has been analyzed with Raman Spectroscopy in order to identify the degree of conversion of the luting cement.

In order to perform the RS measurements, the BWTEK modular portable Raman spectrometer was exploited. In particular, the instrument is equipped with a monochromatic excitation laser (wavelength: 785 nm) and BTC675N spectrometer (range: $65 - 3350$ cm^{-1}, resolution 6 cm^{-1}) coupled with a CCD sensor. In addition, the instrument was connected to the BAC151 compact Raman microscope.

The following parameters were employed: laser power of 100 mW, integration time of 20 s, 24 repetitions for each area, microscopic objective of $80\times$ (analysed area of about 20 μm).

For each sample, several measurements were acquired. In particular, the points of analysis were chosen along with the cement, at the cervical, middle and occlusal areas of the specimens, for a total of three points for each sample. A representative scheme of the point of analysis is shown in Fig. 1. In addition, a specimen of unpolymerized cement (G-Cem One, GC) was measured as a reference.

The degree of conversion was evaluated as the ratio of the residual aliphatic and aromatic bonds collected by Raman spectroscopy in the specimens before and after polymerization. In particular, the DC on all samples was calculated by comparison of the ratio of the aliphatic carbon-carbon double bond C=C, at 1640 cm^{-1}, with that at 1610 cm^{-1} of the aromatic C=C bond for both the cured and uncured cement. The vibrational mode at 1610 cm^{-1} is characteristic of the aromatic bonds and remains constant during the light-curing process. On the other hand, the aliphatic C=C double bonds are converted into C–C single bonds along with the curing, even if a certain amount of unreacted double bonds could remain within the cement. Therefore, it is possible to extract the degree of conversion using Equation 1:

$$DC\% = (1 - \frac{(I_{1640}/I_{1610})_{cured}}{(I_{1640}/I_{1610})_{uncured}}) * 100 \tag{1}$$

where I_{1640} and I_{1610} are the intensity of the vibration modes at 1640 cm^{-1} and 1610 cm^{-1}, respectively.

C. Nanoindentation

In order to perform the nanoindentation measurements, the specimens were specifically prepared to provide a stable supporting base for the test. In particular, all samples were enclosed in acrylic resin (Technovit 4071, Heraeus Kulzer, Hanau, Germany). The measurements were acquired on the layer of the dual-curing cement, in the same area analyzed by Raman Spectroscopy. The Nanoindenter XP (MTS System Corporation, Eden Prairie, MN, USA) was employed. The instrument is equipped with a diamond Berkovich indenter, with a theoretical force resolution of $50\ \mathrm{nN}$ and a theoretical displacement resolution lower than $0.01\ \mathrm{nm}$. Before the acquisition of data, a standard procedure was used for the calibration of the shape function of the indenter and the frame stiffness of the instrument [21].

Fig. 2 shows a schematic representation of the principal phases of a nanoindentation test. The input curve is defined by two phases, the loading, and unloading ones, imposing a strain rate value of $0.1\ \mathrm{s}-1\ \mathrm{s}$. The maximum load value is achieved in correspondence to the set nanoindentation depth and it was maintained constant for $30\ \mathrm{s}$. The measurements were acquired in displacement control, by setting a maximum value of indentation depth of $2000\ \mathrm{nm}$. The cross-section value obtained from the calibration procedure at the set indentation depth is compatible with the cement width. These experimental conditions are necessary to limit restrict the investigation of the mechanical properties only to the region of interest, considering the compatible dimensions of the area under the indenter and the indented portion of the tooth slice. The Oliver-Pharr method [22] was employed in order to analyze the loading-displacement curves for the quantification of the plastic and elastic micromechanical properties through the nanoindentation hardness.

III. Results and Discussion

In Fig. 3 representative Raman spectra of the two typologies of samples (Group 1 and Group 2) are reported, together with a spectrum collected on the reference unpolymerised sample of G-Cem One cement. On the right side of the figure, a magnification of the Raman spectra is reported, focusing on the peaks relevant for the computation of the Degree of Conversion.

It is possible to observe that the intensity of the peak at $1640\ \mathrm{cm}^{-1}$ decreases in the cured sample, with respect to the uncured one. At the same time, the peak at $1610\ \mathrm{cm}^{-1}$ does not present a modification of intensity and therefore can be exploited as an internal reference in order to extract the degree of conversion value, as described in Equation 1.

The extracted DC$\%$ values in function of the position on the sample are reported in Fig. 4 and Fig. 5. For Group 1, the DC$\%$ assumes a maximum value of 84.59% and a minimum value of 50.48%. On the other hand, in Group 2 the cement has reached a maximum degree of conversion of 79.97% and a minimum one of 42.95%.

In addition, no evident correlation between the degree of conversion and the position of analyses is present, since there is no significant variation of the DC value along with the cement layer. Therefore, it could be assessed that the curing protocols tested in the present study do not influence the conversion degree of the tested cement, as well as the distance from the curing light. In general, the chemical composition of dual-curing self-adhesive cements enables the full adhesion of the material to the tooth structure, by both chemical-curing and light-curing processes, also in the areas not reached directly by light. Nevertheless, some authors [1], [23] suggested that dual cements could achieve weaker mechanical properties, which

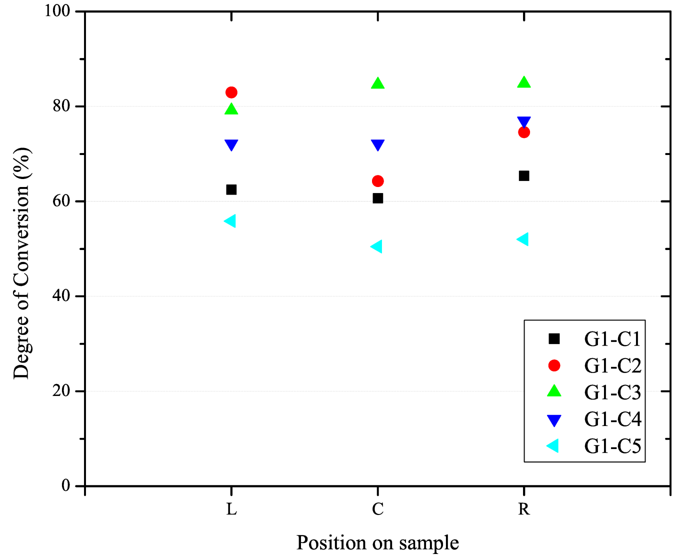

Fig. 4. Scatter plot of the Degree of Conversion $(\%)$ acquired on samples of group 1 (G1). Measurements were performed on three position along the cement layer, on the left (L), centre (C), and right (R) side as reported in Fig. 1.

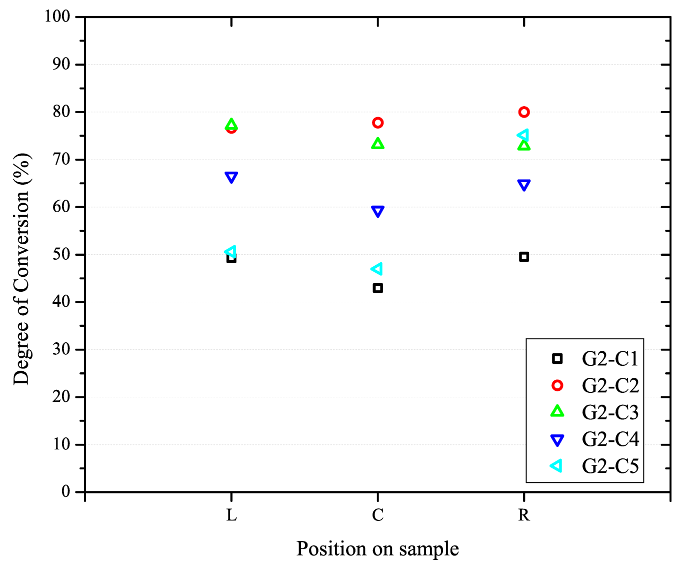

Fig. 5. Scatter plot of the Degree of Conversion $(\%)$ acquired on samples of group 2 (G2). Measurements were performed on three position along the cement layer, on the left (L), centre(C), and right (R) side as reported in Fig. 1.

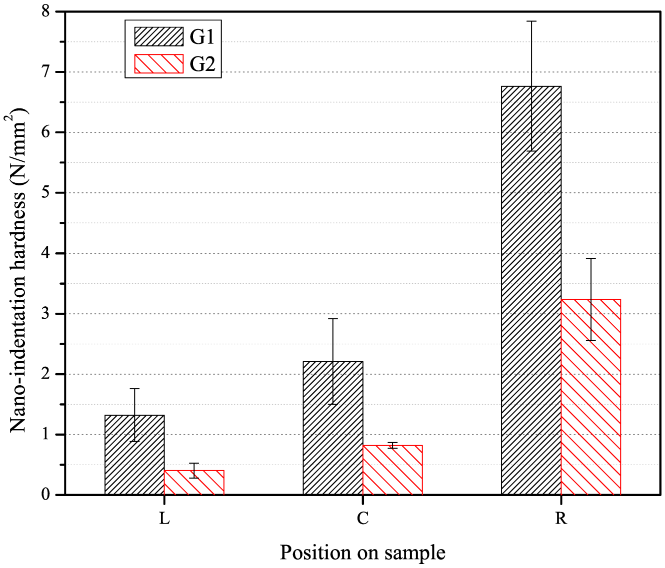

Fig. 6. Histogram plot of the mean value of the nanoindentation hardness for the two group of samples, group 1 (G1) and group 2 (G2), in function of the analysed area, left (L), centre (C), and right (R) side, together with standard deviation values.

might not be sufficient for clinical application when the material is not properly light-cured. This can be due to the early vitrification induced by insufficient light-activation, which can interfere with subsequent self-polymerization, compromising the overall curing process of dual-cure resin cements.

However, Ferracane et al. [24] showed that, if the light can easily pass through the indirect restoration, thanks to its reduced thickness, a sufficient final degree of conversion could be reached, as observed in the present study.

The nanoindentation results expressed as $\mathrm{N/mm^2}$, are represented in Fig. 6 as a histogram plot, together with the values of standard deviation. From the data, it is possible to state that the nanoindentation modulus is lower in Group 2 than in Group 1. Thus, it could be assessed that the progressive irradiation performed in Group 1, which led to a longer initial self-curing time, could let the cement arrange better and thus achieve better mechanical properties [25]. In addition, it can be observed that greater values of the nanoindentation modulus are reached on the right side of the cement layer. This could be due to the different distribution of the light used to cure the cement, which could affect the mechanical properties of the material in the proximal regions.

IV. Conclusions

In this study, a measuring approach that involves the use of Raman spectroscopy and nanoindentation was exploited for the study of the degree of conversion and hardness of a dual-cure luting cement on which two different light-curing protocols were applied.

Within the limitations of the present in-vitro study, Raman spectroscopy and nanoindentation measurements showed a different trend when applied to test the luting cement layer used to bond ceramic crown. In particular, the preliminary results highlighted that for both curing protocols a good value of polymerization was reached, without significant differences in the degree of conversion along the cement-tooth interfacial surface, given the evidence of an almost constant ratio of the Raman vibration characteristic peaks. However, the nanoindentation modulus was lower in the case of the tack-cured protocol. Further studies will be focused on the investigation of the best nanoindentation technique to extract the mechanical properties which could not be affected by the chemical composition of the polymer.

Acknowledgment

The authors acknowledge Francesca Doria, Angela Rulfo, and Sara Peano for their help in preparing the samples.

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