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Influence of *N*-(2-hydroxyethyl)acrylamide addition in light- and dual-cured resin cements

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ABSTRACT

Objective: To develop experimental light-cured (L) and dual-cured (D) resin cements containing *N*-(2-hydroxyethyl)acrylamide and evaluate the physicochemical and optical properties.

Methods: Experimental resin cements were formulated using bisphenol A-glycidyl dimethacrylate (70%) and 2-hydroxyethyl methacrylate (30%), in the control groups, and, bisphenol A-glycidyl dimethacrylate (70%) and *N*-(2-hydroxyethyl)acrylamide (30%). Polymerization kinetics were evaluated by differential scanning calorimetry (n = 3), softening in solvent (ΔKHN) evaluated by the difference of Knoop microhardness before (KHN_1) and after (KHN_2) ethanol solution immersion (n = 5), radiopacity in mmAl (n = 5), film thickness (n = 3) and color stability were evaluated. Mechanical properties as ultimate tensile strength (UTS) and micro-shear bond strength (μSBS) were analyzed immediately and after 6 months. Results were analyzed using ANOVA, Tukey's test and Student's *t*-test (α = 0.050).

Results: The L_{HEAA1} group had no statistical difference from the control group regarding polymerization kinetics, KHN_1, ΔKHN and color stability ($p > 0.050$). In dual-cured cements, the acrylamide groups presented a lower degree of conversion and higher ΔKHN than the $D_{HEMA0.6}$ group, which obtained a higher rate of polymerization ($p < 0.050$). There was no statistical difference in radiopacity and film thickness ($p > 0.050$). Dual-cured cements with *N*-(2-hydroxyethyl)acrylamide showed higher color change than methacrylates. Immediate mechanical properties were lower for acrylamide groups ($p < 0.050$), with higher hydrolytic stability.

Conclusions: The addition of N-(2-hydroxyethyl)acrylamide negatively affected the properties of the dual-cured resin cements. LHEAA1 did not differ in physicochemical and optical properties from the control, with higher hydrolytic stability.

Clinical significance: The results of the study indicate that acrylamides increased mechanical properties over time independently of the curing system mode, with more hydrolytic stability. The clinical performance of experimental resin cements should be evaluated.

1. Introduction

Resin cements have become popular in dentistry due to their ability to bond to teeth and to the restoration [1,2]. The modes of activation through light-cured or dual-cured resin cements were the most used in clinical practice [1,3,4]. Examples of their clinical applications include the adhesion of laminate veneers, onlays, inlays, crowns, bridges and intracanal posts [1]. Resin cements are the material of choice because of their excellent esthetics, favorable mechanical properties and strong bond to the tooth structure [4]. The composition of the polymeric matrix can influence the physical, chemical and optical properties of the resin cements [5–11].

Resin cements are usually based on methacrylate monomers, and bisphenol A-glycidyl dimethacrylate (Bis-GMA) in the polymeric matrix is known to be responsible for improving the mechanical properties [12]. The monomer 2-hydroxyethyl methacrylate (HEMA) is often present in resin cements' composition [13] and has a concern about the hydrolytic degradation over time due to the ester group [14,15]. HEMA allows an increase in the water uptake [16], which may result in a decrease of the mechanical properties and degradation of the polymeric matrix [13]. Camphorquinone (CQ) is usually used as an initiator in several resin cements and requires an amine co-initiator component,

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which suffers oxidation over time [17,18]. A dual polymerization usually involves free-radical initiators such as benzoyl peroxide that react with a tertiary amine [19]. The amines form by-products during the polymerization reaction, which may cause a yellowish to brown discoloration [17], affecting the color stability of resin cements [20,21]. Recently, one of the concerns regarding resin cements is to prevent hydrolytic degradation [14] and to find new formulations that could eliminate the tertiary amine as co-initiator [22], which leads to an unfavorable color change [23]. Even the light-cured resin cement has higher color stability than dual-cured cement [24], in which its mode of activation will influence the degree of conversion [25–27].

Potential alternative monomers to HEMA have been studied to improve dental resin properties [13,28,29]. *N*-(2-Hydroxyethyl)acrylamide (HEAA) has an organic compound carbamide that has two $–NH_2$ groups joined by a carbonyl (C═O) functional group. This amide is more hydrolytically stable than esters considering the lower reactivity of its carbonyl group [28]. It was postulated that the –NH group in acrylamide might act as a tertiary amine co-initiator in the polymerization process [29]. Such co-initiator would reduce the need for those components that contribute to oxidative color changes [30]. Because of carboxylate groups and the similarity to the amino acids that compose collagen fibrils, the acrylamides could facilitate hydrogen bonding between collagen and amide groups (N—H) [31].

Only one study so far has tested acrylamides in a light-cured resin cement compared with HEMA [13]. The polymer matrix was composed of urethane dimethacrylate (UDMA) and *N*-methylacrylamide, in which only flexural strength and flexural modulus of elasticity were evaluated. Furthermore, the dual-cured resin cements with the addition of acrylamide have not been attempted before in the literature. The aim of this study was to develop experimental light-cured and dual-cured resin cements containing *N*-(2-hydroxyethyl)acrylamide and evaluate the physicochemical and optical properties. The null hypothesis was that the addition of *N*-(2-hydroxyethyl)acrylamide does not influence resin cement properties.

2. Materials and methods

2.1. Formulation

Three experimental light-cured and six experimental dual-cured resin cements were formulated mixing Bis-GMA and HEMA; and, Bis-GMA and HEAA in a 70:30 mass ratio (Bis-GMA:HEMA and Bis-GMA:HEAA) (Table 1). The initiation system of light-cured resin cements was composed of CQ (1 mol%) and ethyl 4-(dimethylamino) benzoate (EDAB) (1 mol%). Only in the group L_{HEAA0}, the tertiary amine (EDAB) was not added. The activation/initiation system of dual-cured resin cements was composed of CQ (1 mol%), benzoyl peroxide (1 mol%) and *N*,*N*-dihydroxyethyl-*p*-toluidine (DHEPT). The tertiary amine DHEPT was added in different concentrations: 0, 0.25 or 0.6 mol %. The inhibitor BHT (butylated hydroxytoluene) was added at 0.01 wt % to all resin cements. All of these components were purchased from Sigma-Aldrich (Aldrich Chemical Co.; St. Louis, USA). The dual-cured resin cements were separated in base paste and catalyst paste. Ytterbium trifluoride (Nanostructured & Amorphous Materials; Houston, USA) was added as filler at 40 wt% for all groups. Initiators and filler were hand mixed with monomers and ultrasonicated for 480 s. To perform photoactivation of resin cements' samples, except for the polymerization kinetics test, a light-emitting diode unit (Radii Cal., SDI Ltd., Melbourne, Australia) was used. An irradiation value of 1200 mW/cm^2 was confirmed with a digital power meter (Ophir Optronics, Jerusalem, Israel).

2.2. Degree of conversion and polymerization kinetics

The degree of conversion (DC) and polymerization kinetics for each experimental resin cement were evaluated via differential scanning calorimetry (DSC; DSC-Q2000, TA Instrument Co., New Castle, USA) with a photocalorimetric accessory (PCA). The intensity and wavelength range of the PCA were adjusted to 100 mW/cm^2 and 390–500 nm, respectively. Three samples per group (n = 3) [27] with approximately 16 mg were polymerized in open aluminum DSC pans and covered with a quartz lid. An additional empty aluminum pan was used as control. The lamp was switched on for 3–7 min and heat flow was recorded. The analysis was performed with a nitrogen flow rate of 50 mL/min. Assuming that the amount of heat involved is proportional to the reacted molar amount, the degree of conversion was determined according to the following Eq. (1):

$$\alpha\ (\text{mol}\%) = 100\ (([M]0 - [M]) \div [M]0) = 100\ Q \div (\Delta Hp,0 \div \Delta Hp)\ Qtot, \quad (1)$$

where $\Delta H_{p,0}$ (kJ mol^{-1}) corresponds to the heat of polymerization for a total conversion, ΔH_p (kJ mol^{-1}) the heat of polymerization obtained by the apparent area of the curve that corresponds to the total heat of reaction Q_{tot} ($J\ g^{-1}$), and Q corresponds to the heat released as partial area under the curve of a time, t. The $\Delta H_{p,0}$ value for a double bond of methacrylate has been reported to be −56 J mol^{-1}, and for acrylamides, –82.9 J mol^{-1} [32,33]. The rate of polymerization (Rp) is proportional to the heat flow released in the isotherm as a function of irradiation time (t). Thus, Rp (mmol × g^{-1} × s^{-1}) at any point during the reaction can be derived from the heat flow using the $\Delta H_{p,0}$ of the monomer according to the following equation (2):

$$Rp = (dH \div dt) \times (M \div \Delta Hp,0 \times n),$$

where dH ÷ dt is the heat flow in J mol^{-1} × s^{-1}, M the concentration of the monomer, and n is the number of double bonds per molecule of monomer.

2.3. Softening in the solvent

Five specimens of each experimental resin cement (n = 5) were

Table 1
Composition of light-cured and dual-cured resin cements.

Curing mode	Groups	Paste A	Paste B
Light-cured	L_{HEMA}	70% BisGMA#; 30% HEMA#; 1% CQ*; 1% EDAB*	Ø
	L_{HEAA0}	70% BisGMA#; 30% HEAA#; 1% CQ*	Ø
	L_{HEAA1}	70% BisGMA#; 30% HEAA#; 1% CQ*; 1% EDAB*	Ø
Dual-cured	D_{HEMA0}	70% BisGMA#; 30% HEMA#; 1% CQ*	70% BisGMA#; 30% HEMA#; 0.6% PB*
	$D_{HEMA0.25}$	70% BisGMA#; 30% HEMA#; 1% CQ*; 0.25% DHEPT*	70% BisGMA#; 30% HEMA#; 0.6% PB*
	$D_{HEMA0.6}$	70% BisGMA#; 30% HEMA#;1% CQ*; 0.6% DHEPT*	70% BisGMA#; 30% HEMA#; 0.6% PB*
	D_{HEAA0}	70% BisGMA#; 30% HEAA#; 1% CQ*	70% BisGMA#; 30% HEAA#; 0.6% PB*
	$D_{HEAA0.25}$	70% BisGMA#; 30% HEAA#; 1% CQ*; 0.25% DHEPT*	70% BisGMA#; 30% HEAA#; 0.6% PB*
	$D_{HEAA0.6}$	70% BisGMA#; 30% HEAA#; 1% CQ*; 0.6% DHEPT*	70% BisGMA#; 30% HEAA#; 0.6% PB*

* mol; #wt; Ø resin cement with a single paste; BisGMA (Bisphenol A glycidyl dimethacrylate); HEMA (2-Hydroxyethyl methacrylate); HEAA (N-Hydroxyethyl acrylamide); CQ (Camphoroquinone); EDAB (ethyl 4-dhymetyl aminobenzoate); DHEPT (NN-dihydroxyethyl p-toluidine); PB (benzoyl peroxide).

obtained using a polyvinylsiloxane matrix (5 mm diameter and 1 mm thickness) and photoactivated for 40 s on each side. The group L_{HEAA0} was photoactivated for 60 s. Samples were stored for 24 h at 37 °C in the absence of light. The cylindrical samples were embedded in acrylic resin and polished (Model 3v; Arotec, Cotia, Brazil) using #1200 and #2000 grit silicon carbide sandpapers. Three indentations were made in each sample with a Knoop indenter with 10 g load for 5 s, 100 µm equidistant from each other (HMV 2; Shimadzu, Tokyo, Japan). The initial Knoop hardness number (KHN_1) was recorded and the specimens were immersed in 70% ethanol solution at 37 °C for 2 h, and the final hardness (KHN_2) was then determined. The percentage of hardness reduction (ΔKHN) between KHN_1 and KHN_2 was calculated [34].

2.4. Radiopacity

The resin cements samples (10 mm ± 0.5 mm diameter and 1 mm ± 0.1 mm thickness) were radiographed with aluminum stepwedge, according to ISO 4049:2009 [33]. The radiographic images were acquired with a phosphorus plate system (VistaScan; Dürr Dental GmbH & Co, Bietigheim-Bissingen, Germany) and X-ray machine operating at 70 kV and 8 mA. The exposure time was 0.4 s and focus-to-object distance was 40 cm. All exposed plates were scanned immediately after exposure. The resulting images were transferred in tiff image files to a personal computer for further analysis with software (Image J; Wayne Rasband, National Institutes of Health, USA). On each image, an area of interest with a size of 25 mm^2 was selected on each specimen and step of aluminum stepwedge image and the reference mean gray values were calculated.

2.5. Film thickness

The film thickness was determined based on ISO 4049:2009 requirements [35]. The resin cements (n = 3) were hand mixed. Two glass squares, having a contact surface area of 200 ± 25 mm^2 and a thickness of 5 mm were used. The combined thickness of the two optically stacked flat glass plates was initially measured using a digital caliper. The upper plate was removed and 0.1 mL of the mixed cement was placed in the center of the lower plate. The upper plate was positioned centrally in the same orientation as in the original measurement. A vertical load of 150 N was applied immediately for 180 s and after that photoactivated for 80 s. The final measurement was made immediately after photoactivation and the subtraction of the thickness of final and initial measurements was made.

2.6. Color stability

The same specimens used in radiopacity evaluation were subjected to color stability analysis. Color measurements were performed using a spectrophotometer (UV–vis-NIR CARY 5000; Agilent Technologies, Santa Clara, USA) equipped with a diffuse reflectance accessory DRA-1800 Integrating Sphere. The samples were positioned over a standard white background. A dark mask containing a circular slit measuring 4 mm in diameter was placed over the infiltrated surface to set the limits of analysis. The color of each sample (n = 5) was measured and quantified in terms of three coordinate values (L*, a* and b*), as established by the Commission Internationale de l'Eclairage (CIE). The color of the resin cements was assessed and recorded under standardized conditions according to the CIE L*a*b* system. The overall changes in color impression (ΔE) were calculated using the following formulas:

$\Delta L = L\ (6\ months) - L\ (baseline)$

$\Delta a = a\ (6\ months) - a\ (baseline)$

$\Delta b = b\ (6\ months) - b\ (baseline)$

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

2.7. Micro-shear bond strength

Premilled blocks (IPS e.max CAD; Ivoclar Vivadent, Schaan, Liechtenstein) were used. Sections were prepared from the CAD/CAM blocks using a precision sectioning saw (LowSpeedSaw; Isomet; Buehler, USA) with a thickness of 1 mm. Block surfaces were measured with a roughness meter and were flattened under water cooling with #600 and #1200-grit silicon carbide sandpaper. The specimens were positioned in a polyvinyl chloride cylinder with dimensions of 2.5 cm × 1.7 cm and embedded in an acrylic resin (JET; Artigos Odontológicos Clássico, Sao Paulo, Brazil). The sections from CAD/CAM blocks were randomly divided into nine groups. All the ceramic surfaces were etched with 10% hydrofluoric acid gel (FGM, Joinville, Brazil) for 20 s and rinsed with distilled water for 20 s and air-dried. A silane coupling agent (RelyX; 3 M ESPE, St Paul, USA) was applied on the surface for 20 s and air-blown for 5 s. An adhesive resin was applied (Adhesive Adper Scotchbond Multi-Purpose; 3 M ESPE, St Paul, USA) and light-cured for 20 s. The custom-made polyvinylsiloxane matrix was used to produce 12 resin cement cylinders 1 mm in diameter and 1 mm in height. Each cylinder was light-cured for 40 s. Half of the specimens were stored in distilled water at 37 °C for 7 days and the other specimens for 6 months. The specimens were tested using a universal testing machine (EZ–SX; Shimadzu, Kyoto, Japan) and loaded at a crosshead speed of 1.0 mm/min until fracture occurred at 0.2 mm in diameter stainless steel wire placed as close as possible to the bonded interface. Micro-shear bond strength was calculated by dividing the maximum load at failure (N) with the bonding area (mm^2) and recorded in MPa. Mean values and standard deviations were calculated. Failure modes were evaluated under a stereomicroscope 40 ×. Failure was assessed as adhesive, cohesive within the resin cement, or mixed.

2.8. Ultimate tensile strength test

Twelve samples per group were prepared in a metallic matrix with an hourglass design measuring 8 mm long, 2 mm wide and 1 mm thick, with a cross-sectional area of 1 mm^2 at the constriction. The resin cements were light-cured for 30 s on each side, except for the group L_{HEAA0}, which was photoactivated for 40 s on each side. The samples were stored in distilled water at 37 °C for 24 h and 6 months before testing. Before being tested they were fixed with a cyanoacrylate adhesive in a metallic device, and the tests were performed in a universal testing machine (EZ-SX; Shimadzu, Kyoto, Japan) at a crosshead speed of 1 mm/min with values expressed in MPa.

2.9. Statistical analysis

The normality of the data was evaluated using the Shapiro–Wilk test in SigmaPlot software (Systat Software Inc., San Jose, USA). One-way analysis of variance (ANOVA) and Tukey's post hoc test were performed to evaluate the degree of conversion, polymerization rate, radiopacity and film thickness. The difference between KHN_1 and KHN_2 was assessed using the paired Student's *t*-test. KHN_1, ΔKHN, ΔE were assessed by one-way ANOVA. For micro-shear bond strength and ultimate tensile strength (UTS), a two-way ANOVA was performed. The failure patterns were evaluated using stereomicroscopy. A level of significance of 0.05 was considered for all tests.

3. Results

Figs. 1 and 2 show the degree of conversion and polymerization kinetics of light-cured and dual-cured resin cements, respectively. Among light-cured resin cements, the DC of L_{HEAA1} (35.9%) was not significantly different from control L_{HEMA1} (40.64%) (p = 0.090).

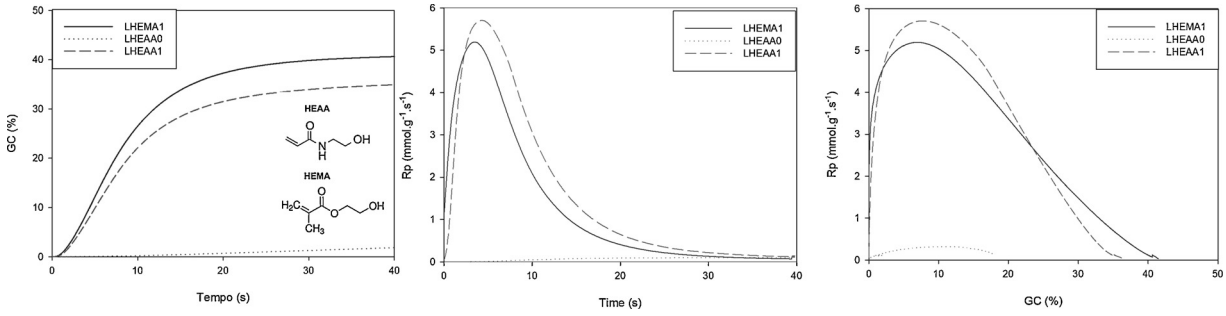

Fig. 1. Degree of conversion and polymerization rate of experimental light-cured resin cements (L_{HEMA1}, L_{HEAA0}, L_{HEAA1}).

L_{HEAA0} showed a lower value than the other light-cured groups ($p < 0.050$). The rate of polymerization (Rp) for L_{HEMA1} and L_{HEAA1} groups was comparable ($p = 0.29$), but for the L_{HEAA0} group a statistically lower Rp was found ($p < 0.0001$). For dual-cured resin cements, $D_{HEMA0.6}$ had the highest DC and Rp values ($p < 0.050$). Acrylamide groups did not differ significantly between them independently of tertiary amine concentration both for DC and Rp ($p > 0.050$).

Maximum degree of conversion (DC max) and polymerization kinetics values, hardness before (KHN_1) and after (KHN_2) immersion in ethanol and the percentage reduction between KHN_1 and KHN_2 (ΔKHN) are shown in Table 2. The group L_{HEAA1} did not differ from control group regarding DC max ($p > 0.050$). In dual-cured resin cements, the groups containing HEAA had no statistical difference between them ($p > 0.050$), while the methacrylate groups had lower DC max than $D_{HEAA0.6}$ ($p < 0.050$). The groups L_{HEMA1} and L_{HEAA1} had higher KHN_1 values than the L_{HEAA0} resin cement ($p = 0.600$ and $p < 0.0001$, respectively). The absence of tertiary amine in the light-cured group showed higher degradation (ΔKHN) ($p < 0.050$). The $D_{HEMA0.6}$ group had the highest value for KHN_1 ($D_{HEMA0.6} > D_{HEMA0,25} = D_{HEAA0} = D_{HEAA0.25} = D_{HEAA0.6} > D_{HEMA0} - p < 0.050$). $D_{HEMA0.6}$ had the lowest degradation for dual-cured groups (ΔKHN) ($p < 0.050$). Significant differences between the initial and final hardness values for each group independently of activation mode were observed ($p < 0.0001$).

The results of radiopacity and film thickness are shown in Table 3. Both light-cured and dual-cured showed no statistical difference in all groups ($p > 0.050$). Table 4 presents the results of color stability of the resin cements evaluated after 6 months of storage in distilled water and mineral oil. In the light-activated resin cements groups stored in distilled water, the control group with methacrylate had the lowest color change value, with no statistical difference from the L_{HEAA1} group ($p = 0.777$). In dual-cured cements, $D_{HEMA0.6}$ and all groups containing HEAA showed the greatest changes in color ($p < 0.050$). Color changes in mineral oil storage showed no statistical differences in both resin cements, except for the L_{HEAA1} group ($\Delta E = 6.97, p < 0.050$). Based on analysis of changes in lightness (L*), the methacrylate groups proved to lighten up, whereas most acrylamide groups darkened in distilled water. Comparing changes in reddish-green hue (a*) and bluish-yellow hue (b*), the methacrylate groups varied less in mineral oil. In distilled water, all acrylamide groups had greater changes toward the red color. In dual-cured resin cement, the methacrylate and acrylamide groups with higher tertiary amine concentration had greater changes in the direction of yellow color. Fig. 3 shows the samples of resin cements after 6 months of distilled water and oil mineral storage.

The averages and standard deviations for UTS and micro-shear bond strength (μSBS) are shown in Table 5. Initial UTS and μSBS for light-cured resin cements were significantly lower for all acrylamide groups ($p < 0.050$). There was a statistically significant interaction between storage time and resin cements ($p < 0.0001$ and $p = 0.050$ for UTS and μSBS, respectively). After 6 months of water storage, the L_{HEAA1} group showed no statistical difference from L_{HEMA1} ($p > 0.050$) for both tests. Among the dual-cured resin cements, initial UTS were lower for all acrylamide groups ($p < 0.0001$). $D_{HEMA0.6}$ showed the highest immediate μSBS value ($p < 0.050$). There was a statistically significant interaction between storage time and resin cements ($p < 0.0001$ for UTS and μSBS). All acrylamide groups had long-term storage UTS and μSBS values higher than initial ones ($p < 0.0001$), except for the D_{HEAA0} in UTS, with no statistical difference from the $D_{HEMA0.6}$ group ($p > 0.050$). The failure mode of light-cured and dual-cured resin cements is shown in Fig. 4 and was predominantly adhesive between ceramic and resin cement for all resin cements.

4. Discussion

Dental resin cements are composed of resin monomers, initiators/co-initiators, inhibitors and inorganic fillers. Light-cured and dual-cured resin cements containing HEAA with the presence or not of tertiary amine were evaluated. In the present study, the polymerization process was affected depending on the chemical component used. Physicochemical and optical properties were evaluated and the addition of HEAA influenced the polymerization behavior, initial and long-term mechanical properties and color stability of the experimental resin cements. Thus, the null hypothesis must be rejected.

In light-cured resin cement groups, a methacrylate group without EDAB was not formulated. The presence of tertiary amine as initiator has been reported as indispensable for polymerization of resin materials with CQ because even with acrylamide, the polymerization reaction

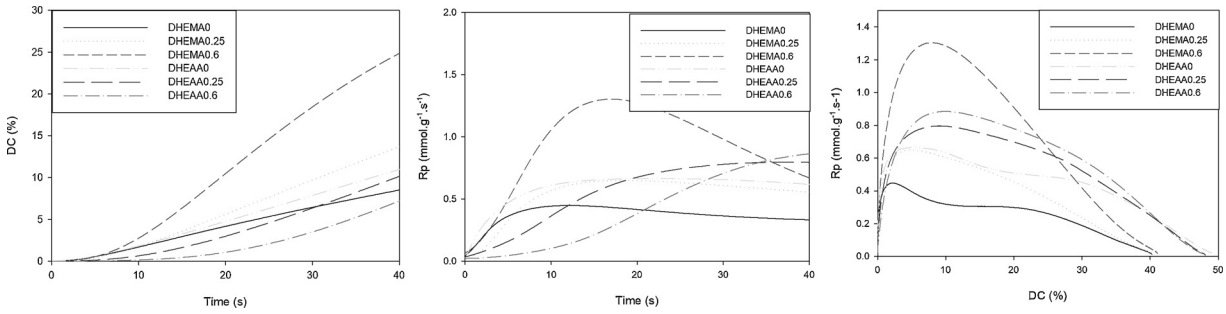

Fig. 2. Degree of conversion and polymerization rate of experimental dual-cured resin cements (D_{HEMA0}, $D_{HEMA0.25}$, $D_{HEMA0.6}$, D_{HEAA0}, $D_{HEAA0.25}$, $D_{HEAA0.6}$).

Table 2
Mean and standard deviation values of degree of conversion (DC) and polymerization rate (Rp). Hardness of the experimental light-cured and dual-cured resin cements before (KHN1) and after the immersion in solvent (KHN2) and the percentage reduction of Knoop hardness after ethanol immersion (ΔKHN).

Curing mode	Groups	DC max (%)	Rp (mmol. $g^{-1}.s^{-1}$)	KHN1	KHN2	ΔKHN%
Light-cured	L_{HEMA1}	41.47 (1.87)^{A}	5.20 (0.59)^{A}	21.66 (1.46)^{Aa}	10.27 (1.38)^{b}	52.02 (8.70)^{A}
	L_{HEAA0}	31.2 (2.51)^{B}	0.30 (0.03)^{B}	2.43 (0.53)^{Ba}	0.84 (0.14)^{b}	64.35 (5.46)^{B}
	L_{HEAA1}	36.52 (2.74)^{AB}	5.73 (0.33)^{A}	22.66 (2.31)^{Aa}	9.10 (1.71)^{b}	59.53 (6.35)^{AB}
Dual-cured	D_{HEMA0}	40.26 (5.91)^{B}	0.44 (0.06)^{C}	8.32 (2.25)^{Ca}	2.72 (1.73)^{b}	68.37 (13.56)^{B}
	$D_{HEMA0.25}$	40.33 (1.63)^{B}	0.65 (0.08)^{B}	15.49 (2.32)^{Ba}	4.8 (1.16)^{b}	69.22 (3.89)^{B}
	$D_{HEMA0.6}$	41.05 (2.28)^{B}	1.30 (0.03)^{A}	21.22 (0.45)^{Aa}	10.3 (0.9)^{b}	51.46 (4.72)^{C}
	D_{HEAA0}	49.4 (3.25)^{A}	0.66 (0.08)^{BC}	14.56 (1.18)^{Ba}	2.87 (1.05)^{b}	79.92 (8.03)^{A}
	$D_{HEAA0.25}$	48.12 (1.27)^{AB}	0.79 (0.15)^{B}	13.67 (2.08)^{Ba}	2.33 (0.8)^{b}	78.54 (5.01)^{B}
	$D_{HEAA0.6}$	48.42 (0.7)^{AB}	0.88 (0.12)^{B}	12.25 (1.04)^{Ba}	3.6 (0.86)^{b}	71.12 (4.78)^{B}

Different capital letters indicate statistically significant difference in the same column, within the same type of cement (light-cured or dual-cured) ($p < 0.05$). Different small letters indicate statistically significant difference in the line within the same test ($p < 0.05$).

Table 3
Mean and standard deviation of radiopacity and film thickness of light-cured and dual-cured resin cements.

Curing mode	Groups	Radiopacity (mmAl)	Film Thickness (μm)
Light-cured	L_{HEMA1}	0.99 (0.62)^{A}	46.66 (5.77)^{A}
	L_{HEAA0}	1.33 (0.19)^{A}	46.66 (5.77)^{A}
	L_{HEAA1}	1.48 (0.28)^{A}	40.00 (10.00)^{A}
Dual-cured	D_{HEMA0}	1.02 (0.17)^{A}	23.33 (5.77)^{A}
	$D_{HEMA0.25}$	1.08 (0.27)^{A}	36.66 (5.77)^{A}
	$D_{HEMA0.6}$	1.16 (0.62)^{A}	36.66 (11.54)^{A}
	D_{HEAA0}	1.23 (0.35)^{A}	23.33 (5.77)^{A}
	$D_{HEAA0.25}$	1.12 (0.20)^{A}	26.66 (11.54)^{A}
	$D_{HEAA0.6}$	1.11 (0.32)^{A}	33.33 (5.77)^{A}

Different capital letters indicate statistically significant difference in the same column, within the same type of cement (light-cured or dual-cured) ($p < 0.05$).

does not occur properly [29]. The dual-cured groups were formulated considering the least amount of DHEPT required for chemical polymerization of the acrylamide group. Thus, the corresponding groups with methacrylate and different tertiary amine concentrations were formulated as controls. The groups D_{HEMA0} and D_{HEAA0} did not polymerize under chemical conditions, only by light activation. However, they were submitted to the tests to see how the acrylamide group (possibly co-initiator) with free-amine initiator would behave because a more color-stable dual-cured resin cement has been proposed with a self-cure initiator system without tertiary amine already [22]. In dual-cured systems, radical production in the redox system appears to proceed via initial ionic displacement by the nitrogen of the amine on the peroxide linkage [32]. Free radicals are transferred to the monomer, which will react with other monomers, until the formation of a stable molecule [5]. Probably, the nitrogen present in HEAA cannot initiate the autopolymerization alone, requiring the presence of an amine co-initiator, however, in lower concentration.

The binary CQ/amine photoinitiator/co-initiator system is the most common combination used in commercially available products that are activated by visible light [18]. In addition, a dual polymerization usually involves free-radical initiators such as benzoyl peroxide that react with a tertiary amine [19]. It is known that DC is influenced by the CQ:amine ratio [23]. The amount of amine present in resin cements significantly influenced the results. These results are related to the fact that sufficient amine is necessary to act as a hydrogen donor for CQ to start the polymerization process [23]. Thus, the absence of EDAB in light-cured groups leads to a reduced DC and Rp and a longer period of time to complete the monomer conversion, corroborating a previous study [29]. Instead, the methacrylate and acrylamide groups with tertiary amine obtained similar DC and Rp. Furthermore, decreasing concentrations of tertiary amine (DHEPT) in methacrylate-based dual-cured resin cements, the Rp also decreased from 1.30 to 0.44 mmol.$g^{-1}.s^{-1}$. The acrylamide groups, however, maintained the Rp independently of amine concentration from 0.88 to 0.66 mmol.$g^{-1}.s^{-1}$. The results did not reveal a difference in the reactivity between HEMA and HEAA. Nevertheless, from the literature, it is well known that acrylamides are more reactive than HEMA [13,29]. These studies evaluated the polymerization kinetics of HEAA and *N*-methylacrylamides in dental adhesives as monofunctional monomer or in association with another dimethacrylate. Instead, this study has the presence of filler content and did not analyze the homopolymer and co-polymer separately. The filler increases the viscosity of resin cement leading to a lower degree of conversion, probably due to reduced mobility of the monomers in viscous materials [6]. In general, the maximum degree of conversion reached by resin cements is around 60% [7–9], whereas the resin cements analyzed by DSC-PCA in this study obtained lower values.

Highly cross-linked polymers are more resistant to degradation and solvent uptake, whereas linear polymers present more space and pathways for solvent molecules to diffuse within their structure [36]. The absence or decrease in tertiary amine concentration reduced initial hardness for the acrylamide group in light-cured and dual-cured resin

Table 4
Mean and standard deviation of ΔL*, Δa*, Δb* and ΔE of luting materials evaluated after 6 months in distilled water and mineral oil.

Curing mode	Groups	Distilled water				Mineral oil			
		ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE
Light-cured	L_{HEMA1}	1.50	−0.24	−0.41	2.55 (1.41)^{A}	−1.45	0.14	−0.29	1.74 (0.89)^{A}
	L_{HEAA0}	6.59	0.05	1.07	6.74 (2.85)^{B}	−0.29	0.40	−0.89	2.61 (1.37)^{A}
	L_{HEAA1}	−3.24	0.84	0.46	3.49 (1.95)^{AB}	5.80	0.18	0.05	6.97 (1.86)^{B}
Dual-cured	D_{HEMA0}	2.43	1.53	−1.56	4.81 (1.18)^{A}	−3.05	0.16	−1.88	3.69 (1.65)^{A}
	$D_{HEMA0.25}$	1.46	1.19	−0.23	5.22 (1.46)^{AB}	−1.35	0.16	−0.80	4.44 (1.17)^{A}
	$D_{HEMA0.6}$	2.27	1.78	3.32	5.83 (1.63)^{ABC}	−3.09	0.55	−1.93	4.39 (1.64)^{A}
	D_{HEAA0}	−3.49	3.06	−0.19	6.70 (0.61)^{ABC}	−1.73	0.48	1.61	3.73 (1.20)^{A}
	$D_{HEAA0.25}$	−0.33	1.89	0.11	7.49 (1.04)^{BC}	−0.58	0.70	−0.22	5.38 (1.35)^{A}
	$D_{HEAA0.6}$	−2.87	3.89	6.24	8.03 (1.08)^{C}	0.30	0.80	2.80	5.40 (1.02)^{A}

Different capital letters indicate statistically significant difference in the same column, within the same type of cement (light-cured or dual-cured) ($p < 0.05$).

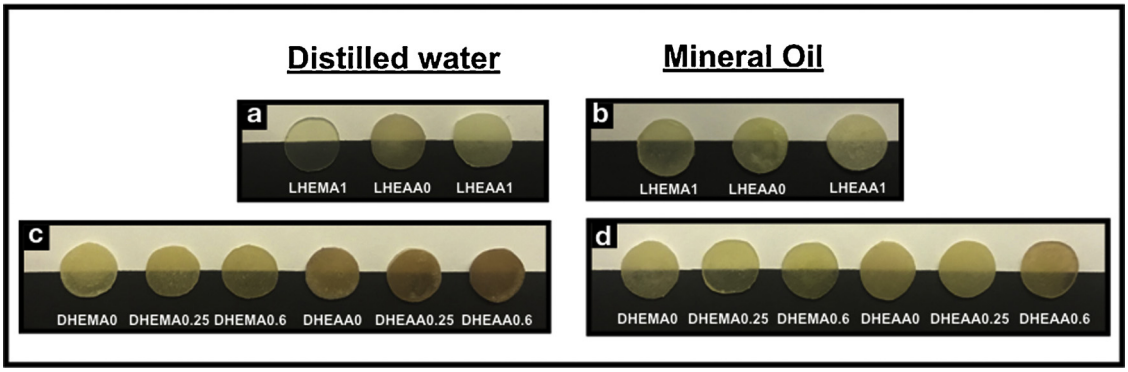

Fig. 3. Photographs of light-cured and dual-cured experimental resin cements specimens after 6 months of distilled water or mineral oil storage. a) Light-cured experimental resin cements stored in distilled water. b) Light-cured experimental resin cements stored in mineral oil. c) Dual-cured experimental resin cements stored in distilled water. d) Dual-cured experimental resin cements stored in mineral oil.

Table 5
Mean and standard deviation values (immediate and after 6 months of water storage) of the UTS test and μSBS teste of light-cured and dual-cured resin cements.

Curing mode	Groups	UTS (24 h)	UTS (6 m)	μSBS (1 w)	μSBS (6 m)
Light-cured	L_{HEMA1}	35.93 (6.84)^{Aa}	31.83 (5.76)^{Aa}	15.64 (3.74)^{Aa}	15.25 (7.09)^{Aa}
	L_{HEAA0}	6.25 (2.02)^{Cb}	19.06 (4.85)^{Ba}	7.92(4.78)^{Ba}	8.14 (2.79)^{Ba}
	L_{HEAA1}	15.82 (2.91)^{Bb}	29.00 (8.21)^{Aa}	8.65 (3.91)^{Bb}	13.89 (5.19)^{Aa}
Dual-cured	D_{HEMA0}	30.28 (7.09)^{Ba}	19.05 (2.83)^{Bb}	3.69 (0.88)^{Ca}	4.98 (0.95)^{Ba}
	$D_{HEMA0.25}$	42.90 (5.69)^{Aa}	23.86 (4.34)^{Ab}	6.52 (3.00)^{Ba}	7.24 (1.51)^{Ba}
	$D_{HEMA0.6}$	40.00 (10.30)^{Aa}	26.81 (3.71)^{Ab}	10.83 (4.90)^{Aa}	12.26 (2.5)^{Aa}
	D_{HEAA0}	19.62 (2.96)^{Ca}	22.56 (5.84)^{Aa}	4.26 (0.81)^{Bb}	13.8 (5.25)^{Aa}
	$D_{HEAA0.25}$	19.00 (2.81)^{Cb}	23.67 (6.05)^{Aa}	4.65 (1.52)^{Bb}	17.26 (4.86)^{Aa}
	$D_{HEAA0.6}$	20.81 (7.00)^{Cb}	24.91 (4.54)^{Aa}	4.72 (2.17)^{Bb}	14.90 (3.82)^{Aa}

Different capital letters indicate statistically significant difference in the same column, within the same type of cement (light-cured or dual-cured) ($p < 0.05$).Different small letters indicate statistically significant difference in the line within the same test ($p < 0.05$).

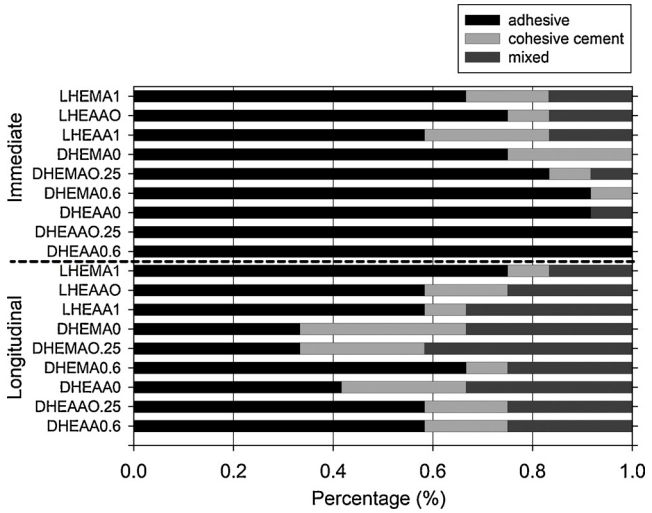

Fig. 4. Incidence of failure mode (%) of resin cements analyzed by stereomicroscope.

cements containing methacrylate monomer. However, despite different concentrations in dual-cured acrylamide groups, there was no difference in the initial hardness, but still they are lower than the $D_{HEMA0.6}$ group. If ethanol has the capacity to penetrate the polymer network, the efficiency of secondary molecular interactions could be reduced, leading to leaching of unreacted monomers and higher degradation rate [36]. Based on the overall results of this study, it is possible to affirm that with the higher Rp, a greater initial hardness and a lower degradation value of resin cements are observed. Furthermore, a higher degradation in the acrylamide groups is probably due to a linear polymer formation and more HEAA monomers converted than Bis-GMA due to the high reactivity of HEAA [29].

Chemical composition, components of the organic matrix and the amount and atomic number of the filler influences the radiopacity [37]. Ytterbium trifluoride (YbF_3) was added as filler in all resin cements. Because of the higher atomic number (z = 70), the element can absorb or reflect more X-rays, leading to an opaque radiographic image [38]. In this study, all groups had no statistical difference in radiopacity because all resin cements received the same amount of filler. The addition of YbF_3 at 40 wt% was due to higher acrylamide viscosity [13], besides most commercial resin cements have 50–60% filler content [4]. Some studies also added a lower filler content around 25 wt% and mechanical properties were comparable to those obtained with thiourethane addition to the modified commercial materials [9,10]. It was expected that the low water solubility of YbF_3 could prevent the long-term degradation of dental cements [39]. In addition, a higher refractive index could decrease the absorption of emitted light through the reflection of photons at the surfaces [40]. YbF_3 has a refractive index of approximately 1.5 [40], which allows more light to pass through the resin cement, probably being the reason for the resin cements' polymerization in amine-free groups D_{HEMA0} and D_{HEAA0}. In addition, the benzoyl peroxide generates radicals that act as initiators with the possible interaction of nitrogen from acrylamide [32]. In relation to film thickness, the ISO standards require a thickness no greater than 50 μm for resin-based cements [35]. Apart from acrylamides being more viscous than HEMA [13], there was no statistical difference in both types of resin cement. Thus, all resin cements are in accordance with ISO 4049 limits.

Light-cured resins generally have acceptable initial color and color stability after polymerization [24]. Nevertheless, the dual-cured resins have a much darker initial yellow color and a larger color shift (ΔE*) for a darker shade of yellow after polymerization [22]. Color stability is influenced by intrinsic factors such as the composition of the resin matrix, conversion rate and type of initiator [11]. Previous studies

report ΔE ≤ 3.3 as clinically acceptable [20,22]. The color changes (ΔE) in the present study ranged from 2.55 to 6.74 in light-cured resin cements and 4.81 to 8.03 in dual-cured resin cements when stored in distilled water for 6 months. Usually, the storage time of color stability is shorter [28] or in most cases induced by accelerated aging [20,22]. The accelerated aging protocol, however, cannot reliably simulate the clinical situation [17]. In this study, all the samples' surfaces were in contact with water during the whole evaluated period, which is considered to be a greater challenge when compared with the clinical situation. The mineral oil storage could represent the changes in color considering internal surfaces that are not in contact with water. Only L_{HEMA1} reached the ΔE that is clinically acceptable. However, L_{HEMA1} and L_{HEAA1} showed no statistical difference and according to a previous study, clinicians are more tolerant of shade mismatch in a clinical scenario, than in vitro conditions, which mean acceptability tolerance for 95% of observers was 4.0 ΔE units [41]. The absence of EDAB in acrylamide light-cured resin cement led to a greater color change due to low monomer conversion and degradation of polymer matrix. Incompletely converted monomer undergoes further oxidation that generates a yellowing of the resin [23]. Leaching of the monomer can occur if significant amounts of unreacted monomers remain in a poorly polymerized resin mass, which leads to porosity and enhanced potential for extrinsic staining [21]. Storage in distilled water showed higher ΔE values than mineral oil, which may prevent the effects of water [42]. The L_{HEAA1} group showed the highest ΔE (6.97) in mineral oil storage, however, it can be attributed to increased lightness ($\Delta L^* = 5.8$), which became more opaque, explaining the greater color variation.

The high initial color and color shift are greatly influenced by the initiator system such as CQ and amine in light-curing mode and tertiary aromatic amine and benzoyl peroxide in dual-curing mode. Color changes are more evident due to tertiary aromatic amines that are more like to oxidize [17]. The ΔE was dependent on the amount of amine, i.e., the higher the amine content, the higher the yellowing effect [23]. As the amine concentration decreased in dual-cured groups, less color change was observed. Composites with higher viscosity had higher b* values, i.e., were more yellow than materials with lower viscosity in the baseline color evaluation. Increasing co-monomer viscosity might reduce the efficiency of photoinitiator diffusion through the reaction medium leaving excited but unreacted CQ molecules to return to their original, yellow state [23]. Acrylamide groups in dual-cured resin cements had a considerable color change, probably due to benzoyl peroxide and tertiary amine interaction, where the acrylamide also presents a nitrogen in its molecular structure, which leads to the formation of a radical in the redox system [32], leading to a higher color change.

Addition of HEAA in light-cured and dual-cured resin cements showed lower initial mechanical properties. However, the acrylamide groups increased the mechanical properties after storage. The storage time of this work was 6 months, nevertheless it is expected that 1 year of water storage could lead to a higher degradation of methacrylate groups, which are prone to hydrolytic degradation [14]. Higher water sorption can facilitate the degradation of the polymer matrix and also leads to a decrease in the mechanical properties. HEMA is characterized by low reactivity and lack of hydrolytic stability [15]. A luting composite was formulated based on the monomer *N*-methyl-*N*-(2-hydroxyethyl)acrylamide, which has an additional methyl group compared with HEAA in this study, being an alternative to increase the initial mechanical properties. The additional methyl group tends to form a cross-linked polymer, instead of a linear polymer, but high hydrophilicity of this monomer may compromise the durability [13].

Acrylamides seem to have a function in polymerization. The homopolymer HEAA is more reactive than HEMA and played an important role in the earlier stages of polymerization of acrylamide groups and followed by Bis-GMA conversion in the later stages [29]. It can result in unreacted double bonds of dimethacrylate Bis-GMA, which could link to HEAA in later stages of polymerization. In dual-cured resin cements, autopolymerization could continue for two weeks, even after light polymerization has been completed and the rate of dual polymerization differs according to the time after mixing and tends to increase with time [25]. It has been speculated that a delay in light activation would enhance the resin cement properties [26]. Thus, the autopolymerization promoters are allowed to react to some extent before being entrapped by the polymeric chains as soon as the photoactivation begins [27].

The results of the present study suggest that HEAA alone is not effective in polymerization when there is no tertiary amine present. The addition of HEAA monomer negatively affected the properties of the dual-cured resin cements. The bond strength of resin cements with acrylamide monomer was negatively affected. Despite the recommendation of the manufacturer of lithium disilicate to use hydrofluoric acid (HF) at 5% before cementation, the authors used 10% HF. The use of 10% HF was based on previous studies that showed no difference between concentrations of 5% and 0% [43,44]. The light-cured resin cement L_{HEAA1} had no difference in its physicochemical and optical properties compared with the control, however, with long-term hydrolytic stability. Less degradation of the polymeric matrix is desired for a longer durability of the bond interface between restoration and tooth structure.

5. Conclusions

Physicochemical and optical properties of light-cured and dual-cured resin cements were influenced by *N*-(2-hydroxyethyl)acrylamide addition. The dual polymerization showed lower polymerization kinetics and KHN_1, leading to a higher monomer degradation that underwent a significant color change. The L_{HEAA1}, instead, did not differ from the control in relation to physicochemical and optical properties, however, with long-term hydrolytic stability.

Declaration of Competing Interest

The authors declared no conflict of interest.

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