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ORIGINAL ARTICLE

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Impact of photoinitiator quality on chemical-mechanical properties of dental adhesives under different light intensities

Impacto da qualidade de fotoiniciadores nas propriedades químico mecânicas de adesivos dentais sob diferentes intensidades de luz

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ABSTRACT

Objective: Evaluate the mechanical properties of experimental adhesive models with different photoinitiators (PI) polymerized by LED units of different power densities. **Material and Methods:** Three groups of adhesive models based on HEMA/BisGMA (45/55) were prepared in association with different PI combinations: G2 (control) – 2 PI: 0.5% CQ, 0.5% EDMAB; G3 - 3 PI: 0.5% CQ; 0.5% DMAEMA, 0.5% DPIHP; G4 - 4 PI: 0.5% CQ; 0.5% EDMAB; 0.5% DMAEMA; 0.5% DPIHP. The three formulations were polymerized at two different LED power densities: 550 mW/cm^2 and 1200 mW/cm^2. The degree of conversion (DC) of adhesive monomers was monitored *in situ* through the FTIR for 600 s. Specimens were prepared for each formulation for analysis of flexural strength (FS), modulus of elasticity (ME), sorption (SOR) and solubility (SOL). Data were submitted to two-way ANOVA and Tukey tests (5%). **Results:** DC: there is a significant difference among adhesive systems (G2<G3<G4). FS and ME: significant differences were found between densities, with the lowest average for 550 mW/cm^2. SOR and SOL: adhesives polymerized at 1200 mW/cm^2 presented higher sorption and solubility. **Conclusion:** The mechanical properties of the adhesive models are directly related to the types of photoinitiators and the LED power densities.

KEYWORDS

Dental adhesive; Irradiance; Light-curing; Photoinitiators; Physicochemical phenomena.

RESUMO

Objetivo: Avaliar as propriedades mecânicas de modelos adesivos experimentais com diferentes fotoiniciadores (PI) polimerizados por unidades de LED de diferentes densidades de energia. **Material e Métodos:** Três grupos de modelos adesivos baseados em HEMA/BisGMA (45/55) foram preparados em associação com diferentes combinações de PI: G2 (controle) – 2 PI: 0,5% CQ, 0,5% EDMAB; G3 - 3PI: 0,5% CQ; 0,5% DMAEMA, 0,5% DPIHP; G4 - 4 PI: 0,5% CQ; 0,5% EDMAB; 0,5% DMAEMA; 0,5% DPIHP. As três formulações foram polimerizadas em duas densidades de potência de LED: 550 mW/cm2 e 1200 mW/cm^2. O grau de conversão (DC) dos monômeros adesivos foi monitorado *in situ* através do FTIR durante 600 s. Amostras foram preparadas para cada formulação para análise de resistência à flexão (FS), módulo de elasticidade (ME), sorção (SOR) e solubilidade (SOL). Os dados foram submetidos aos testes ANOVA 2-fatores e Tukey (5%). **Resultados:** DC: houve diferença significativa entre os sistemas adesivos (G2<G3<G4). FS e ME: foram encontradas diferenças significativas entre as densidades, com as menores médias para 550 mW/cm^2. SOR e SOL: adesivos polimerizados a 1200 mW/cm^2 apresentaram

maior sorção e solubilidade. **Conclusão:** As propriedades mecânicas dos modelos adesivos estão diretamente relacionadas com os tipos de fotoiniciadores e as densidades de potência LED.

PALAVRAS-CHAVE

Fotoiniciadores; Fotopolimerização; Irradiação; Propriedades físico-químicas; Sistemas adesivos.

INTRODUCTION

Adhesion represents the main mechanism by which resin materials bond to a dental substrate, and it remains the most fragile link in long-term clinical performance. The durability of the adhesive system at the interface may be affected by incomplete polymerization, prevention of infiltration of demineralized dentin by the presence of dentin fluids, phase separation and hydrolytic-enzymatic degradation of the adhesive [1-4]. Knowledge of the behavior of light-polymerized adhesives and the generation of more effective adhesive models that enhance the longevity of restorations in a wet environment are necessary to improve current dental practice [5].

Adhesive systems comprise a resinous phase, an aqueous phase, photoinitiators, and co-initiators. The resinous phase is rich in Bis-GMA, a highly hydrophobic monomer and polymerizable because it has branched chains that provide good mechanical properties for the adhesive system but inadequate penetration into the demineralized and moist dentin. The aqueous phase is rich in HEMA, an aggregate monomer for increasing water compatibility and adhesive infiltration on the demineralized and wet dentin substrate. However, HEMA has a linear chain that does not have the same polymerization potential as Bis-GMA, which provides a poorly polymerized adhesive interface favoring longitudinal degradation [5-9].

Photoinitiators, of which camphorquinone is the most commonly used in current adhesive systems, are added to the adhesive formulations for polymerization reaction. With hydrophobic characteristics, camphorquinone remains associated with Bis-GMA in the resinous phase, ensuring excellent polymerization [2,7].

However, in view of the moist substrate and adhesive phase separation, the polymerization rate and degree of conversion are affected, inducing a nonhomogeneous polymerization structure of the adhesive. This may lead to a mechanism for degradation. Therefore, in addition to camphorquinone, other photoinitiators with hydrophobic characteristics, such as ethyl-4-(dimethylamino) benzoate (EDMAB) and hydrophilic characteristics, such as 2-(dimethylamino) ethyl methacrylate (DMAEMA), are used in adhesive systems to improve polymerization in the presence of water. In addition, a new co-initiator, DHIHP (salt) has been introduced into adhesive systems to replace inactive radicals with active radicals of both camphorquinone and phenyl, optimizing polymerization [7,10].

Analysis of mechanical properties of the new adhesive systems *in vitro* offers a significant reference for their behavior under clinical conditions [5]. These mechanical properties are also directly related to the effectiveness of the photopolymerizing units and the intensity and spectrum of light emission [11,12]. Currently, LED devices are the most commonly used for photopolymerization [13]. Recent developments have increased the output of LED devices from a power density between 300 mW/cm^2 and 650 mW/cm^2 to more than 1200 mW/cm^2. The increase in light intensity may result in a higher degree of conversion and, consequently, better mechanical properties [14,15]. However, it may generate higher tensile stresses from polymerization contraction.

The present study optimized the incorporation of a combination of hydrophilic and hydrophobic photoinitiators to improve the degree of conversion of the adhesive systems, mainly in the hydrophilic phase. The evaluation of different photopolymerization power densities should provide better adhesiveness and strength, both of which are important to the maintenance of restorations in the oral environment. Thus, the aim of this study was to evaluate the mechanical properties of experimental models of adhesive systems polymerized by LED units of different power densities. The null hypotheses tested were that no significant differences would be found among the photoinitiators regarding the mechanical properties of the adhesive systems tested and that no significant differences would be found among the LED intensities used.

MATERIAL AND METHODS

Model adhesive compositions

Experimental models of adhesive systems similar to commercially available adhesive systems were fabricated. The model adhesive consisted of hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, St. Louis, MO, USA) and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA, Sigma-Aldrich, St. Louis, MO, USA) with a mass ratio of 45/55 (HEMA/BisGMA) as monomers widely used in dentin adhesives [7]. In association, 2, 3, and 4 different photoinitiators were added:

- *G2* - 2 photoinitiators: 0.5% camphorquinone (CQ, Sigma-Aldrich, St. Louis, MO, USA); 0.5% ethyl-4-(dimethylamino) benzoate (EDMAB, Sigma-Aldrich, St. Louis, MO, USA).
- *G3* - 3 photoinitiators: 0.5% CQ; 0.5% 2-(dimethylamino) ethyl methacrylate (DMAEMA, Sigma-Aldrich, St. Louis, MO, USA); 0.5% diphenyliodonium hexafluorophosphate (DPIHP, Sigma-Aldrich, St. Louis, MO, USA).
- *G4* - 4 photoinitiators: 0.5% CQ; 0.5% EDMAB; 0.5% DMAEMA; 0.5% DPIHP.

The experimental adhesive systems were prepared in a brown glass vial and shaken (Orbit 300, LabNET International Inc., Woodbridge, NJ, USA) for 48 h to yield well-mixed adhesive resin solutions.

Degree of conversion

The photopolymerization of the experimental adhesive models was monitored *in situ* with an infrared spectrometer (FT-IR, PerkinElmer, Waltham, MA, EUA) with a resolution of 4cm^{-1} in the attenuated total reflection (ATR) mode and a transmission range of 650 cm^{-1} to 4000 cm^{-1} [7]. The technique consisted of collecting the reflected radiation from the interface between the adhesive and the crystal (ATR), providing evidence for the transformation of carbon double bonds (C=C) in the intensity range of 1638 cm^{-1} and of single bonds (C-C) in the 1608 cm^{-1} range [4,16].

A volume of 10 μL of experimental adhesive system was placed on the ATR crystal, and a transparent coverslip was attached with a piece of tape placed on the specimen to prevent the evaporation of components [15]. Three formulations were evaluated according to the power density used for photopolymerization [13], as measured with a radiometer (Curing Radiometer Model 100, Demetron Research Corporation, Danbury, CT, USA):

- Group 550 - LED unit (Emitter A, Schuster, Santa Maria, RS, Brazil), with light intensity of 550 mW/cm^2.
- Group 1200 – LED unit (Demi Light Curing System, Kerr Corporation, São Paulo, SP, Brazil), with light intensity of 1200mW/cm^2.

The LED units were positioned at a distance of 2 mm perpendicular to the horizontal platform where the ATR was located. A time-resolved spectrum collector (Spectrum TimeBase, Perkin-Elmer, MA, USA) was used for the continuous and automatic collection of spectra during polymerization.

The decrease in band ratio profile for intensity at 1638 cm^{-1} to that at 1608 cm^{-1} was monitored continuously during polymerization [16-18]. The degree of conversion (DC) was determined using the following formula, which was based on the intensity band ratios before and after light-polymerization [10,16]:

$$DC(\%) = \left(1 - \left(\frac{\frac{1638cm-1}{1608cm-1}cured}{\frac{1638cm-1}{1608cm-1}uncured}\right)\right)\times 100 \qquad (1)$$

All experiments were carried out in triplicate, and the results were averaged.

Adhesive flexural strength and modulus of elasticity

Ten specimens were prepared for each adhesive system formulation (n=60). The specimens were made in rectangular silicone molds (12 mm length × 2 mm width × 2 mm height) [19]. Unpolymerized adhesive was dropped onto the molds, covered with a mylar strip, and light polymerized for 20 s according to the different LED power densities (550 mW/cm^2 and

1200 mW/cm^2). The specimens were stored in brown glass until testing [18].

The flexural properties were evaluated using a three-point flexural strength test performed with a universal testing machine (EMIC DL-2000MF, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/min using a 10 kgf load cell. Flexural strength was obtained by measuring the load at the fracture point, and the modulus of elasticity was calculated based on the recorded load deflection curves [20].

Adhesive sorption and solubility

For each experimental adhesive system formulation, ten disc-shaped specimens (n=60) were fabricated using a silicone mold (6 mm diameter × 2 mm height). Unpolymerized adhesive models were placed in the silicone mold, a mylar strip and a glass slide were placed onto the silicone mold, and the adhesive was light-polymerized for 20 s [20], according to the LED power densities (550 mW/cm^2 and 1200 mW/cm^2).

The specimens were stored in a desiccator containing freshly dried silica gel. After 24 h, the specimens were weighed using a 0.0001 mg precision scale (Mettler, Toledo, OH, USA). This cycle was repeated until a constant mass (M1) was obtained. The specimens were immersed in 1 ml of distilled water at 37°C for 28 days [21]. Every 24 h, the specimens were removed, blotted dry, reweighed (M2 - sorption), and returned to the water. After 28 days, the specimens were again dried in the desiccator and weighed daily until a constant mass was achieved (M3 - solubility).

Water sorption was calculated by the ratio between the difference M1 and M2 by the specimen volume [22], according to the following equation:

$$\%SOR = 100\left(M2 - M1 / V\right). \quad (2)$$

Water solubility was calculated by the ratio between the difference M1 and M3 by the specimen volume of the according to the formula: $\%SOL = 100\ (M1 - M3 / V)$.

Statistical analysis

Data collected on degree of conversion (%DC), flexural strength (in MPa), modulus of elasticity (in MPa), water sorption (%SOR) and solubility (%SOL) were statistically analyzed using two-way ANOVA (adhesive models; LED power densities) and the Tukey test (5%).

RESULTS

Table I shows the mean values and standard deviation of flexural strength (FS), modulus of elasticity (ME), degree of conversion (%DC), sorption (%SOR), and solubility (%SOL) obtained in the groups. The highest means of FS, ME, and DC were observed in the G4 group, independently of the LED power density. For sorption and solubility, the greatest mean values were obtained in the G4 group, which was photopolymerized with 1200 mW/cm^2.

According to two-way ANOVA, the LED power densities showed a statistically significant effect ($p = 0.0095$; F = 7.934) for the modulus of elasticity. Flexural strength presented a statistically significant difference according to LED intensity ($p = 0.0125$; F = 7.293). Water solubility showed statistically significant differences according to adhesive model ($p = 0.0053$; F = 6.58) and LED power density ($p = 0.0001$; F = 23.27). For water sorption, the adhesive model ($p = 0.0001$; F = 19.0) and LED intensity ($p = 0.0005$; F = 16.43) were statistically significant.

For the degree of conversion, the adhesive models had statistically significant differences ($p = 0.0001$; F=201.15). The representative results from kinetic study for the adhesive formulations, according to the degree of conversion, are presented (Figure 1). The G2 adhesive groups exhibited a lower degree of conversion means than the formulation of G3 and G4 groups.

The measurements of the conversion and the polymerization rate as a function of time are shown in Figure 1. Figure 1A shows the conversion of the monomers of the G2 adhesive subjected to 550 and 1200 W, where it is possible to notice that all the curves present the same behavior, with an abrupt increase in conversion, in 25 seconds, followed by a saturation in 45 seconds. The saturation values were different for the two conditions, the highest with 550 W with ≈ 57% and the lowest with 1200 W with ≈ 55%. The samples from groups G3 and G4 showed a curve like G2 with a reaction start at 20 and 25 seconds respectively, followed

Table I - Mean (SD) and Tukey test: Flexural strength (FS), Modulus of elasticity (ME), Degree of conversion (DC), Water sorption (%SOR), Water solubility (%SOL) of the adhesive systems evaluated

	FS (MPa)		ME (GPa)		DC (%)		% SOR		% SOL	
	550 W	1200 W	550 W	1200 W	550 W	1200 W	550 W	1200 W	550 W	1200 W
G2	86.3 (10.72) Ab	116.7 (5.73) Aa	0.74 (0.25) Aa	1.48 (0.40) Ab	55.09 (0.94) Aa	51.58 (2.70) Ab	8.53 (0.26) Aa	9.03 (0.51) Aa	-1.41 (0.63) Aa	-1.84 (0.38) ABa
G3	96.1 (23.99) Aab	125.0 (19.58) Aa	1.22 (0.55) ABa	1.66 (0.26) Aa	68.21 (1.66) Ba	69.22 (0.87) Ba	9.12 (0.34) ABa	9.91 (0.49) Bb	-1.21 (0.41) Aa	-2.35 (0.31) Bb
G4	114.6 (28.62) Aa	113.8 (20.58) Aa	1.43 (0.32) Ba	1.46 (0.46) Aa	72.91 (1.27) Ca	72.26 (1.78) Ba	9.63 (0.49) Ba	10.16 (0.24) Bb	-1.97 (0.20) ABa	-2.53 (0.33) Bb

Different letters show statistically significant differences ($p<0.05$); capital letters refer to columns; lowercase letters refer to lines.

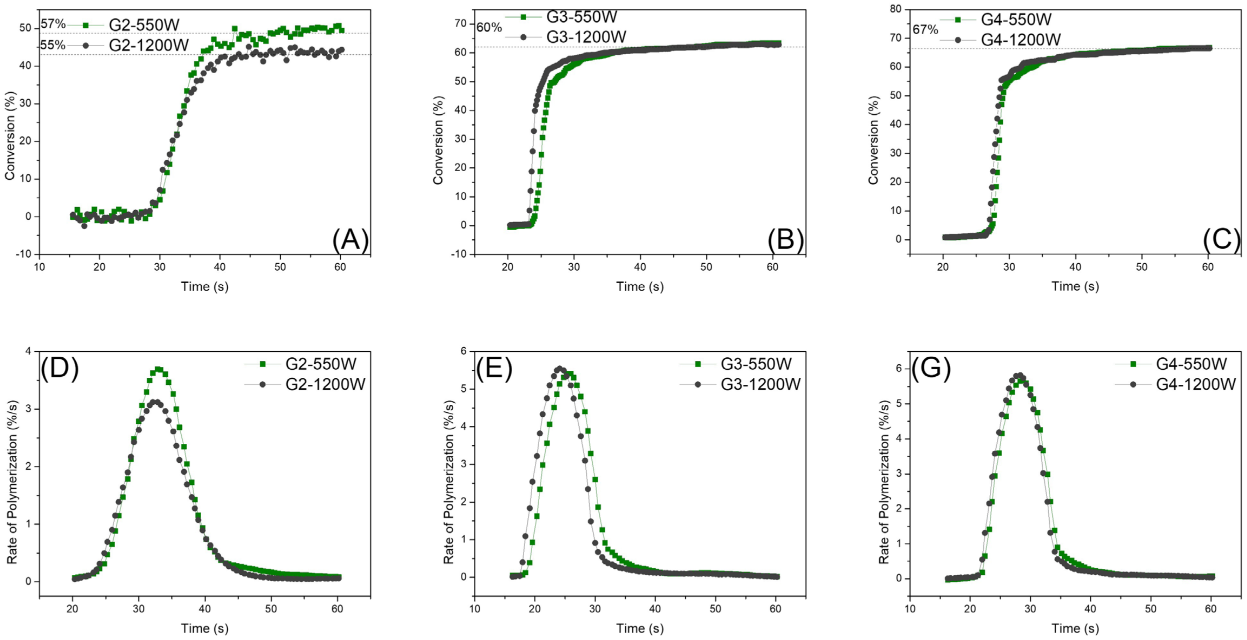

Figure 1. Polymerization kinetics of adhesives with different formulations, varying the light power and relating the conversion of monomers over time and the polymerization rate by time.

by a saturation at 30 and 35 seconds, respectively, these reactions being faster than that observed in the G2 sample. Another relevant point observed is that the change in light intensity did not result in a significant difference in monomer conversion.

When analyzing the monomer conversion rate by time, shown in Figure 2, it is possible to conclude that the G2 sample for both LED powers densities presented the same curve profile, and 500 W presented a higher polymerization rate when compared to 1200 W. On the other hand, G3 showed similar polymerization rates, but with the highest potency, it generated a shift in the curve for shorter times. As for G4, it is not possible to observe a significant visual difference for the two potencies used.

Table II presents the kinetic constants referring to the auto-catalytic model adjusted to the experimental results. This model lists four constants: *k* (speed constant), *m* (exponent of the autocatalytic term), *n* (exponent of the reaction order term), and *a* (reaction yield). G2 did not show a significant increase in its rate constant as a function of the LED power densities used to initiate the reaction. However, the constant m that correlates with the propagation of chains reduced and the constant *n* that correlates with the termination of chains increased. This suggests that at 1200 W it favors the chain termination mechanisms and at 500 W it favors the propagation mechanism and therefore there was an increase in the conversion of monomers. The G3 did not show significant changes in the values of *m* and *n* as a function of the light power used, however, there was an increase in the values of *k* with 1200 W, indicating that this

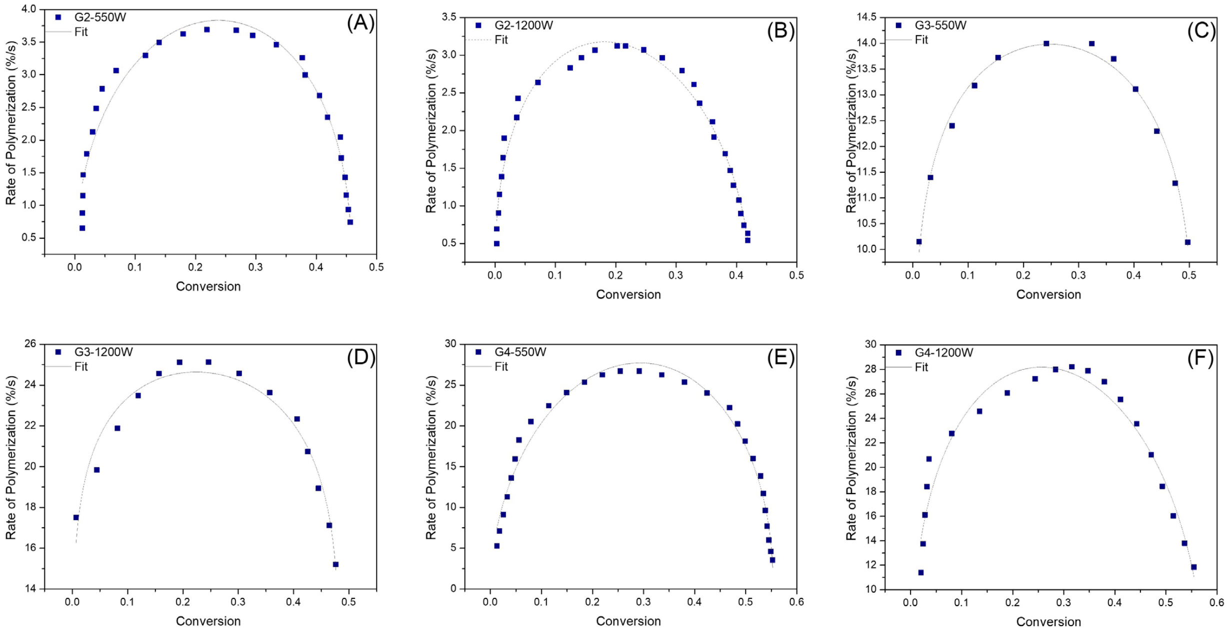

Figure 2. Polymerization kinetics of adhesive models with different formulations.

Table II - Kinetic constants referring to the autocatalytic model adjusted to the experimental results presented in Figure 2

Groups		k*	m	n	a
G2	550 W	14.15 ± 1.8	0.46 ± 0.03	0.43 ± 0.05	0.46 ± 0.003
	1200 W	13.40 ± 1.2	0.40 ± 0.01	0.53 ± 0.04	0.42 ± 0.002
G3	550 W	20.92 ± 0.6	0.14 ± 0.01	0.15 ± 0.01	0.51 ± 0.005
	1200 W	38.85 ± 2.42	0.15 ± 0.02	0.17 ± 0.02	0.48 ± 0.005
G4	550 W	99.80 ± 7.6	0.53 ± 0.03	0.47 ± 0.05	0.55 ± 0.002
	1200 W	79.84 ± 10.4	0.38 ± 0.03	0.47 ± 0.05	0.55 ± 0.002

*k (speed constant), m (exponent of the autocatalytic term), n (exponent of the reaction order term), and a (reaction yield).

condition favored the polymerization process in relation to 500 W. The G4 presented the higher values of *k* having a small percentage reduction with increasing power and a small reduction in the constant *m*, however due to the high values of *k* it was not possible to notice a significant change in the conversion.

DISCUSSION

In vitro studies represent an important tool for understanding adhesive models and for predicting and validating the behavior of materials before clinical use. The hydrolytic degradation caused by phase separation of the adhesive under clinical conditions of the presence of intrapulpal fluid requires adhesive systems with improved performance in hydrophilic environments. Therefore, the evaluation of the behavior of new combinations of hydrophilic and hydrophobic photoinitiators is relevant to optimize resistance to degradation with no prejudice to the mechanical properties [10].

Commercially available adhesive systems typically have a composition based on cross-linking polymerizations between the hydrophobic monomers (Bis-GMA) and hydrophilic (HEMA) monomers. The Bis-GMA molecule has two binding sites, whereas HEMA has only one, which helps raise the rate of polymerization of the adhesive systems. After polymerization, Bis-GMA shows two outstanding hydroxyl radicals, which allows water sorption and increases the risk of degradation [6,7]. Due to the moisture from the demineralized dentin, adhesive phase separation occurs, with Bis-GMA tending to migrate to the resin phase (hydrophobic) and HEMA to the aqueous phase (hydrophilic). The polymerization of the resin phase is more efficient than the aqueous phase, weakening the adhesive bond [3,7,23].

In case of phase separation, an improved photoinitiator system should be able to generate sufficient hydrophilic and hydrophobic radicals to improve the integrity of the adhesive interface. Under *in vivo* conditions, photopolymerization is usually carried out in the presence of endogenous water and other factors that limit the durability of the adhesive layer in dentin. Problems such as incomplete polymerization, partial infiltration in the demineralized dentin matrix, phase separation and enzymatic degradation of adhesive system and demineralized collagen have been reported [1,7].

Most current photoinitiator systems use a combination of camphorquinone with an aromatic amine co-initiator (EDMAB) and exhibit a highly hydrophobic profile that compromises their performance in humid environments. New photoinitiators, such as DMAEMA and DPIHP (hydrophilic profile), have been associated with formulations that could improve the degree of conversion in the presence of moisture [1,10].

Therefore, this study compared three photoinitiator systems, G2 formulation with hydrophobic characteristics, G3 with hydrophilic photoinitiators, and G4 with a combination of hydrophilic and hydrophobic components to verify the physical-mechanical profile of each adhesive model. The results of the present study support the hypothesis that the combination of hydrophilic and hydrophobic photoinitiators would affect the polymerization of adhesive systems based on the BisGMA/HEMA model, independently of the energy intensity applied during photopolymerization, similar to the previous study [24]. For the degree of conversion, the G4 formulation produced statistically better results compared with G3 (hydrophilic) and G2 (hydrophobic), as shown in Figure 1.

The influence of DPIHP on adhesive polymerization provided a higher degree of conversion to G3 and G4 in relation to G2 (which was not present). This showed that a combination of hydrophobic and hydrophilic photoinitiators can provide effective polymerization in an adhesive system. Thus, the first null hypothesis was rejected.

The beneficial effects of DPIHP were observed in another study with respect to the mechanical properties [7]. The authors reported that formulations with hydrophobic photoinitiators showed poor mechanical durability but that a combination of hydrophilic and hydrophobic co-initiators significantly improved these properties. Considering the model of flexural strength and modulus of elasticity according to ISO 4049, the results of this study did not show statistically significant differences in the flexural strength and modulus of elasticity in relation to type of photoinitiator, despite the greater mean values presented by G4 and G3 regarding G2 (Table I). The LED power density used for photopolymerization showed a significant effect on adhesive models. As a result, the second null hypothesis was rejected.

Different intensities of LED power density (550 mW/cm^2 and 1200 mW/cm^2) were evaluated to determine the influence of the light source on the presence of photoinitiators in the physical-mechanical properties of the adhesive models [11,12]. Statistically significant differences were observed for G2, which had a higher flexural strength, modulus of elasticity, and degree of conversion when photopolymerized with an LED intensity of 1200 mW/cm^2. A higher light intensity is required to obtain adequate mechanical properties because of the hydrophobic characteristics of adhesive systems. In the G3 and G4 groups, the presence of different photoinitiators reduced the influence of light, which may have practical value as clinicians may use defective or aging LED units.

Also, statistically significant differences were observed for the LED intensity factor for water sorption and solubility ($p < 0.05$). It was found that 1200 mW/cm^2 promoted higher sorption and greater solubility, which present highly hydrophilic characteristics. Probably, the higher intensity promoted faster polymerization of the resin monomers, reducing the gel phase of the material and favoring the degradation of the polymer matrix and the stability of the material. The results showed that LED intensity had a direct influence on the physical-mechanical properties of the adhesive models tested; however, the interaction may depend on the adhesive composition.

The results obtained for water sorption showed the best behavior for G2, with lower mean values when compared with those of G3 and G4 (Table I). Studies have suggested that the water sorption of adhesive systems is influenced by the composition and hydrophilicity of the material [9,25-27]. This fact was observed in this study, since the hydrophobic composition of G2 favored lower water sorption in relation to the adhesives with hydrophilic composition such as G3 and G4. Consequently, higher sorption promoted the greater solubility of the unreacted hydrophilic monomers [18,28] and monomers for G3 and G4 groups, relating the composition of the adhesive models to the effects of the presence of water in the oral environment. Although the combination of different photoinitiators improved the degree of conversion of the experimental adhesive models, the water sorption characteristics deteriorated.

The addition of other initiators to the adhesives impacted the propagation and termination steps of the reaction as seen by the changes in the values of *m* and *n*. However, its main effect is to increase the speed constant, which is one of the factors that most influence the degree of conversion.

The evaluation of the physical properties of sorption and solubility is relevant to the profile of adhesive systems [9], as both can lead to extensive chemical and physical processes with deleterious effects on mechanical properties such as flexural strength, modulus of elasticity, and degree of conversion. These can affect the deformation mechanisms [29] and the structure and function of the polymers [27,28].

The results of this study indicate that the selection and combination of photoinitiator components should be based on the polymerization behavior of the resin monomers under conditions of higher or lower moisture, as in the previous studies [5,7,11,12]. Further research should be conducted to find the optimal percentage of photoinitiator components that can provide a homogeneous and stable blend and maintain mechanical properties in the long term.

CONCLUSION

Within the limitations of this study, it can be concluded that the mechanical properties of the experimental adhesive systems were directly related to the type of photoinitiator and the LED density.

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Author's Contributions

TMS, SEPG: Conceptualization. TMS, NFP, SEPG: Methodology. RPM: Software. TMS, SEPG: Validation. TMS, TMBC: Investigation. TMS, SEPG: Resources. TMS, NFP, TMBC: Data Curation. TMS, SEPG: Writing – Original Draft Preparation. RPM, JPSJ, TMBC, SEPG: Writing – Review & Editing. NFP, RPM, JPSJ, TMBC: Visualization. SEPG: Supervision. TMS, SEPG: Project Administration.

Conflict of Interest

No conflicts of interest declared concerning the publication of this article.

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Regulatory Statement

This study was conducted in accordance with all the provisions of the local research subjects oversight committee guidelines and policies: no human or animals was used in this research.

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