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Evaluation of physico-mechanical properties and filler particles characterization of conventional, bulk-fill, and bioactive resin-based composites

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ABSTRACT

Objective: This study evaluated physical and mechanical properties and characterized the filler particles of seven composites.

Materials and methods: Filtek Supreme (FS, 3M Oral Care), Forma (FO, Ultradent), Charisma Diamond (CD, Kulzer), Spectra Smart (SS, Dentsply), Filtek Bulk Fill (FB, 3M Oral Care), Tetric N-Ceram Bulk Fill (TB, Ivoclar), and Cention N (Ivoclar) in self- (CNSC) or dual-curing (CNDC) were evaluated. Fillers size, shape, and content were analyzed by scanning electron microscopy (SEM) and X-ray dispersive energy spectroscopy (EDX). Disk-shaped specimens (n = 5) were prepared for sorption (SP) and solubility (SL). Flexural strength and elastic modulus were tested at 24 h and 12 months (n = 10). Degree of conversion (DC%) and maximum rate of polymerization (Rp^{max}) were evaluated using micro-Raman spectroscopy. SP and SL results were submitted to Kruskal-Wallis one-way ANOVA and Dunn's pairwise test ($\alpha = 0.05$). Mechanical properties were analyzed by 2-way ANOVA and Tukey's test ($\alpha = 0.05$). DC% of CNSC and CNDC was compared by independent t-test ($\alpha = 0.05$). Rp^{max} results were analyzed by 1-way ANOVA and Tukey's test ($\alpha = 0.05$).

Results: The composites differed regarding filler size, shape, and content. CD and CNSC showed lower SP than FS. SS had lower SL than CNSC and CNDC. CNDC presented higher DC% than CNSC. CD, TB, and CNDC showed the highest Rp^{max}. TB, CNSC, and CNDC showed the lowest 24-h flexural strengths. Mechanical properties of CD did not decrease, while FO, TB, and CNSC showed a significant reduction after storage.

Conclusions: Monomer composition and fillers characteristics greatly influenced the physico-mechanical properties of the tested composites.

1. Introduction

In the past decades, resin composites have become a useful tool for direct restorations, as these materials do not require invasive tooth preparations (Wilson, 2007). Also, the use of amalgam alloys in restorative dentistry has been reduced over the past decades due to the Minamata convention (2013), which demanded a global effort for the gradual elimination of mercury-containing materials from dentistry,

given its potential release in the oral environment (Chesterman et al., 2017). Hence, resin composites have been widely used for dental restorations, mostly because of their esthetic appeal, coupled with adequate mechanical properties. These features make resin composites suitable for the restoration of either anterior or posterior teeth, as well as allow for more conservative tooth preparations that preserve as much dental tissue as possible.

The first developed resin-based restorative material required manual

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mixing of two pastes for the onset of chemical polymerization, which caused the incorporation of bubbles in the bulk composite, impairing its final mechanical properties and polishing. Later, these materials were enhanced by advancements regarding methacrylate-based monomers, inorganic filler particles, and silane coupling agents, accompanied by the introduction of photoinitiator systems (Ferracane, 2011; Fronza et al., 2017). The most commonly used photoinitiator system is composed of camphorquinone (CQ) and tertiary amine. When composites containing this photoinitiator system are exposed to visible light irradiation at around 450-nm wavelength, the C=C bonds of resin monomers are converted to C—C bonds, forming highly-resistant, cross-linked polymers. However, most of the effective light energy emitted by a light-curing unit (LCU) during polymerization does not reach homogeneously more than 2 mm in depth through the composite layer, which is due to light dispersion happening inside the material (Schneider et al., 2008; Soto-Montero et al., 2020).

The organic matrix of most dental composites presents the methacrylate-based monomer Bis-GMA (bisphenol-A diglycidyl dimethacrylate), characterized by its high molecular weight. However, there are many other monomers that can be used in composite formulations in order to adapt the material to various purposes (Ferracane, 2011). A high conversion of the monomers C=C bonds would be desirable to provide satisfactory mechanical properties for the resulting polymer, but it would also cause high polymerization shrinkage stresses due to the approximation of the monomer units during the curing process of the material, which might negatively impact the durability of the dental restoration. Furthermore, long-term clinical trials have showed composite restoration failures related mainly to marginal breakdown, reducing their service time in the oral cavity (Opdam et al., 2014).

The mechanical properties of composites are highly dependent on the features of their filler particles, like size, composition, and content. This is an important observation, considering there are several resin-based materials with different types of fillers in their composition available in the dental market (Leprince et al., 2012). Filler particles represent the inorganic content of dental composites, usually incorporated into the material at a rate of approximately 60% of its total volume, and they can be composed of quartz, silica, zirconia, barium aluminosilicate, ytterbium trifluoride, lithium borohydride, or a combination of those (Di Francescantonio et al., 2016; Ruivo et al., 2019). The development of polymerization shrinkage stresses in a composite is related to the volume or weight% of filler particles in its composition, as well as to the depth of the cavity, and the amount of energy delivered to the restoration by the light-curing unit, which are all factors to determine the magnitude of the volumetric shrinkage of the restorative material (Atria et al., 2018; Prager et al., 2018).

Therefore, the layering technique has been recommended to ensure complete cure and reduce polymerization shrinkage stresses of the resin-based material during clinical procedures (Ferracane, 2011; Finan et al., 2013; Fronza et al., 2017). This technique recommends the use of multiple 2 mm-thick layers of composite to fill a tooth cavity, which are inserted without connecting opposite walls, with a separate light-activation step for each composite layer. However, placing composite restorations became time-consuming, especially in large cavities (Wang et al., 2019), while concerns have also been raised regarding the high technical sensitivity of incremental-filling restorative approaches (Hirata et al., 2015).

In order to overcome the limitations related to conventional resin-based materials and their associated restorative techniques, changes in filler particles (amount, shape, or surface treatment), monomer chemistry, or alterations of polymerization dynamics have been introduced (Ilie and Hickel, 2011), resulting in the development of composites for bulk placement, which have been introduced and marketed as “low polymerization shrinkage” materials (Sebold et al., 2020). The so-called bulk-fill resin-based products might contain modified monomers (mostly not fully disclosed by manufacturers), higher content of inorganic fillers, or more efficient photoinitiator systems as an effort to

reduce polymerization shrinkage stress (Ilie et al., 2013; Sebold et al., 2020). Due to the modifications, these materials can enable clinicians to perform direct posterior restorations with a single 4–5 mm thick layer of composite (depending on manufacturer’s recommendations), making restorative procedures faster and less technique-sensitive (Bucuta and Ilie, 2014; Leprince et al., 2014; Lynch and Wilson, 2013).

Moreover, primary caries has been suggested as the main reason for restoration placement, while recurrent caries remains the most common reason for replacing existing restorations (Eltahlah et al., 2018). Considering this problem, fluoride-releasing agents, which are believed to play an important role in the process of de- and remineralization (Naoum et al., 2011), have been incorporated into composites (Davis et al., 2014; Khan et al., 2013). One of these products is the bioactive, dual-cured composite Cention N, which was recently introduced by Ivoclar, delivered as powder (inorganic particles) and liquid (monomers and initiator systems) for hand mixing before application. According to manufacturer’s claims, the alkaline fillers of Cention N can release “acid-neutralizing” ions (such as fluoride, hydroxide, and calcium) in order to avoid or reduce demineralization of adjacent dental hard tissues during acidic challenges (Todd, 2016). Theoretically, this material would not require light-curing to polymerize in depth, but the use of additional light-curing could be an option depending on the preference of the professional. Nonetheless, the effectiveness of fluoride-releasing restorative materials, and the influence of fluoride addition on their mechanical properties have not been completely clarified, as current clinical results are not conclusive (Cury et al., 2016).

Hence, since resin composite technology rapidly evolves, with new products being released in the market every year, research on the physical and mechanical properties of these materials is of the utmost importance for academics, as well as for clinicians to understand the restorative materials they use. The aim of this study was to evaluate and compare the content and features of filler particles, and also physical and mechanical properties of seven different dental composites available in the market, including conventional, bulk-fill, and bioactive dual-cure materials. The null hypotheses were: (1) the tested dual-cure, bioactive composite would not present statistically different degrees of conversion when self-cured or dual-cured; (2) maximum rate of polymerization (R_p^{\max}) values would not differ among the tested composites; (3) there would be no differences in composition, size, or shape of fillers between the tested composites; (4) after seven days of water storage, the tested materials would not differ regarding water sorption or solubility; (5) the investigated composites would not present any differences in flexural strength or elastic modulus; and (6) these mechanical properties would not be significantly reduced/increased after 12 months of water storage.

2. Materials and methods

2.1. Resin-based composites selected for the study

Seven dental composites were evaluated: four conventional, methacrylate-based composites (Filtek™ Supreme Ultra Universal Restorative, 3M Oral Care, St. Paul, MN, USA - FS; Forma Zirconia Nano-Hybrid Composite, Ultradent do Brasil, Indaiatuba, SP, Brazil - FO; Charisma® Diamond, Kulzer GmbH, Hanau, Germany - CD; and Spectra Smart, Dentsply Sirona, Pirassununga, SP, Brazil - SS); two bulk-fill composites (Filtek™ Bulk Fill Posterior Restorative, 3M Oral Care, St. Paul, MN, USA - FB; and Tetric® N-Ceram Bulk Fill, Ivoclar Vivadent AG, Schaan, Liechtenstein - TB); as well as a chemically-cured, fluoride-releasing composite with optional light-curing (Cention® N, Ivoclar Vivadent AG, Schaan, Liechtenstein), which was tested in the self-cure (only chemical polymerization - group CNSC), and in the dual-cure (chemical + light polymerization - group CNDC) modes. Commercial names, manufacturers, composition, filler content/size, and batch numbers of the tested composites are presented in Table 1.

Table 1

Group acronyms, commercial names, manufacturers, composition, filler content/size, and batch numbers of the tested composites.

Acronym	Commercial name	Manufacturer	Composition	Filler size/content (vol% or wt%)	Batch number
FS	Filtek™ Supreme Ultra Universal Restorative	3M Oral Care	Silane treated ceramic; silane treated silica; UDMA; Bis-EMA; Bis-GMA; silane treated zirconia; PEGDMA; TEGDMA.	20 nm (silica); 4–11 nm (zirconia); 0.6–20 µm (silica-zirconia cluster fillers) (63.3 vol% or 78.5 wt%)	N697117
FO	Forma Zirconia Nano-Hybrid Composite	Ultradent do Brasil	Bis-GMA; Bis-EMA; TEGDMA; BHT; PEGDMA; UDMA; ytterbium trifluoride; fillers based on silane-treated ceramic, silane-treated silica, silane-treated silica-zirconium oxide, and barium glass.	0.7 µm (mean particle size) (67 wt%; vol% not disclosed by manufacturer)	150,416
CD SS	Charisma® Diamond Spectra Smart	Kulzer GmbH Dentsply Sirona	TCD-urethaneacrylate; UDMA; barium aluminum fluoride glass. Glass powder; silica; hydrophobic colloid; dimethacrylate; benzophenone III; EDAB; flublau concentrate; camphorquinone; BHT butylated hydroxytoluene; yellow iron oxide; red iron oxide; black iron oxide; titanium dioxide.	5 nm - 20 µm (64 vol% or 81 wt%)* Information not disclosed by the manufacturer	010054A 2468901
FB	Filtek™ Bulk Fill Posterior Restorative	3M Oral Care	Silane treated ceramic; aromatic UDMA; ytterbium dimethacrylate; UDMA; silane treated silica; DDDMA; silane treated zirconia; water; modified methacrylate monomer; EDMAB; benzotriazol.	100 nm (ytterbium trifluoride); 20 nm (silica); 4–11 nm (zirconia) (58.4 vol% or 76.5 wt%)	N689744
TB	Tetric® N-Ceram Bulk Fill	Ivoclar Vivadent AG	Bis-GMA; UDMA; Bis-EMA; barium glass; prepolymer; ytterbium trifluoride; mixed oxide.	0.04–3 µm (mean particle size: 0.6 µm) (53–55 vol% or 75–77 wt%)	U22999
CNSC (self-cure) CNDC (dual-cure)	Cention® N	Ivoclar Vivadent AG	Liquid: UDMA; DCP; aromatic aliphatic-UDMA; PEG-400 DMA. Powder: barium aluminum silicate glass filler; ytterbium trifluoride; Isofiller (Tetric N-Ceram technology); calcium barium aluminium fluorosilicate glass filler; calcium fluorosilicate (alkaline) glass filler.	0.1–35 µm (57.6 vol% or 78.4 wt%)	W13521

Abbreviations: UDMA (urethane dimethacrylate); Bis-EMA (bisphenol-A ethoxylate dimethacrylate); Bis-GMA (bisphenol-A diglycidyl dimethacrylate); PEGDMA (polyethylene glycol dimethacrylate); TEGDMA (triethylene glycol dimethacrylate); BHT (butylhydroxytoluene); EDAB (ethyl 4-dimethylamine benzoate); DDDMA (1,12-dodecane dimethacrylate); EDMAB (ethyl 4-dimethyl aminobenzoate); DCP (tricyclodecan-dimethanol dimethacrylate); PEG-400 DMA (polyethylene glycol 400 dimethacrylate); aromatic aliphatic-UDMA (tetramethyl-xylylendiurethane dimethacrylate).

* Filler wt% reported by Cao et al. (2013).

2.2. Measurements of degree of conversion (DC) and maximum rate of polymerization (R_p^{\max})

Micro-Raman spectroscopy analysis was chosen to evaluate the DC and the R_p^{\max} of the tested composites. Measurements were undertaken throughout 40 s of light-curing for all composites, except for Cention N, which had a chemical-setting time of 5 min; therefore, measurements were made during 5 min for the self-cure group, and during 5 min and 40 s for the dual-cure group. A multiple-peak light-emitting diode (LED) light-curing unit (Valo, Ultradent Products, Inc., South Jordan, UT, USA) was employed in close contact and parallel to the surface of the samples. The light-curing unit delivered approximately 16.8 J/cm² to the samples during 10 s of exposure, as verified on a previous study of our research group (Sahadi et al., 2018), using an anterior sensor in the MARC patient simulator (MARC-PS, BlueLight Analytics Inc., Halifax, Canada).

The micro-Raman spectrophotometer (Xplora, Horiba JobinYvon, Paris, France) was calibrated by a silicon standard sample supplied by its manufacturer. Then, a HeNe laser with a power of 3.2 mW and a wavelength of 532 nm was used with a spatial resolution of 1.5 µm, and 2.5 cm⁻¹ spectral resolution coupled with 10× magnification lenses (Olympus, London, UK). DC was calculated according to the following formula (Araujo-Neto et al., 2018):

$$DC\% = \left(1 - \frac{R_{\text{cured}}}{R_{\text{uncured}}}\right) \times 100$$

Where R is the ratio between the heights of 1639 cm⁻¹ and 1609 cm⁻¹ peaks of uncured and cured materials. Three readings were undertaken on the top surface of each specimen (Miletic and Santini, 2012). On the other hand, the R_p^{\max} (percent/s) corresponded to the highest rate of polymerization, and it was calculated based on the differences between DC values measured in sequential, 1-s intervals throughout the whole analysis of each specimen (Arrais et al., 2009).

Since a valid comparison between different products is not possible

for DC (Fronza et al., 2015), only data of the Cention N groups were compared among themselves regarding curing modes (self-cure or dual-cure) by an independent samples t-test with a significance level of 95%, which was performed after checking the results passed the Shapiro-Wilk normality test and Levene's test for equality of variances. R_p^{\max} data were analyzed regarding normality by the Shapiro-Wilk test, followed by one-way ANOVA (1- resin composites), and Tukey's test with a 95% confidence interval.

2.3. Filler particles characterization

Approximately 1 g of each unpolymerized composite was successively treated in 6 mL of different organic solvents (centrifuged at 1,000 rpm in 99.5% acetone for 5 min; centrifuged at 1,000 rpm in 99.8% chloroform for 5 min; and immersed in absolute ethanol for 24 h). This procedure was performed in order to remove the organic portion and obtain the inorganic content of the tested composites. Supernatant (mixture of solvent and monomeric portion) was removed, followed by one last solvent bath until supernatant was clear (Aguiar et al., 2012; Ruivo et al., 2019). After ethanol immersion, the remaining content was dried at 37 °C in an incubator for 24 h. A small amount of the obtained smear was placed over metallic stubs and sputter-coated with gold (SDC 050 Sputtercoater, Bal-Tec, Balzers, Liechtenstein) (Di Francescantonio et al., 2016; Fronza et al., 2017) to analyze the size and shape of inorganic fillers by scanning electron microscopy (SEM) at 5,000x and 10,000× magnifications. The remaining smear was placed on plastic stubs and carbon-coated (MED 010 Baltec, Balzers, Liechtenstein) for examination by X-ray dispersive-energy (EDX) microanalysis using a detection system (X-Act; Oxford Instruments, Abingdon, Oxfordshire, UK) coupled to a scanning electron microscope (JEOL, JSM-5600LV, Tokyo, Japan). EDX analysis was performed to identify the chemical elements of the recovered insoluble filler particles. Each spectrum of the EDX analysis was acquired for 100 s with a voltage of 15 kV, 20–25% dead time, and a working distance of 20 mm). Images showing the identified chemical

elements, and their relative concentrations were obtained from five different analyzes of each material at different regions of the samples.

2.4. Water sorption and solubility

Water sorption and solubility tests were performed following specifications from ISO 4049:2009 (Dentistry — Polymer-based filling, restorative and luting materials, International Organization for Standardization). Forty disk-shaped specimens (15.0 ± 0.1 mm of diameter \times 1.0 ± 0.1 mm of thickness, $n = 5$) were prepared from the above-mentioned composites. Specimens were analyzed after 7 days of water immersion. In regard to the Cention N composite, different specimens were prepared for the self-cured group, and for the dual-cured group.

Composites were placed into pre-fabricated silicone molds, and a piece of Mylar strip was placed on the top surface, and pressed gently using a microscope glass slide in order to reduce oxygen inhibition, prevent defects in the body of the material, and create a flat surface (Marghalani, 2012). As a way to standardize the light-curing procedure, all specimens were light-cured using a multiple-peak LED light-curing unit (Valo, Ultradent Products, Inc., South Jordan, UT, USA) for 40 s, with a single exposure at their center, using the same power and distance parameters described in section 2.2.

For the Cention N composite, powder and liquid were handled according to manufacturer's instructions: 2 measuring scoops of powder and 2 drops of liquid (4.6:1 wt ratio) were dispensed on a mixing pad; the liquid was spread out to enlarge the surface, while the powder was divided into two equal parts, and both components were mixed with a plastic spatula for 45–60 s. Then, the resulting composite was placed over the silicone mold, and covered with a Mylar strip until the chemical-setting time was reached (5 min from the start of mixing, according to manufacturer). No further procedures were performed for the chemical-curing group (CNSC). However, for the chemical and light-curing group (CNDC), specimens were light-cured as described above right after their setting time.

Afterwards, specimens were carefully removed from their molds, and stored in a light-proof container at 37°C for 1 h. Then, excess material was removed by holding the periphery of the specimens against a non-rotating table using a 1,000-grit silicon carbide paper, as advised by ISO 4049:2009. The volume (V in cm^3) of each specimen was calculated according to their dimensions measured by a digital caliper (Mitutoyo Sul Americana Ltda., Suzano, SP, Brazil). Specimens were placed in a desiccator at $37 \pm 2^\circ\text{C}$ and weighed every 24 h using an analytical balance (JK-180, Chiyo Balance Corp., Tokyo, Japan) with an accuracy of 0.1 mg until a constant mass (m_1) was reached (i.e., until each specimen did not lose more than 0.1 mg of mass within a period of 24 h).

Specimens were individually stored in deionized water for 7 days, according to their group. Following water immersion, the disk-shaped specimens were washed with deionized water, blot-dried with absorbent paper, and weighed again (m_2). Then, specimens were placed in a desiccator, and their mass was recorded every 24 h until it was constant (m_3), as described before. The values of water sorption (WS) and solubility (SL) were calculated (in $\mu\text{g}/\text{mm}^3$) using the following equations:

$$WS = \frac{m_2 - m_3}{V}$$

$$SL = \frac{m_1 - m_3}{V}$$

Where " m_1 " is the constant mass of the specimens (in μg) prior to immersion in water; " m_2 " is the mass (in μg) after immersion in water for 24 h or 7 days; " m_3 " is the constant mass of the specimens (in μg) after being reconditioned in the desiccator; and " V " is the volume of each specimen (in mm^3). Nonparametric data regarding WS and SL were statistically analyzed by a Kruskal-Wallis one-way ANOVA, followed by Dunn's pairwise test with a 95% confidence level.

2.5. Three-point bending test

One hundred and sixty bar-shaped composite specimens ($n = 10$) were made for the three-point bending test in order to measure their flexural strength and elastic modulus. Specimens were produced according to ISO 4049:2009 (Dentistry — Polymer-based filling, restorative and luting materials, International Organization for Standardization), which recommends the use of a mold 25 mm long, 2 mm wide, and 2 mm high. Resin composites were placed into polytetrafluoroethylene molds and covered with Mylar strips and glass slides from both sides, top and bottom. All specimens were light-cured following the same procedures described above for the water sorption and solubility tests. However, due to the length of the specimens, light-curing was performed in three non-overlapping irradiation cycles, since the tip of the light-curing unit was about 10 mm wide. Handling and curing of the Cention N composite was also performed as above-mentioned. Once again, the LED light-curing unit Valo (Ultradent Products, Inc., South Jordan, UT, USA) was employed using the same parameters (power and distance) as in section 2.2. Then, specimens were lightly polished using a 1,000-grit SiC paper and stored in deionized water at 37°C for 24 h or 12 months prior to testing. Afterwards, specimens were blot-dried and submitted to flexural stress in a universal testing machine (4411, Instron Co., Norwood, MA, USA), with a load cell of 100 g, at a speed of 0.5 mm/min, until fracture. The resulting data was analyzed regarding normality by the Kolmogorov-Smirnov test, followed by Levene's test for equality of variances. Since the flexural strength results did not pass Levene's test, they were transformed as a function of \log_{10} . Afterwards, data was submitted to two-way ANOVA (1- resin composites; 2- time of evaluation), and Tukey's test with a 95% confidence level.

3. Results

3.1. Filler particles characterization

Fig. 1 shows the composition and morphology of filler particles according to the tested composites. FS presented spherically-shaped fillers organized in clusters of varied dimensions, which were composed mainly of silicon and zirconium. The chemical elements barium, aluminum, ytterbium, and silicon were found in the composition of Forma's filler particles, which were irregularly-shaped, ranging from 500 nm to 2 μm . EDX analysis showed fillers in CD were made of aluminum, silicon, and barium, with an irregular shape, and varied dimensions (300 nm - 3 μm). The inorganic composition of SS included barium, aluminum, and silicon. This material consisted mainly of irregularly-shaped fillers ranging from 500 nm to 5 μm . Conversely, FB contained rhomboid-shaped fillers (100 nm - 5 μm) made of silicon and zirconium, with traces of other elements, as iron, copper, silver, potassium, calcium, and chromium. The bulk-fill composite TB revealed the presence of ytterbium, aluminum, silicon, and barium in the composition of its fillers, with minor amounts of barium and copper. Fillers of this composite ranged from 300 nm to 3 μm with an irregular shape. Cention N's filler particles composition was found to include several chemical elements, but mainly ytterbium, silicon, calcium, and barium. These particles were also irregularly-shaped, and presented large dimensions, ranging from 1 μm to 4 μm .

3.2. DC%, Rp^{max} , water sorption and solubility

DC, Rp^{max} , as well as water sorption and solubility results are summarized in Table 2. All composites presented a final DC above 80%, except for Cention N in the self-cure mode (78.5%). When both Cention N groups were compared (self-cure vs dual-cure), the group in which the composite was not light-cured resulted in a lower DC than the group that received additional light-curing ($p = 0.003$). Moreover, CNSC had the lowest numeric Rp^{max} mean, although it did not differ from FS and SS (p

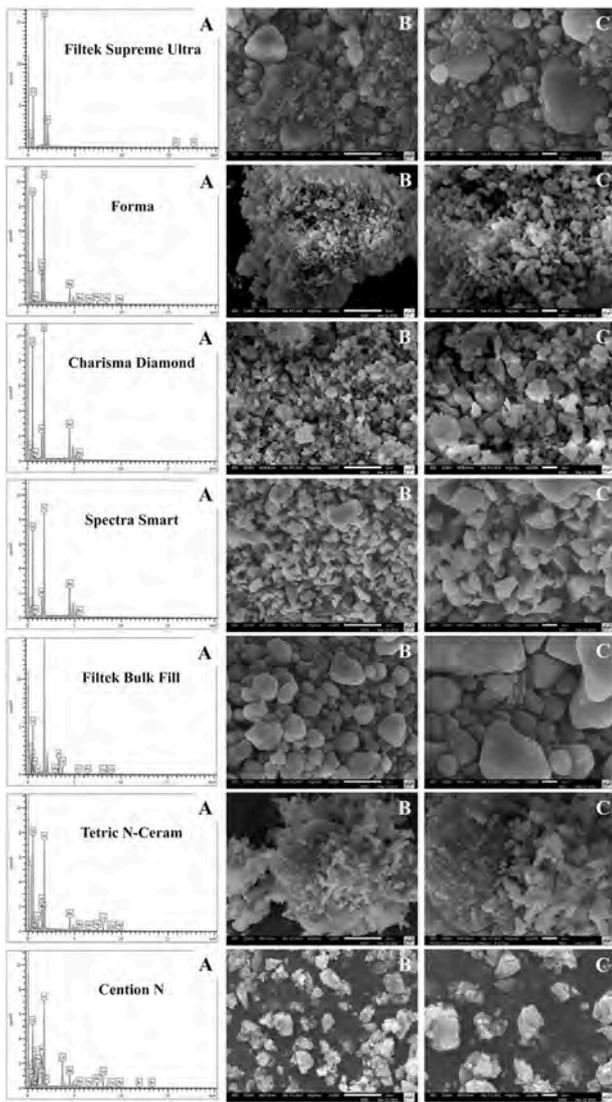


Fig. 1. X-ray dispersive energy charts showing the elemental composition of filler particles (A), and scanning electron micrographs of filler particles at 5,000x (B) and 10,000× (C) magnifications for each of the tested composites.

> 0.05). CD resulted in a higher Rp^{max} compared to FS ($p = 0.002$), SS ($p = 0.039$), and CNSC ($p < 0.001$). Also, the Rp^{max} of CNDC was significantly higher than that of CNSC ($p = 0.007$).

According to the Kruskal-Wallis one-way ANOVA, there was strong evidence of a difference between the mean ranks of at least one pair of groups for both water sorption ($p < 0.001$) and solubility ($p = 0.001$). Regarding water sorption results, FS presented a higher median compared to CD ($p = 0.008$, adjusted using the Bonferroni correction) and CNSC ($p = 0.048$, adjusted using the Bonferroni correction), while no statistically significant differences were found among the remaining groups ($p > 0.05$, adjusted using the Bonferroni correction). As for water solubility, SS led to a lower median compared to both Cention N groups, CNSC ($p = 0.09$, adjusted using the Bonferroni correction) and CNDC ($p = 0.05$, adjusted using the Bonferroni correction). Also, CNDC presented higher solubility than TB ($p = 0.043$, adjusted using the Bonferroni correction), and SS ($p = 0.005$, adjusted using the Bonferroni correction). No statistical differences were found among the other composites ($p > 0.05$, adjusted using the Bonferroni correction).

3.3. Flexural strength and elastic modulus

Results of the three-point bending test at 24 h and 12 months are

Table 2

Mean (\pm standard deviation) degree of conversion (%) and maximum rate of polymerization (%/s), and medians (minimum value; maximum value) of water sorption and solubility ($\mu\text{g}/\text{mm}^3$) for the tested composites.

Group	DC	Rp^{max}	Sorption	Solubility
FS	92.8 (± 0.7)	2.3 (± 0.3)	25.0 (23.5; 27.5) A	7.6 (1.6; 11.8)
FO	89.5 (± 2.0)	4.6 (± 1.3)	19.3 (17.8; 27.7)	4.6 (0.6; 6.6) ABC
CD	91.1 (± 1.0)	8.2 (± 2.4) A	12.4 (9.2; 14.8) B	5.4 (2.9; 7.2) ABC
SS	85.3 (± 0.6)	4.0 (± 0.2)	11.8 (10.7; 29.7)	1.6 (0.6; 1.7) C
FB	88.3 (± 1.5)	4.8 (± 2.1)	22.0 (18.8; 23.7)	4.1 (1.6; 6.5) ABC
TB	83.4 (± 1.2)	5.4 (± 1.9)	18.9 (17.6; 34.6)	2.7 (0.0; 6.0) AC
CNSC	78.5 (± 0.6)	0.6 (± 0.3) C	12.9 (11.9; 14.9) B	10.6 (7.8; 11.6)
CNDC	87.3 (± 2.3)	5.8 (± 0.6)	13.0 (11.3; 16.0)	9.8 (8.6; 11.7) B

Uppercase letters compare different composites/groups for the same property (DC, Rp^{max} , water sorption, or water solubility). Means or medians followed by the same letters did not present statistically significant differences among them ($p > 0.05$).

presented in Table 3. The flexural strength of CD and FB was not reduced significantly after 12 months of storage ($p > 0.05$), while FS, CD, and CNDC did not show a decrease in elastic modulus when tested at 12 months ($p > 0.05$).

At 24 h, CNSC had the lowest flexural strength compared to the other groups ($p \leq 0.05$), TB and CNDC led to intermediate values that were statistically similar ($p = 0.387$), while the remaining composites (FS, FO, CD, SS, and FB) showed the highest means and did not differ among them ($p > 0.05$). At 12 months, the highest flexural strength values were obtained with CD and FB, which did not differ statistically ($p = 0.182$); SS showed a lower mean compared to CD ($p = 0.043$), did not differ from FB ($p = 0.483$), but its results were higher than all the other composites ($p \leq 0.05$). FO did not differ from TB ($p = 0.709$), which showed no statistically significant difference compared to FS ($p = 0.103$). CNDC was statistically similar to FS ($p = 0.421$), while CNSC presented the lowest flexural strength outcome ($p \leq 0.05$).

In regard to the elastic modulus results at 24 h, FS, CD, and FB showed the highest values with no statistical difference ($p > 0.05$).

Table 3

Mean (\pm standard deviation) flexural strength (in MPa) and elastic modulus (in GPa) of the tested composites according to time of evaluation (24 h or 12 months).

Groups	Flexural Strength		Elastic Modulus	
	24 h	12 months	24 h	12 months
FS	133.8 (± 14.5)	77.6 (± 16.4)	9.60 (± 0.97)	9.38 (± 0.90)
FO	126.8 (± 11.9)	92.2 (± 22.5) Bc	8.04 (± 0.84)	6.94 (± 1.32)
CD	147.4 (± 30.1)	128.3 (± 24.5)	9.92 (± 1.87)	9.38 (± 1.11)
SS	137.8 (± 20.4)	107.5 (± 15.3)	8.13 (± 0.91)	9.82 (± 1.35)
FB	133.3 (± 26.0)	115.5 (± 25.1)	8.86 (± 1.90)	10.61 (± 0.89)
TB	103.7 (± 17.3)	88.5 (± 17.2)	8.04 (± 0.72)	6.78 (± 1.59)
CNSC	82.1 (± 12.7)	53.9 (± 5.5) Bf	7.11 (± 1.08)	5.29 (± 1.12)
CNDC	96.4 (± 15.9)	71.9 (± 12.4) Be	8.12 (± 0.95)	8.23 (± 1.54)

Means followed by the same letter did not present a statistically significant difference between them ($p > 0.005$). Uppercase letters compare the same composite at different times of evaluation (rows), while lowercase letters compare different composites within the same time of evaluation (columns).

Moreover, FB did not differ from FO ($p = 0.141$), SS ($p = 0.193$), TB ($p = 0.143$), and CNDC ($p = 0.184$), while the latter three composites were also statistically similar to CNSC ($p > 0.05$). On the other hand, when elastic modulus was evaluated at 12 months, FB presented the highest mean, although it did not differ from SS ($p = 0.158$), which was also similar to the intermediate results obtained by FS ($p = 0.430$) and CD ($p = 0.421$). CNDC had higher elastic modulus compared to FO ($p = 0.021$), TB ($p = 0.010$), and CNSC ($p < 0.001$), while CNSC presented the lowest elastic modulus among all groups ($p \leq 0.05$).

4. Discussion

Properties, expected behavior, and biocompatibility of polymer-based restorative materials are largely determined by their degree of conversion (Ferracane et al., 2017). Although a minimum DC% for a clinically acceptable composite restoration has not been accurately established yet, previous literature suggests composites placed in load-bearing areas require a DC% of at least 55% (Ferracane et al., 1997; Silikas et al., 2000). According to the parameter used in this study to calculate degree of conversion, all composites tested reached values between 78.5% and 92.8%.

Statistical comparison for DC% was not performed among the evaluated composites, except between the two groups of Cention N, which differed regarding polymerization modes (self or light-cured) but had the exact same material. When testing distinct, commercially available resin-based composites, these materials usually present completely different monomer blends, photoinitiator systems, filler particles, and inhibitors, i.e. there are several uncontrolled variables involved in study design. Thus, direct comparisons among such different materials would not be fair, as due to their composition, their maximum DC% would probably be different, even if tested under the same conditions. Moreover, a DC% between 70-80% might be considered adequate for a certain material, while another could reach over 90%, but that would not necessarily mean the latter performs better than the first one.

This limitation underlines the biggest benefit of testing and comparing composite model or experimental formulations instead of commercially available materials, which is the possibility of precisely individualizing study variables and obtaining reliable and accurate results about specific modifications made to dental composites. Previously published papers reported data on experimental resin-based composition, comparing materials with the same monomer blend and photoinitiator system, but different filler particle content (Arai et al., 2020; Guimaraes et al., 2020). The same rationale can be observed in other studies, varying only monomer type (Czech et al., 2020; dos Santos et al., 2018; Fugolin et al., 2020) or photoinitiator system (Bertolo et al., 2017; Brandt et al., 2013). Although this approach might be desirable from a study design point of view, usually it includes experimental composites that are not yet available for clinical use, which limits the immediate applicability of scientific data to help practitioners make sense of some properties and features of new materials constantly released in the market.

In the present study, Cention N exhibited higher DC% and Rp^{\max} when light-cured compared to the self-cured group. Therefore, the null hypothesis that the DC of Cention N would not be influenced by polymerization mode (self- or dual-curing) was rejected. These results are in accordance with a previous publication (Ilie, 2018) that showed additional light-curing had a significant influence on degree of conversion and polymerization kinetics of Cention N. Although light-curing helps initiate polymerization faster, which can shorten the restorative procedure, its effect on the final degree of conversion might be considered low, as both curing methods did not differ past 11 min of setting (Ilie, 2018). However, self-curing might be preferred from a bioactivity point of view, since light-cured Cention N led to significantly lower fluoride release due to the formation of a tightly bound and less hydrophilic matrix (Gupta et al., 2019).

The Rp^{\max} corresponds to the highest rate of polymerization at 1-s

intervals based on the difference between degree of conversion values measured throughout the time of analysis of each composite (Denis et al., 2012). In other words, the Rp^{\max} is a point in the polymerization reaction in which the highest reaction rate is achieved, followed by an abrupt decrease (Denis, 2012). This property allows researchers to imply the speed of the polymerization process reaction and compare it among materials (Arrais et al., 2009). Slower monomer conversion, as observed for chemical curing, might delay the gel phase and allow a higher flow of resin from the unbounded surface, reducing shrinkage (Wang et al., 2019) due to the easier rearrangement of molecules that can dissipate some of the contraction-induced stress (Braga et al., 2002).

According to Table 2, the composites Charisma Diamond, Tetric N-Ceram Bulk Fill, and Cention N (light-cured) led to the highest numerical Rp^{\max} , although not statistically different from Forma and Filtek Bulk Fill. These results might be due to the presence of alternative photoinitiator systems in the formulation of most of the tested composites with high Rp^{\max} values. Charisma Diamond contains, besides camphorquinone (CQ), phenyl-propanedione (PPD) and diphenyl (2, 4, 6-trimethylbenzoyl)-phosphine oxide (TPO) as photoinitiators. Tetric N-Ceram Bulk Fill has a photoinitiator system based on a mixture of CQ, TPO, and bis-(4-methoxybenzoyl)diethylgermane (Ivocerin), while Cention-N, a product from the same manufacturer, can polymerize through two different photoinitiator systems: a chemically-curable one, comprising copper salt, peroxide, and thiocarbamide, and a light-curable one, composed of phenylbis (2, 4, 6-trimethylbenzoyl)-phosphine oxide (BAPO) and Ivocerin.

Interestingly, PPD has been shown to react slower than CQ when LED light-curing units were used to polymerize an experimental composite (Brandt et al., 2011), which might be explained by its lower absorbed power density and lower interaction with co-initiator compared to CQ (Schneider et al., 2008). On the other hand, TPO presents two-fold faster reactivity than CQ, accelerating the conversion kinetics of polymers (Vaidyanathan et al., 2017), as it can generate two free radicals per molecule compared to a single one produced by CQ (Neumann et al., 2005). The manufacturer of Ivocerin claims it presents high quantum efficiency and high absorption capacity (Hirt et al., 2013), which could fasten the polymerization process. In fact, a recent publication found that Ivocerin promoted higher Rp^{\max} compared to CQ when incorporated into methacrylate- or methacrylamide-based monomer systems due to its higher quantum yields of conversion (Barcelos et al., 2020). Also, the addition of 1 mol% BAPO to a model resin composite resulted in a significant increase of reactivity, with higher Rp^{\max} and a less abrupt deceleration phase during polymerization, which was probably due to the fact that the α -cleavage process BAPO undergoes during exposure to light may occur twice, rendering this photoinitiator capable of producing up to four free radicals per molecule (Meereis et al., 2014).

Some photoinitiators can be classified as Norrish type I, which means they have low-energy bonds that can be cleaved upon light exposure to generate free radicals (Pratap et al., 2019). All the aforementioned photoinitiators, except for CQ, belong to the Norrish type I class, and present light-absorbance peaks (λ_{\max}) near ultra-violet with some overlap into visible light (PPD - $\lambda_{\max} = 398$ nm; TPO - $\lambda_{\max} = 385$ nm; Ivocerin - $\lambda_{\max} = 408$ nm; and BAPO - $\lambda_{\max} = 371$ nm) (Hirt et al., 2013; Meereis et al., 2014; Oliveira et al., 2016; Vaidyanathan et al., 2017). Therefore, the tested composites with Norrish type I photoinitiators might have benefited from the multiple-peak light-curing unit used in the present study, which is capable of delivering light within the range of 385–515 nm, with peaks at 400, 450, and 460 nm (Andre et al., 2018), leading to higher Rp^{\max} values.

Three of the tested composites (Filtek Supreme, Spectra Smart, and Cention N in self-cure mode) presented lower Rp^{\max} compared to the remaining products, which leads to the rejection of the null hypothesis that states Rp^{\max} values would not differ among composites. The remarkable variation in filler particle size and monomer blends among the tested composites must be considered when analyzing parameters related to polymerization. Although at first look most of the tested

materials seem to present overlapping filler particle size ranges (Fig. 1), an evaluation of 17 commercially-available composites showed their fraction of fillers smaller than 500 nm was lower than 20 wt% of the total filler content, even for those products marketed as “nanohybrids” (Randolph et al., 2016), and the distribution of the largest micron-sized fillers could also be identified as “monomodal” (particles limited between 1-2 μm) or “bimodal” (much larger particles up to 30 μm) (Randolph et al., 2016).

A previous publication demonstrated that smaller filler particles (hence larger surface area) and higher filler loading led to increased composite viscosity, which caused the polymerization rates to be slowed down (Habib et al., 2018). The viscosity of a composite can affect its polymerization kinetics by reducing the mobility of the polymer chains, decreasing the termination rate, and increasing the rate of polymerization (Odian, 2004). Literature also suggests the type of base monomer included in the composite formulation can affect its rate of polymerization due to structural characteristics that render the material more flexible or reactive, while also influencing its overall viscosity (Fonseca et al., 2017; Froes-Salgado et al., 2015).

Furthermore, the reaction process leading to the formation of a polymer is dependent on light reflection, scattering, and absorption, which are phenomena highly influenced by the composition of the resin-based material (Fronza et al., 2017). Fujita et al. (2011) found that increasing the particle size of silica filler from 0.05 to 2.0 μm resulted in a drastic decrease of the maximum transmittance (visible light passing through the composite sample) from 68.6% to 9.7% (Fujita et al., 2011). Therefore, even if some of the tested materials present similar monomer composition (Forma and Filtek Supreme) or filler particle content (Forma and Spectra Smart or Filtek Bulk Fill and Filtek Supreme), a difference regarding polymerization kinetics could still be expected (Satterthwaite et al., 2009; Turssi et al., 2005), given the many factors influencing the polymerization reaction process. Considering SEM micrographs showed in Fig. 1 and the influence filler particles can have in the properties of composites, the null hypothesis that the tested composites would not present differences in composition, size, or shape of fillers was rejected.

Sorption and solubility of the tested materials were also evaluated, which is important for light-curable polymeric composites, considering they can absorb water and release unreacted monomers when exposed to an aqueous environment as the oral cavity (Sideridou et al., 2003). The water uptake by resin-based composites might result in chemical degradation, causing a hydrolytic breakdown of the filler-matrix interface (Szczesio-Wlodarczyk et al., 2020), accompanied by softening and plasticization of the polymer network (Ferracane, 2006; Froes-Salgado et al., 2015), with a consequent decrease of its mechanical properties (Ito et al., 2005; Soderholm et al., 1984). In regard to water sorption, all the tested materials presented statistically similar values, except for Charisma Diamond and Cention N (self-cured), which presented lower sorption medians compared to Filtek Supreme, even though Cention N (self-cured) did not differ from its dual-cured counterpart (Table 2).

Although both phases of resin-based composites, organic and inorganic, can influence their water diffusion characteristics, the contribution of the polymeric organic matrix is remarkably predominant (Goncalves et al., 2008). Many factors are well known to affect the sorption-desorption process of dimethacrylates, namely the hydrophilicity of the polymer, the difference in solubility parameter between polymer and solvent, as well as the crosslinking density and porosity of the polymer network (Sideridou et al., 2007). Also, the specific monomer selected for a composite strongly influences its uptake of liquids, swelling, and overall stability (Sideridou et al., 2007), since the monomer chemical structure is a key-factor to determine polymer chain elasticity and hydrophilicity (Barszczewska-Rybarek, 2019).

Compared to Charisma Diamond and Cention N, Filtek Supreme is composed of a monomer blend containing Bis-GMA and TEGDMA, which are not present in the other two products. This might explain the higher water uptake by Filtek Supreme, since Bis-GMA and TEGDMA

provide polar groups in their molecules ($-\text{OH}-$ and $-\text{O}-$, respectively), which makes the resulting polymer matrix more hydrophilic (Goncalves et al., 2008). Bis-GMA and TEGDMA can be considered relatively hydrophilic monomers (Imazato et al., 1999; Sideridou et al., 2003) that might exacerbate water sorption, leading to long-term degradation (Ruivo et al., 2019). Moreover, Charisma Diamond is based on tricyclodecane-urethane acrylate (TCD-urethane), while Cention N is composed of tetramethyl-xylylenediurethane dimethacrylate (aromatic aliphatic-UDMA), and both monomers might have influenced the results.

TCD-urethane is a high-molecular weight, low-viscosity monomer prepared through the reaction between hydroxyalkyl (meth)acrylic acid esters and diisocyanates, with a subsequent reaction involving polyols (Ilie and Hickel, 2011). Due to its low viscosity, TCD-urethane does not require the addition of diluent monomers in the composite, which coupled with its hydrophobic nature, might contribute to a reduction in water sorption (Durner et al., 2012). Although our results corroborate with this hypothesis, also supported by manufacturers claims, no differences regarding the aging and storage behavior of Venus Diamond (commercial name of Charisma Diamond in American and European markets) compared to other composites based on alternative methacrylates have been reported in literature (Schmidt and Ilie, 2012).

On the other hand, aromatic aliphatic-UDMA can be synthesized by adding hydroxyl group-containing methacrylates to α , α , α' , α' -tetramethyl-m-xylylene diisocyanate (TMXDI) (Moszner et al., 2008), which would combine the favorable properties of aliphatic (low tendency to discolor) and aromatic (stiffness) diisocyanates, according to the manufacturer of Cention N. A reduction of 25–40% in water sorption was reported in a previous study when pendant phenyl methoxy or ethyl substituents were added to the structure of UDMA (Kerby et al., 2009). This result was attributed to an increase in the dipole moment and dielectric constant of the modified monomers, accompanied by their hydrophobic nature, and also due to the bulky characteristic of the phenyl methoxy substituents (Kerby et al., 2009). Therefore, a similar effect might have played a role in the lower water uptake observed for Cention N compared to Filtek Supreme. However, literature on this dual-cured, fluoride-releasing restorative material is still lacking, and a direct comparison between Ivoclar's aromatic aliphatic-UDMA technology with the monomers of the aforementioned study (Kerby et al., 2009) would not be adequate, since the modifications carried out in the urethane dimethacrylate molecule are not fully disclosed and clearly explained by the manufacturer.

The water uptake and swelling of polymers is just the first stage of their dissolution process, followed by the disintegration of the polymeric matrix into true solutions (Ravve, 2012). Therefore, water sorption is closely related to solubility, which can be defined as the separation of the molecules of a solid from each other, leaving spaces that will be occupied by solvent molecules (Morrison and Boyd, 2002). Considering the degree of conversion of most dental composites remains well below 100% at room temperature (Ferracane et al., 2017), unreacted substances such as monomers, co-monomers, initiators, stabilizers, decomposition products, or contaminants can be released in the oral cavity (Van Landuyt et al., 2011) as a consequence of solubility. The elution of these unreacted compounds raises concerns regarding the biocompatibility of dental composites, due to *in vitro* cytotoxic, teratogenic, estrogenic, and/or genotoxic effects that have been reported in literature (Bakopoulou et al., 2009; Jun et al., 2020; Libonati et al., 2011; Schwengberg et al., 2005; Yang et al., 2018). Furthermore, hydrolytic degradation of filler-matrix bonds and leaching of filler particles have been suggested to influence the mechanical properties of resin composites (Berger et al., 2009; Drummond et al., 2004; Sideridou et al., 2003).

Cention N (light-cured) showed higher solubility than Tetric N-Ceram Bulk Fill and Spectra Smart, and it showed higher solubility than Spectra Smart when used in the self-cure mode (CNSC). However, additional light-curing did not lead to lower solubility for Cention N

when compared to the self-cure group. This material is mainly composed of low-viscosity monomers with a dual-cure photoinitiator system, and it is likely to result in a more porous composite compared to conventional products delivered as a paste in a syringe, which is due to its need for hand-mixing. Therefore, Cention N seems to be remarkably similar to resin-based luting agents, known to present higher solubility compared to high-viscosity resin-based composites (Bortolotto et al., 2013).

In addition, approximately 24.6 wt% of Cention N corresponds to alkaline filler particles, which are supposed to be released under water immersion, as part of its proposed remineralizing effect characterized by the release of fluoride, hydroxide, and calcium ions (according to the manufacturer) (Todd, 2016). A higher solubility can be expected from fluoride-releasing restorative materials, since they require a certain amount of water diffusion in order to be effective (McCabe and Rusby, 2004). Also, the release of fluoride ions from these materials through dissolution of their fillers has been suggested to create vacancies on their surface, which could contribute to a decrease in microhardness (Park et al., 2007). Therefore, such aspects might have influenced the mass measurements of Cention N, leading to a higher solubility compared to other tested composites. Nevertheless, since the tested materials differed regarding sorption and solubility after seven days, this null hypothesis was rejected.

The mechanical test performed in this study was useful for the evaluation of two parameters of the tested composites: flexural strength, and elastic modulus. Elastic modulus describes the relative stiffness of a material, while flexural strength is the maximum stress needed to fracture a specimen subjected to flexural loading (Anusavice et al., 2012). At 24 h, both Ivoclar's composites, Tetric N-Ceram Bulk Fill and Cention N, showed lower flexural strength than the remaining materials ($p \leq 0.05$). The 24-h elastic modulus of these composites was also lower than the values found for Filtek Supreme, Charisma Diamond, and Filtek Bulk Fill ($p \leq 0.05$). Thus, the null hypothesis that expected no differences in flexural strength or elastic modulus among the investigated composites was rejected. A reasonably large amount of the filler particles inside Ivoclar's products is composed of so-called "isofillers", i.e. pre-polymerized filler particles containing dimethacrylates (17 wt% for Tetric N-Ceram Bulk Fill, and 15–25 wt% for Cention N), which is part of the stress-relieving approach taken by the manufacturer. However, the introduction of this type of particles as inorganic fillers may render the material less resistant due to a lower percentage of glass or ceramic-based fillers (Benalcázar Jalkh et al., 2019; Randolph et al., 2016), as also supported by the present results.

Another interesting finding regarding the mechanical performance of Cention N is that the dual-cured group showed higher flexural strength than the self-cured group at both evaluation times (24 h or 12 months, Table 3). For the elastic modulus, on the other hand, a benefit from the additional light-curing step was observed only after storage for 12 months, since at 24 h there was no statistically significant difference between the two Cention N groups (Table 3). Even though the dual-cured group showed higher degree of conversion compared to the self-cured group (Table 2), previous studies have failed to find a clear correlation between DC% and mechanical properties (da Silva et al., 2008; Leprince et al., 2014).

However, the Cention N self-cured group had a lower R_p^{\max} value than the dual-cured group. A low initial cure rate has been suggested to activate a minor portion of photoinitiator, leading to the formation of fewer growth centers, which results in a predominantly linear polymer chain (Asmussen and Peutzfeldt, 2004). Therefore, when light-cured, Cention N might have resulted in a polymer with higher cross-link density that was, consequently, more resistant to flexural tensions. As for the statistically similar elastic modulus for both polymerization modes at 24 h, this parameter is a constant value that describes the relative stiffness of a material, and thus it is not affected by plastic or elastic deformations the material might be subjected to, as it is not a measurement of resistance (Anusavice et al., 2012).

After twelve months of storage in deionized water, the composite

Charisma Diamond was the most mechanically stable among the tested materials, as there was no significant reduction of its flexural strength or elastic modulus (Table 3). This low susceptibility of Charisma Diamond to water-induced deleterious effects might be explained by its lower water sorption (Table 2), due to monomer composition (Durner et al., 2012), and high filler content of approximately 81 wt% (Randolph et al., 2016). Interestingly, two of the tested composites, Spectra Smart and Filtek Bulk Fill, showed a significant increase of their elastic modulus after storage in water. However, this did not translate into stable long-term flexural strength for Spectra Smart, which still presented a decrease in its mechanical resistance (Table 3). We hypothesize these composites might have resulted in densely-packed, highly cross-linked polymer chains, given their high flexural strength results, which could have influenced the effects of swelling and plasticization caused by water sorption (Sideridou et al., 2003). Therefore, hydrogen-bonded water molecules that were accommodated within the polymer structure might have formed clusters and acted as filler particles rather than plasticizers (Patil et al., 2000; Ping et al., 2001).

Conversely, the composites Forma, Tetric N-Ceram Bulk Fill, and Cention N (self-cured) resulted in significantly lower mechanical properties after water storage (Table 3). Dental polymers go through swelling (volumetric expansion) and plasticization (reduction of surface and bulk mechanical properties) when immersed in water, which may occur more intensely depending on their chemical characteristics (Ferracane, 2006). Additionally, as previously mentioned, the loss of filler particles from the composite (Abuna et al., 2016; Berger et al., 2009), as well as the leaching of unreacted monomers, additives, and filler components caused by solubility (Van Landuyt et al., 2011), might also contribute to increase even further composite hydrolytic degradation. Hence, all these factors played a role in the unreliable mechanical properties of the aforementioned materials when they were exposed to water for a long period of time. Therefore, the final null hypothesis that the mechanical properties of composites would not be significantly changed after 12 months of storage was rejected.

5. Conclusions

Considering the results obtained in the present study, the following conclusion can be drawn:

- 1 Monomer composition and characteristics of filler particles greatly influenced the physico-mechanical properties of the tested composites.
- 2 Additional light-curing improved the degree of conversion, flexural strength, and resistance to water degradation of Cention N compared to its self-cure mode.
- 3 The presence of alternative photoinitiator systems more reactive than camphorquinone led to higher maximum rates of polymerization for Charisma Diamond, Tetric N-Ceram Bulk Fill, and Cention N (light-cured). Also, the size of the filler particles contained in the tested composites influenced their rates of polymerization.
- 4 Sorption and solubility phenomena were greatly affected by monomer compositional variability.
- 5 The materials containing pre-polymerized filler particles showed lower mechanical properties compared to the other composites.
- 6 Charisma Diamond was the most hydrolytically stable among the tested materials, while the mechanical properties of Forma, Tetric N-Ceram Bulk Fill, and Cention N (self-cured) were reduced after 12 months of water storage.

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CRedit authorship contribution statement

Vitaliano Gomes de Araújo-Neto: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - review & editing. **Maicon Sebald:** Conceptualization, Data curation, Formal analysis, Investigation, roles, Writing - original draft, Writing - review & editing. **Eduardo Fernandes de Castro:** Conceptualization, Data curation, Investigation, Methodology, Writing - review & editing. **Victor Pinheiro Feitosa:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing - review & editing. **Marcelo Giannini:** Conceptualization, Data curation, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Abuna, G., Feitosa, V.P., Correr, A.B., Cama, G., Giannini, M., Sinhoreti, M.A., Pashley, D. H., Sauro, S., 2016. Bonding performance of experimental bioactive/biomimetic self-etch adhesives doped with calcium-phosphate fillers and biomimetic analogs of phosphoproteins. *J. Dent.* 52, 79–86. <https://doi.org/10.1016/j.jdent.2016.07.016>.
- Aguiar, T.R., Di Francescantonio, M., Bedran-Russo, A.K., Giannini, M., 2012. Inorganic composition and filler particles morphology of conventional and self-adhesive resin cements by SEM/EDX. *Microsc. Res. Tech.* 75, 1348–1352. <https://doi.org/10.1002/jemt.22073>.
- Andre, C.B., Nima, G., Sebald, M., Giannini, M., Price, R.B., 2018. Stability of the light output, oral cavity tip accessibility in posterior region and emission spectrum of light-curing units. *Operat. Dent.* 43, 398–407. <https://doi.org/10.2341/17-033-L>.
- Anusavice, K.J., Shen, C., Rawls, H.R., 2012. *Phillips' Science of Dental Materials*, 12th ed. Saunders, St. Louis.
- Arai, Y., Kurokawa, H., Takamizawa, T., Tsujimoto, A., Saegusa, M., Yokoyama, M., Miyazaki, M., 2020. Evaluation of structural coloration of experimental flowable resin composites. *J. Esthetic Restor. Dent.*, e12674 <https://doi.org/10.1111/jerd.12674>.
- Araujo-Neto, V.G., Nobre, C.F.A., De Paula, D.M., Souza, L.C., Silva, J.C., Moreira, M.M., Picanco, P.R.B., Feitosa, V.P., 2018. Glycerol-dimethacrylate as alternative hydrophilic monomer for HEMA replacement in simplified adhesives. *J. Mech. Behav. Biomed. Mater.* 82, 95–101. <https://doi.org/10.1016/j.jmbmm.2018.03.022>.
- Arrais, C.A., Giannini, M., Rueggeberg, F.A., 2009. Kinetic analysis of monomer conversion in auto- and dual-polymerizing modes of commercial resin luting cements. *J. Prosthet. Dent.* 101, 128–136. [https://doi.org/10.1016/S0022-3913\(09\)60008-1](https://doi.org/10.1016/S0022-3913(09)60008-1).
- Asmussen, E., Peutzfeldt, A., 2004. Flexural strength and modulus of a step-cured resin composite. *Acta Odontol. Scand.* 62, 87–90. <https://doi.org/10.1080/00016350310008823>.
- Atria, P.J., Sampaio, C.S., Caceres, E., Fernandez, J., Reis, A.F., Giannini, M., Coelho, P. G., Hirata, R., 2018. Micro-computed tomography evaluation of volumetric polymerization shrinkage and degree of conversion of composites cured by various light power outputs. *Dent. Mater. J.* 37, 33–39. <https://doi.org/10.4012/dmj.2016-430>.
- Bakopoulou, A., Papadopoulos, T., Garefis, P., 2009. Molecular toxicology of substances released from resin-based dental restorative materials. *Int. J. Mol. Sci.* 10, 3861–3899. <https://doi.org/10.3390/ijms10093861>.
- Barcelos, L.M., Borges, M.G., Soares, C.J., Menezes, M.S., Huynh, V., Logan, M.G., Fugolin, A.P.P., Pfeifer, C.S., 2020. Effect of the photoinitiator system on the polymerization of secondary methacrylamides of systematically varied structure for dental adhesive applications. *Dent. Mater.* 36, 468–477. <https://doi.org/10.1016/j.dental.2020.01.020>.
- Barszczewska-Rybarek, I.M., 2019. A guide through the dental dimethacrylate polymer network structural characterization and interpretation of physico-mechanical properties. *Materials* 12, 4057. <https://doi.org/10.3390/ma12244057>.
- Benalcázar Jalkh, E.B., Machado, C.M., Giannini, M., Beltrami, I., Piza, M., Coelho, P. G., Hirata, R., Bonfante, E.A., 2019. Effect of thermocycling on biaxial flexural strength of CAD/CAM, bulk fill, and conventional resin composite materials. *Operat. Dent.* 44, E254–E262. <https://doi.org/10.2341/18-146-L>.
- Berger, S.B., Palialol, A.R., Cavalli, V., Giannini, M., 2009. Characterization of water sorption, solubility and filler particles of light-cured composite resins. *Braz. Dent. J.* 20, 314–318. <https://doi.org/10.1590/S0103-64402009000400009>.
- Bertolo, M.V., Moraes, R.C., Pfeifer, C., Salgado, V.E., Correr, A.R., Schneider, L.F., 2017. Influence of photoinitiator system on physical-chemical properties of experimental self-adhesive composites. *Braz. Dent. J.* 28, 35–39. <https://doi.org/10.1590/0103-6440201700841>.
- Bortolotto, T., Guillarme, D., Gutemberg, D., Veuthey, J.L., Krejci, I., 2013. Composite resin vs resin cement for luting of indirect restorations: comparison of solubility and shrinkage behavior. *Dent. Mater. J.* 32, 834–838. <https://doi.org/10.4012/dmj.2013-153>.
- Braga, R.R., Cesar, P.F., Gonzaga, C.C., 2002. Mechanical properties of resin cements with different activation modes. *J. Oral Rehabil.* 29, 257–262. <https://doi.org/10.1046/j.1365-2842.2002.00821.x>.
- Brandt, W.C., Silva, C.G., Frollini, E., Souza-Junior, E.J., Sinhoreti, M.A., 2013. Dynamic mechanical thermal analysis of composite resins with CQ and PPD as photo-initiators photoactivated by QTH and LED units. *J. Mech. Behav. Biomed. Mater.* 24, 21–29. <https://doi.org/10.1016/j.jmbmm.2013.04.010>.
- Brandt, W.C., Tomaselli Lde, O., Correr-Sobrinho, L., Sinhoreti, M.A., 2011. Can phenyl-propanedione influence Knoop hardness, rate of polymerization and bond strength of resin composite restorations? *J. Dent.* 39, 438–447. <https://doi.org/10.1016/j.jdent.2011.03.009>.
- Bucuta, S., Ilie, N., 2014. Light transmittance and micro-mechanical properties of bulk fill vs. conventional resin based composites. *Clin. Oral Invest.* 18, 1991–2000. <https://doi.org/10.1007/s00784-013-1177-y>.
- Cao, L., Zhao, X., Gong, X., Zhao, S., 2013. An in vitro investigation of wear resistance and hardness of composite resins. *Int. J. Clin. Exp. Med.* 6, 423–430.
- Chesterman, J., Jowett, A., Gallacher, A., Nixon, P., 2017. Bulk-fill resin-based composite restorative materials: a review. *Br. Dent. J.* 222, 337–344. <https://doi.org/10.1038/sj.bdj.2017.214>.
- Cury, J.A., de Oliveira, B.H., dos Santos, A.P., Tenuta, L.M., 2016. Are fluoride releasing dental materials clinically effective on caries control? *Dent. Mater.* 32, 323–333. <https://doi.org/10.1016/j.dental.2015.12.002>.
- Czech, Z., Kabatc, J., Bartkowiak, M., Mozelewska, K., Kwiatkowska, D., 2020. Influence of an alkoxylation grade of acrylates on shrinkage of UV-curable compositions. *Polymers* 12. <https://doi.org/10.3390/polym12112617>.
- da Silva, E.M., Poskus, L.T., Guimaraes, J.G., 2008. Influence of light-polymerization modes on the degree of conversion and mechanical properties of resin composites: a comparative analysis between a hybrid and a nanofilled composite. *Operat. Dent.* 33, 287–293. <https://doi.org/10.2341/07-81>.
- Davis, H.B., Gwinner, F., Mitchell, J.C., Ferracane, J.L., 2014. Ion release from, and fluoride recharge of a composite with a fluoride-containing bioactive glass. *Dent. Mater.* 30, 1187–1194. <https://doi.org/10.1016/j.dental.2014.07.012>.
- Denis, A.B., Viana, R.B., Plepis, A.M.G., 2012. Kinetic parameters and monomeric conversion of different dental composites using standard and soft-start photoactivation modes. *Laser Phys.* 22, 1099–1104. <https://doi.org/10.1134/s1054660x12060011>.
- Denis, A.B., 2012. *Evaluation of Degree of Monomer Conversion, the Polymerization Kinetic Parameters and Determination of Residual Monomers in Experimental Resins*. University of São Paulo, São Carlos.
- Di Francescantonio, M., Pacheco, R.R., Aguiar, T.R., Boaro, L.C.C., Braga, R.R., Martins, A.L., Giannini, M., 2016. Evaluation of composition and morphology of filler particles in low-shrinkage and conventional composite resins carried out by means of SEM and EDX. *J. Clin. Dent. Res.* 13, 49–58. <https://doi.org/10.14436/2447-911x.13.1.049-058.oar>.
- dos Santos, A., Andre, C.B., Martim, G.C., Schuquel, I.T.A., Pfeifer, C.S., Ferracane, J.L., Tominga, T.T., Khalil, N.M., Radovanovic, E., Giroto, E.M., 2018. Methacrylate saccharide-based monomers for dental adhesive systems. *Int. J. Adhesion Adhes.* 87, 1–11. <https://doi.org/10.1016/j.ijadhadh.2018.09.009>.
- Drummond, J.L., Andronova, K., Al-Turki, L.I., Slaughter, L.D., 2004. Leaching and mechanical properties characterization of dental composites. *J. Biomed. Mater. Res. B Appl. Biomater.* 71, 172–180. <https://doi.org/10.1002/jbm.b.30074>.
- Durner, J., Obermaier, J., Draener, M., Ilie, N., 2012. Correlation of the degree of conversion with the amount of elutable substances in nano-hybrid dental composites. *Dent. Mater.* 28, 1146–1153. <https://doi.org/10.1016/j.dental.2012.08.006>.
- Eltahlah, D., Lynch, C.D., Chadwick, B.L., Blum, I.R., Wilson, N.H.F., 2018. An update on the reasons for placement and replacement of direct restorations. *J. Dent.* 72, 1–7. <https://doi.org/10.1016/j.jdent.2018.03.001>.
- Ferracane, J.L., 2006. Hygroscopic and hydrolytic effects in dental polymer networks. *Dent. Mater.* 22, 211–222. <https://doi.org/10.1016/j.dental.2005.05.005>.
- Ferracane, J.L., 2011. Resin composite—state of the art. *Dent. Mater.* 27, 29–38. <https://doi.org/10.1016/j.dental.2010.10.020>.
- Ferracane, J.L., Hilton, T.J., Stansbury, J.W., Watts, D.C., Silikas, N., Ilie, N., Heintze, S., Cadenaro, M., Hickel, R., 2017. *Academy of Dental Materials guidance-Resin composites: Part II-Technique sensitivity (handling, polymerization, dimensional changes)*. *Dent. Mater.* 33, 1171–1191. <https://doi.org/10.1016/j.dental.2017.08.188>.
- Ferracane, J.L., Mitchem, J.C., Condon, J.R., Todd, R., 1997. Wear and marginal breakdown of composites with various degrees of cure. *J. Dent. Res.* 76, 1508–1516. <https://doi.org/10.1177/00220345970760081401>.
- Finan, L., Palin, W.M., Moskwa, N., McGinley, E.L., Fleming, G.J., 2013. The influence of irradiation potential on the degree of conversion and mechanical properties of two bulk-fill flowable RBC base materials. *Dent. Mater.* 29, 906–912. <https://doi.org/10.1016/j.dental.2013.05.008>.
- Fonseca, A.S., Labruna Moreira, A.D., de Albuquerque, P.P., de Menezes, L.R., Pfeifer, C. S., Schneider, L.F., 2017. Effect of monomer type on the CC degree of conversion, water sorption and solubility, and color stability of model dental composites. *Dent. Mater.* 33, 394–401. <https://doi.org/10.1016/j.dental.2017.01.010>.
- Froes-Salgado, N.R., Gajewski, V., Ornaghi, B.P., Pfeifer, C.S., Meier, M.M., Xavier, T.A., Braga, R.R., 2015. Influence of the base and diluent monomer on network characteristics and mechanical properties of neat resin and composite materials. *Odontology* 103, 160–168. <https://doi.org/10.1007/s10266-014-0153-6>.

- Fronza, B.M., Ayres, A., Pacheco, R.R., Rueggeberg, F.A., Dias, C., Giannini, M., 2017. Characterization of inorganic filler content, mechanical properties, and light transmission of bulk-fill resin composites. *Operat. Dent.* 42, 445–455. <https://doi.org/10.2341/16-024-L>.
- Fronza, B.M., Rueggeberg, F.A., Braga, R.R., Mogilevych, B., Soares, L.E., Martin, A.A., Ambrosano, G., Giannini, M., 2015. Monomer conversion, microhardness, internal marginal adaptation, and shrinkage stress of bulk-fill resin composites. *Dent. Mater.* 31, 1542–1551. <https://doi.org/10.1016/j.dental.2015.10.001>.
- Fugolin, A.P., de Paula, A.B., Dobson, A., Huynh, V., Consani, R., Ferracane, J.L., Pfeifer, C.S., 2020. Alternative monomer for BisGMA-free resin composites formulations. *Dent. Mater.* 36, 884–892. <https://doi.org/10.1016/j.dental.2020.04.009>.
- Fujita, K., Ikemi, T., Nishiyama, N., 2011. Effects of particle size of silica filler on polymerization conversion in a light-curing resin composite. *Dent. Mater.* 27, 1079–1085. <https://doi.org/10.1016/j.dental.2011.07.010>.
- Goncalves, L., Filho, J.D., Guimaraes, J.G., Poskus, L.T., Silva, E.M., 2008. Solubility, salivary sorption and degree of conversion of dimethacrylate-based polymeric matrices. *J. Biomed. Mater. Res. B Appl. Biomater.* 85, 320–325. <https://doi.org/10.1002/jbm.b.30949>.
- Guimaraes, G.M.F., Bronze-Uhle, E.S., Lisboa-Filho, P.N., Fugolin, A.P.P., Borges, A.F.S., Gonzaga, C.C., Pfeifer, C.S., Furuse, A.Y., 2020. Effect of the addition of functionalized TiO₂ nanotubes and nanoparticles on properties of experimental resin composites. *Dent. Mater.* 36, 1544–1556. <https://doi.org/10.1016/j.dental.2020.09.013>.
- Gupta, N., Jaiswal, S., Nikhil, V., Gupta, S., Jha, P., Bansal, P., 2019. Comparison of fluoride ion release and alkalinizing potential of a new bulk-fill alkasite. *J. Conserv. Dent.* 22, 296–299. <https://doi.org/10.4103/JCD.JCD.74.19>.
- Habib, E., Wang, R., Zhu, X.X., 2018. Correlation of resin viscosity and monomer conversion to filler particle size in dental composites. *Dent. Mater.* 34, 1501–1508. <https://doi.org/10.1016/j.dental.2018.06.008>.
- Hirata, R., Kabbach, W., de Andrade, O.S., Bonfante, E.A., Giannini, M., Coelho, P.G., 2015. Bulk fill composites: an anatomic sculpting technique. *J. Esthetic Restor. Dent.* 27, 335–343. <https://doi.org/10.1111/jerd.12159>.
- Hirt, T., Moszner, N., Burtscher, P., Vogel, K., Todd, J., Heintze, S., Peschke, A., 2013. Patented Ivocerin Light Initiator - a Milestone in Composite Technology, Ivoclar Vivadent Report. Ivoclar Vivadent AG, Schaan, pp. 1–42.
- Ilie, N., 2018. Comparative effect of self- or dual-curing on polymerization kinetics and mechanical properties in a novel, dental-resin-based composite with alkaline filler. Running title: resin-composites with alkaline fillers. *Materials* 11, 108. <https://doi.org/10.3390/ma11010108>.
- Ilie, N., Bucuta, S., Draenert, M., 2013. Bulk-fill resin-based composites: an in vitro assessment of their mechanical performance. *Operat. Dent.* 38, 618–625. <https://doi.org/10.2341/12-395-L>.
- Ilie, N., Hickel, R., 2011. Resin composite restorative materials. *Aust. Dent. J.* 56 (Suppl. 1), 59–66. <https://doi.org/10.1111/j.1834-7819.2010.01296.x>.
- Imazato, S., Tarumi, H., Kato, S., Ebi, N., Ehara, A., Ebisu, S., 1999. Water sorption, degree of conversion, and hydrophobicity of resins containing Bis-GMA and TEGDMA. *Dent. Mater.* 18, 124–132.
- Ito, S., Hashimoto, M., Wadgaonkar, B., Svizero, N., Carvalho, R.M., Yiu, C., Rueggeberg, F.A., Foulger, S., Saito, T., Nishitani, Y., Yoshiyama, M., Tay, F.R., Pashley, D.H., 2005. Effects of resin hydrophilicity on water sorption and changes in modulus of elasticity. *Biomaterials* 26, 6449–6459. <https://doi.org/10.1016/j.biomaterials.2005.04.052>.
- Jun, S.K., Cha, J.R., Knowles, J.C., Kim, H.W., Lee, J.H., Lee, H.H., 2020. Development of Bis-GMA-free biopolymer to avoid estrogenicity. *Dent. Mater.* 36, 157–166. <https://doi.org/10.1016/j.dental.2019.11.016>.
- Kerby, R.E., Knobloch, L.A., Schrickler, S., Gregg, B., 2009. Synthesis and evaluation of modified urethane dimethacrylate resins with reduced water sorption and solubility. *Dent. Mater.* 25, 302–313. <https://doi.org/10.1016/j.dental.2008.07.009>.
- Khan, A.S., Amer, S., Chaudhry, A.A., Wong, F.S., Ur Rehman, I., 2013. Synthesis and characterizations of a fluoride-releasing dental restorative material. *Mater. Sci. Eng. C Mater. Biol. Appl.* 33, 3458–3464. <https://doi.org/10.1016/j.msec.2013.04.029>.
- Leprince, J.G., Leveque, P., Nysten, B., Gallez, B., Devaux, J., Leloup, G., 2012. New insight into the "depth of cure" of dimethacrylate-based dental composites. *Dent. Mater.* 28, 512–520. <https://doi.org/10.1016/j.dental.2011.12.004>.
- Leprince, J.G., Palin, W.M., Vanacker, J., Sabbagh, J., Devaux, J., Leloup, G., 2014. Physico-mechanical characteristics of commercially available bulk-fill composites. *J. Dent.* 42, 993–1000. <https://doi.org/10.1016/j.jdent.2014.05.009>.
- Libonati, A., Marzo, G., Klinger, F.G., Farini, D., Gallusi, G., Tecco, S., Mummolo, S., De Felici, M., Campanella, V., 2011. Embryotoxicity assays for leached components from dental restorative materials. *Reprod. Biol. Endocrinol.* 9, 136. <https://doi.org/10.1186/1477-7827-9-136>.
- Lynch, C.D., Wilson, N.H., 2013. Managing the phase-down of amalgam: Part I. Educational and training issues. *Br. Dent. J.* 215, 109–113. <https://doi.org/10.1038/sj.bdj.2013.737>.
- Marghalani, H.Y., 2012. Sorption and solubility characteristics of self-adhesive resin cements. *Dent. Mater.* 28, e187–198. <https://doi.org/10.1016/j.dental.2012.04.037>.
- McCabe, J.F., Rusby, S., 2004. Water absorption, dimensional change and radial pressure in resin matrix dental restorative materials. *Biomaterials* 25, 4001–4007. <https://doi.org/10.1016/j.biomaterials.2003.10.088>.
- Meereis, C.T., Leal, F.B., Lima, G.S., de Carvalho, R.V., Piva, E., Ogliari, F.A., 2014. BAPO as an alternative photoinitiator for the radical polymerization of dental resins. *Dent. Mater.* 30, 945–953. <https://doi.org/10.1016/j.dental.2014.05.020>.
- Miletic, V., Santini, A., 2012. Micro-Raman spectroscopic analysis of the degree of conversion of composite resins containing different initiators cured by polywave or monowave LED units. *J. Dent.* 40, 106–113. <https://doi.org/10.1016/j.jdent.2011.10.018>.
- Morrison, R.T., Boyd, R.N., 2002. 1.21 solubility. In: *Organic Chemistry*, 6th ed. Prentice Hall of India Private Limited, New Delhi, pp. 31–33.
- Moszner, N., Fischer, U.K., Angermann, J., Rheinberger, V., 2008. A partially aromatic urethane dimethacrylate as a new substitute for Bis-GMA in restorative composites. *Dent. Mater.* 24, 694–699. <https://doi.org/10.1016/j.dental.2007.07.001>.
- Naoum, S., Ellakwa, A., Martin, F., Swain, M., 2011. Fluoride release, recharge and mechanical property stability of various fluoride-containing resin composites. *Operat. Dent.* 36, 422–432. <https://doi.org/10.2341/10-414-L>.
- Neumann, M.G., Miranda Jr., W.G., Schmitt, C.C., Rueggeberg, F.A., Correa, I.C., 2005. Molar extinction coefficients and the photon absorption efficiency of dental photoinitiators and light curing units. *J. Dent.* 33, 525–532. <https://doi.org/10.1016/j.jdent.2004.11.013>.
- Odian, G., 2004. *Principles of Polymerization*, 4th ed. John Wiley & Sons, Inc., Hoboken.
- Oliveira, D.C., Souza-Junior, E.J., Dobson, A., Correr, A.R., Brandt, W.C., Sinhoretto, M.A., 2016. Evaluation of phenyl-propanedione on yellowing and chemical-mechanical properties of experimental dental resin-based materials. *J. Appl. Oral Sci.* 24, 555–560. <https://doi.org/10.1590/1678-775720160058>.
- Opdam, N.J., van de Sande, F.H., Bronkhorst, E., Cenci, M.S., Bottenberg, P., Pallesen, U., Gaengler, P., Lindberg, A., Huysmans, M.C., van Dijken, J.W., 2014. Longevity of posterior composite restorations: a systematic review and meta-analysis. *J. Dent. Res.* 93, 943–949. <https://doi.org/10.1177/0022034514544217>.
- Park, C.A., Hyun, S.H., Lee, J.H., Seol, H.J., Kim, H.I., Kwon, Y.H., 2007. Evaluation of polymerization in fluoride-containing composite resins. *J. Mater. Sci. Mater. Med.* 18, 1549–1556. <https://doi.org/10.1007/s10856-007-3023-8>.
- Patil, R.D., Mark, J.E., Apostolov, A., Vassileva, E., Fakirov, S., 2000. Crystallization of water in some crosslinked gelatins. *Eur. Polym. J.* 36, 1055–1061. [https://doi.org/10.1016/S0014-3057\(99\)00144-5](https://doi.org/10.1016/S0014-3057(99)00144-5).
- Ping, Z.H., Nguyen, Q.T., Chen, S.M., Zhou, J.Q., Ding, Y.D., 2001. States of water in different hydrophilic polymers - DSC and FTIR studies. *Polymer* 42, 8461–8467. [https://doi.org/10.1016/S0032-3861\(01\)00358-5](https://doi.org/10.1016/S0032-3861(01)00358-5).
- Prager, M., Pierce, M., Atria, P.J., Sampaio, C., Caceres, E., Wolff, M., Giannini, M., Hirata, R., 2018. Assessment of cuspal deflection and volumetric shrinkage of different bulk fill composites using non-contact phase microscopy and micro-computed tomography. *Dent. Mater. J.* 37, 393–399. <https://doi.org/10.4012/dmj.2017-136>.
- Pratap, B., Gupta, R.K., Bhardwaj, B., Nag, M., 2019. Resin based restorative dental materials: characteristics and future perspectives. *Jpn. Dent. Sci. Rev.* 55, 126–138. <https://doi.org/10.1016/j.jdsr.2019.09.004>.
- Randolph, L.D., Palin, W.M., Leloup, G., Leprince, J.G., 2016. Filler characteristics of modern dental resin composites and their influence on physico-mechanical properties. *Dent. Mater.* 32, 1586–1599. <https://doi.org/10.1016/j.dental.2016.09.034>.
- Ravve, A., 2012. 2.6 solutions of polymers. In: *Principles of Polymer Chemistry*, third ed. Springer Science+Business Media, LLC, Niles, pp. 48–51.
- Ruivo, M.A., Pacheco, R.R., Sebold, M., Giannini, M., 2019. Surface roughness and filler particles characterization of resin-based composites. *Microsc. Res. Tech.* 82, 1756–1767. <https://doi.org/10.1002/jemt.23342>.
- Sahadi, B.O., Price, R.B., Andre, C.B., Sebold, M., Bermejo, G.N., Palma-Dibb, R.G., Faraoni, J.J., Soares, C.J., Giannini, M., 2018. Multiple-peak and single-peak dental curing lights comparison on the wear resistance of bulk-fill composites. *Braz. Oral Res.* 32, e122. <https://doi.org/10.1590/1807-3107bor-2018.vol32.0122>.
- Satterthwaite, J.D., Vogel, K., Watts, D.C., 2009. Effect of resin-composite filler particle size and shape on shrinkage-strain. *Dent. Mater.* 25, 1612–1615. <https://doi.org/10.1016/j.dental.2009.08.012>.
- Schmidt, C., Ilie, N., 2012. The mechanical stability of nano-hybrid composites with new methacrylate monomers for matrix compositions. *Dent. Mater.* 28, 152–159. <https://doi.org/10.1016/j.dental.2011.11.007>.
- Schneider, L.F., Pfeifer, C.S., Consani, S., Prah, S.A., Ferracane, J.L., 2008. Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites. *Dent. Mater.* 24, 1169–1177. <https://doi.org/10.1016/j.dental.2008.01.007>.
- Schwengberg, S., Bohlen, H., Kleinsasser, N., Kehe, K., Seiss, M., Walther, U.I., Hickel, R., Reichl, F.X., 2005. In vitro embryotoxicity assessment with dental restorative materials. *J. Dent.* 33, 49–55. <https://doi.org/10.1016/j.jdent.2004.08.001>.
- Sebold, M., Lins, R.B.E., Andre, C.B., Martins, L.R.M., Giannini, M., 2020. Flowable and regular bulk-fill composites: a comprehensive report on restorative treatment. *Int. J. Periodontics Restor. Dent.* 40, 293–300. <https://doi.org/10.11607/prd.3932>.
- Sideridou, I., Tserki, V., Papanastasiou, G., 2003. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials* 24, 655–665. [https://doi.org/10.1016/s0142-9612\(02\)00380-0](https://doi.org/10.1016/s0142-9612(02)00380-0).
- Sideridou, I.D., Achilias, D.S., Karabela, M.M., 2007. Sorption kinetics of ethanol/water solution by dimethacrylate-based dental resins and resin composites. *J. Biomed. Mater. Res. B Appl. Biomater.* 81, 207–218. <https://doi.org/10.1002/jbm.b.30655>.
- Silikas, N., Eliades, G., Watts, D.C., 2000. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent. Mater.* 16, 292–296. [https://doi.org/10.1016/s0109-5641\(00\)0020-8](https://doi.org/10.1016/s0109-5641(00)0020-8).
- Soderholm, K.J., Zigan, M., Ragan, M., Fischlschweiger, W., Bergman, M., 1984. Hydrolytic degradation of dental composites. *J. Dent. Res.* 63, 1248–1254. <https://doi.org/10.1177/00220345840630101701>.
- Soto-Montero, J., Nima, G., Rueggeberg, F.A., Dias, C., Giannini, M., 2020. Influence of multiple peak light-emitting-diode curing unit beam homogenization tips on microhardness of resin composites. *Operat. Dent.* 45, 327–338. <https://doi.org/10.2341/19-027-L>.

- Szczeszio-Wlodarczyk, A., Sokolowski, J., Kleczewska, J., Bociog, K., 2020. Ageing of dental composites based on methacrylate resins-A critical review of the causes and method of assessment. *Polymers (basel)* 12. <http://doi.org/10.3390/polym12040882>.
- Todd, J.C., 2016. *Scientific Documentation: Cention N. Ivoclar Vivadent AG, Research and Development. Scientific Service, Liechtenstein*, pp. 1–58.
- Turssi, C.P., Ferracane, J.L., Vogel, K., 2005. Filler features and their effects on wear and degree of conversion of particulate dental resin composites. *Biomaterials* 26, 4932–4937. <https://doi.org/10.1016/j.biomaterials.2005.01.026>.
- Vaidyanathan, T.K., Vaidyanathan, J., Lizymol, P.P., Ariya, S., Krishnan, K.V., 2017. Study of visible light activated polymerization in BisGMA-TEGDMA monomers with Type 1 and Type 2 photoinitiators using Raman spectroscopy. *Dent. Mater.* 33, 1–11. <https://doi.org/10.1016/j.dental.2016.09.002>.
- Van Landuyt, K.L., Nawrot, T., Geebelen, B., De Munck, J., Snauwaert, J., Yoshihara, K., Scheers, H., Godderis, L., Hoet, P., Van Meerbeek, B., 2011. How much do resin-based dental materials release? A meta-analytical approach. *Dent. Mater.* 27, 723–747. <https://doi.org/10.1016/j.dental.2011.05.001>.
- Wang, R., Liu, H., Wang, Y., 2019. Different depth-related polymerization kinetics of dual-cure, bulk-fill composites. *Dent. Mater.* 35, 1095–1103. <https://doi.org/10.1016/j.dental.2019.05.001>.
- Wilson, N.H.F., 2007. *Minimally Invasive Dentistry: the Management of Caries, first ed.* Quintessence Publishing Co., Surrey.
- Yang, Y., Reichl, F.X., Shi, J., He, X., Hickel, R., Hogg, C., 2018. Cytotoxicity and DNA double-strand breaks in human gingival fibroblasts exposed to eluates of dental composites. *Dent. Mater.* 34, 201–208. <https://doi.org/10.1016/j.dental.2017.10.002>.