Assessment of Degree of Conversion and Knoop Microhardness of Different Resin Cementing Agents

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Abstract:
Background: There are still controversies in the literature as to which is the best resinous cementing agent. Due to this fact and the immense availability of types and brands of cementing agents, further studies are needed to evaluate the properties of these important dental materials.

Objective: To assess the degree of monomer conversion (DC) and Knoop microhardness (KHN) of four resin cements: two conventional dual-cured resin cements (EnForce and RelyXARC); one self-etching cement (RelyXU100); and one chemically-activated cement (Cement-Post).

Methods: 20 Pieces were made to assess KHN, and 20 to assess DC (n = 5). The DC was analyzed using a Fourier-transform infrared spectrometer, and KHN of the base and the top of the pieces were assessed using the Future-Tech microhardness tester. The data of KHN were statistically analyzed by two-factor ANOVA, and data related to DC were analyzed by the Kruskal-Wallis non-parametric test. The analysis of the correlation between KHN and DC of the cementing agents was performed by linear regression.

Results: Dual-cured cements exhibited lower average KHN values at the base than at the top of the pieces (p <0.05). The self-etching cement had a significantly higher average KHN value than the other assessed cements (p <0.05). The DC of the dual-cured cement did not differ (p >0.05). The chemically-activated cement exhibited the lowest averages of KHN and DC values (p <0.05). Linear regression analysis indicated a strong correlation between DC and KNH (p = 0.043; R² = 0.96); however, a specific hardness value could not be correlated to a specific DC value.

Conclusion: Preferably, dual-cured resin cements (conventional or self-etching) should be used. Chemically-activated resin cements should be avoided due to their lower averages of DC and KHN values.

Keywords: Dental materials, Resin cements, Dental cements, Polymerization, Hardness tests, Cementation.

1. INTRODUCTION

Resin cements are polymeric materials commonly used in the cementation of indirect restorations due to their high aesthetics, low solubility, high adhesive strength, and superior mechanical properties that help reinforce restorations [1 - 5]. However, resin cements are sensitive to the technique. This way, problems occurring during cementation are one of the main causes of failure in indirect adhesive aesthetic restorations [6 - 8]. Different resin cements can be used in diverse clinical situations. It is worth mentioning that the variations between these materials occur mainly during the polymerization and bonding mechanism [2, 3].

Resin cements can be classified according to their activation modes, namely: chemically activated; photo-activated (physical activation); and dual-cured [6, 9]. In dual activation, the polymerization reaction is initiated both by the emission of visible light and by a chemical reaction (peroxide/amine) [2, 9]. This category reconciles the
advantages of photo-activated cements, such as control of working time and color stability, with the possibility of achieving an adequate degree of monomer conversion (DC), regardless of the presence of light, the main advantage of chemically-activated cements [2, 5, 10].

Another classification has become mandatory since the advent of new resin cements with different bonding mechanisms [2]. This way, cements can also be classified as conventional or self-etching cements [3, 6]. Conventional cements require previous acid etching and hybridization with the adhesive system, so that the union between the resinous material and the dental structure occurs [3, 5, 6]. Self-etchers do not require previous acid conditioning with the adhesive system, reducing the sensitivity inherent to the cementation technique by simplifying the procedure and, consequently, optimizing clinical time [2, 6].

Despite the clinical advantages of self-etching resin cements, some studies have indicated that conventional resin cements exhibited higher DC and better mechanical properties [3, 4, 6]. In this sense, doubts still arise regarding the use of conventional or self-etching resin cements. Due to this fact and the immense availability of types and brands of cementing agents, the goal of the present study was to assess Knoop microhardness (KHN) and the DC of four commercial resin cements. The tested null hypothesis was that there was no significant difference in KHN and DC of the cementing agents assessed.

2. MATERIALS AND METHODS

Four A2-shade resin cements were used: two conventional dual-cured cements; one dual-cured self-etching cement; and one conventional chemically-activated cement (Table 1).

2.1. Knoop Microhardness

Twenty pieces were made in a circular black Teflon matrix (diameter = 4 mm; height = 2 mm). They were randomly distributed into four groups (n = 5), according to the selected resin cementing agents. The cements were inserted with single increments in the matrix, between polyester strips and glass coverslips. Photo-activation was performed by a Light Emitting Diode (LED) (Elipar Freelight 2, 3M ESPE, USA), with irradiance of 800 mW/cm² for 20 seconds. Prior to making the test pieces for each experimental group, the photo-activation unit was measured by a radiometer (LED Radiometer, Kerr, USA).

The groups made with chemical setting cement were not submitted to light irradiation, and were kept between the polyester strips and glass coverslips for four minutes.

Subsequently, they were stored in a biological oven at 37 °C ± 1 and 100% humidity for 24 hours. Prior to carrying out the microhardness tests, the pieces were polished using a polishing machine (DPU-10, Struers, Copenhagen, Denmark) with paper #1200. The hardness measurements were obtained using the Future Tech 700 microdrometer (Future-Tech Corp., Kawasaki, Japan), with a load of 50 grams-force (gf) for 30 seconds, at five equidistant points on the base and top surfaces, totaling ten measurements per piece. The average hardness values of the bases and the tops, and the general average were calculated for each piece.

2.2. Degree of Monomer Conversion

Twenty pieces were made in a Teflon bipartite circular matrix (diameter = 8mm; height = 2mm), and randomly distributed into four groups (n = 5), according to the resin cement agents selected. The protocols for the preparation of the pieces and storage conditions were the same used for the KHN tests.

The base of each piece was eroded in order to obtain 1.5 to 2.0 mg of powder and taken to the Nicolet iS10 Fourier Transform spectrophotometer (Thermo Scientific/Waltham, MA, USA). All spectra were obtained between the 4000 and 750 cm⁻¹ bands, with a resolution of 4 cm⁻¹. The spectra of each sample were transferred to the Origin software (OriginLab Corp., Northampton, MA, USA). The vibrational modes were selected for obtaining better visualization. The absorbance spectrum was acquired by scanning the pieces 32 times, at intervals of 1670 to 1550 cm⁻¹. The calculation of the DC was based on the proportion between the absorbance values at 1638 cm⁻¹, representing the absorption of the double bond of aliphatic carbon of vinyl methacrylate, and at 1608 cm⁻¹, corresponding to the absorption of the double bond of aromatic carbon that remains constant during the polymerization reaction. These values were entered in the equation:

$$DC\% = 100 \times \left(1 - \frac{R_{polymer}}{R_{monomer}}\right)$$

where $R_{polymer}$ = peaks at 1638 cm⁻¹, and $R_{monomer}$ = peaks at 1608 cm⁻¹.

Table 1. Resin cementing agents included in the study: trade name, manufacturer, activation mode, method of union, composition, and batch.

| Trade Name          | Activation Mode | Method of Union | Composition                                                                 | Batch   |
|---------------------|-----------------|-----------------|-----------------------------------------------------------------------------|---------|
| EnForce (Dentsply Caulk, York, EUA) | Dual            | Conventional    | Base: Bis-GMA, TEGDMA, CQ, EDAB, BHT and DHEPT. Catalyst: Bis-GMA, BHT, EDAB, TEGDMA and BPO. | 103515B |
| RelyX ARC (3M ESPE, Sant. Paul, EUA) | Dual            | Conventional    | Paste A: Bis-GMA, TEGDMA, dimethacrylate polymer, CQ, amine. Paste B: Bis-GMA, TEGDMA, dimethacrylate polymer, BPO. | N179452 |
2.3. Statistical Analysis

Data relating to KHN and DC were submitted to the Shapiro-Wilk test and Levene’s test to determine the parametric assumptions of normality and homoscedasticity. Subsequently, the data of KHN were statistically analyzed by ANOVA and post-hoc Tukey’s test. Data relating to DC were analyzed by the Kruskal-Wallis non-parametric test and post-hoc Dwass-Steel-Critchlow-Fligner test. The analysis of the correlation between KHN and DC of the cementing agents was performed by linear regression with the results of the base of the pieces. Statistical calculations were performed using the Jamovi software (version 2.22), with a significance level of 5%.

Table 2. Average and standard deviation of Knoop microhardness values in Kg/mm² according to the cementing agent and measurement location (top and base).

| Resin Cementing Agents | Average Top (SD) | Average Base (SD) |
|------------------------|------------------|-------------------|
| EnForce                | 55.5 (3.88)      | 40.6 (2.72)       |
| RelyX ARC              | 49.3 (4.42)      | 42.4 (0.67)       |
| RelyX U100             | 61.8 (4.78)      | 49.1 (2.90)       |
| Cement-Post            | 26.8 (1.75)      | 23.9 (1.76)       |

SD – standard deviation; values followed by different letters represent a significant difference in the average of the values between the top and base (p<0.05 two-factor ANOVA/Tukey).

3. RESULTS

3.1. Knoop Microhardness

The two-way ANOVA test indicated that the average KHN values were influenced by the different types of resin cements assessed and by the measures taken from the top or base of the pieces (p <0.001). The cements obtained significantly lower average KHN values at the base than at the top of the pieces (p <0.05), except for Cement-Post (p = 0.83). RelyX U100 had the highest KHN average values (p <0.05), followed by EnForce and RelyX ARC, which did not differ statistically from each other. Cement-Post had the lowest average KHN value (p <0.001) (Table 2).

3.2. Degree of Monomer Conversion

The Kruskal-Wallis test indicated a statistical difference between the DC of the resin cements assessed (p = 0.014) (Table 3). The post-hoc test revealed that EnForce, RelyX ARC, and RelyX U100 did not differ statistically from each other (p >0.05). However, only RelyX ARC and RelyX U100 exhibited a statistically significant difference from Cement-Post, the cement with the lowest DC values.

3.3. Correlation Between Degree of Monomer Conversion and Knoop Microhardness

The linear regression analysis indicated a strong positive correlation between DC and KHN (p = 0.043). The higher the DC, the greater the KHN of resin cements. A correlation was observed between the cementing agents, i.e., a specific value of DC was not able to predict KHN if the resin cements being assessed were not specified.

Table 3. The median and interquartile range of the percentage values of the degree of conversion according to the cementing agent.

| Resin Cementing Agents | Median (IQR) |
|------------------------|--------------|
| EnForce                | 35.5 (4.14)  |
| RelyX ARC              | 42.7 (3.13)  |
| RelyX U100             | 38.2 (2.83)  |
| Cement-Post            | 34.3 (1.74)  |

IQR – interquartile range; values followed by different letters represent a significant difference (p<0.05 – Kruskal-Wallis).

4. DISCUSSION

The DC of resin cementing agents is directly proportional to the magnitude of adhesion between the resin material and the dental structure, influencing the physical properties and satisfactory clinical performance of resin cements in indirect procedures [3, 4, 8]. In addition to decreasing bond strength, low DC can lead to pulp sensitivity, decrease in mechanical characteristics, and compromise the clinical success and longevity of the restoration due to detachment, fracture, or secondary caries [2 - 7]. There are several factors that can interfere with the DC of resin cements, for example, the composition of the materials, possible interactions between the adhesive system and the cements, characteristics of the restorations to be cemented, and characteristics of the photo-activation stage [4 - 9].
Their mechanical properties [10, 11]. These cements have the two cements had not exhibited significant differences in average values, confirming the results of previous studies that statistical differences between them, both for the DC and KHN that have double polymerization. They did not exhibit cements with respect to DC.

The results of the present study confirmed the statement that there is a strong positive correlation between the DC and KHN, i.e., microhardness values increase as DC values increase [10, 13]. The DC was able to predict 96% of the variability of KHN in the cementing agents included in the study \( p < 0.05 \). However, KHN can be sensitive to different variables [10, 13], and a specific hardness value cannot be correlated to a specific DC when comparing different material formulations. Therefore, the two techniques should not be used interchangeably as indicative of DC of different resins since each one is sensitive to different variables. The same DC for EnForce and RelyX U100 does not mean the same KHN; however, if the DC is increased, higher KNH values will be obtained for both cements.

Cement-Post had the lowest results when compared to the other assessed cements \( p < 0.01 \). This result can be attributed to the inhibition of oxygen and the increase of the inhibitor in the formulation of chemical cure cements, used to increase the working time of this material [7, 9, 14]. Therefore, the use of dual-cure cement should always be considered for possibly increasing DC through physical and chemical activation of the monomer system [3, 5, 9]. Despite the lower results, Cement-Post was the only cement that did not show statistical differences between the KNH results at the top and base of the pieces, which can be explained by its exclusively chemical activation that occurs without depending on the irradiance of light.

Fig. (1). Correlation between the degree of conversion and the Knoop microhardness of resin cementing agents \( (p = 0.043; R^2 = 0.96) \).
significant differences in KHN and DC.

CONCLUSION

Based on the results obtained and within the limitations of the present in vitro study, we suggest that chemically-activated resin cements should be avoided due to their lower averages of DC and KHN values. Preferably, dual-cure resin cements should be used. Although the self-etching cement assessed exhibited the highest KHN results, the dual-cure resin cements (conventional or self-etching) did not differ among them with respect to the DC. Further conclusive evidence derived from clinical observations is needed to confirm the findings of the present study.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data supporting the findings of the article is available in Zenodo Repository the at: https://zenodo.org/, reference number 10.5281/zenodo.5610313.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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