Stomatologija, Baltic Dental and Maxillofacial Journal, 20: 119-24, 2018

Influence of light-curing unit on the network structure and mechanical properties of model resin cements containing diphenyliodonium compared with a commercial reference

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SUMMARY

Objective. To evaluate the effects of dyphenyliodonium hexafluorophosphate (DPI) on cross-link density (CLD), flexural strength (FS), and flexural modulus (FM) of a light-cured experimental resin cement compared with a commercial dual-cured cement.

Materials and methods. Bis-GMA combined with TEGDMA (50-50%) was used as resin matrix. Silanated barium-aluminum-silica glass was used as inorganic filler. Camphorquinone (CQ) – 1 mol%, 2-(dimethylamino)ethyl methacrylate (DMAEMA) – 2 mol%, and two concentrations of DPI (0 or 0.5 mol%) were used as the photoinitiator system. Two light-curing units (LCUs) were used (a single-peak (Radii-Cal) and a polywave (Bluephase)). The CLD was indirectly assessed in a softening test by Knoop hardness indentation; FS and FM were measured by means of a three-point bending test.

Results. DPI positively influenced Knoop hardness when compared with experimental resin without DPI. The flexural strength of experimental cements was lower than that found with Variolink II. The crosslinking density (obtained by reduction of Knoop hardness) of cement with 0.5% DPI was similar to that of dual – cured Variolink II.

Conclusions. DPI showed an improvement in some of the properties tested but was inferior to the commercial dual-cured resin cement. The LCUs had no influence on the flexural strength of the resin cements.

Key words: diphenyliodonium hexafluorophosphate; dental materials; resin cement; polymers.

INTRODUCTION

In the dental office, the use of resin cements has increased for the repair of indirect restorations and intrarradicular fiberglass posts. Dual-cure resin-based cements are the materials of choice to compensate for the reduced light irradiance promoted by thick ceramic restorations (1, 2), since this reduction can jeopardize the polymerization of light-cured materials (3).

Despite the light-dependence, light-cured resin cements have important advantages over dual- and self-cured materials, such as, longer working time, easy removal of excess, and better color stability (3-5). To improve the reactivity and, consequently, polymerization of light-cured cements, some studies have evaluated the use of onium salts in alternative photoinitiator systems (6-8). Diaryliodonium salts, with a complex metal halide as a weakly nucleophilic counter-ion, are efficient photoinitiators for cationic polymerization.

It is well-known that the degree of conversion (DC) has an important influence on the mechanical properties of dental resin composite and, consequently, its clinical performance, since dental composites must be properly cured to withstand the masticatory stress associated with sudden tempera-

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ture changes (9, 10). However, DC is not the only property responsible for the quality of the network structure. Polymers with similar DCs may present distinct crosslink density (CLD), due to differences in chain formation (11-13), and this can directly influence the chemical-physical properties of the resin materials. In crosslink systems, residual double bonds in the polymer formed do not necessarily indicate remaining monomer, but may also indicate pendant double bonds that are attached to the polymer network (14). Therefore, CLD is an important parameter to predict the network configuration and physical properties of the polymers (15). The CLD can be determined by glass transition temperature (Tg) or by softening of the polymer in ethanol, a well-established method used for the indirect evaluation of the CLD in dental polymers (15, 16).

This study evaluated the influence of single-peak and polywave LCUs on the CLD and flexural strength of model resin cements containing DPI, subjected to thermomechanical cycles. The tested hypothesis was that the addition of DPI and light source would have a positive influence on the properties evaluated.

MATERIALS AND METHODS

Preparation of experimental cements

A model resin formulation was prepared with 2,2-bis[4-(2-hydroxy-3- methacryloxyprop-1-oxy) phenyl]propane (Bis-GMA; Esstech Inc., Essington, PA, USA) and triethylene glycol dimethacrylate (TEGDMA; Esstech Inc.) at a 1:1 mass ratio. The photoinitiator system was composed of 1 mol% of camphorquinone (CQ;Esstech Inc.), 2 mol% of 2-(dimethylamino)ethyl methacrylate (DMAEMA; Sigma-Aldrich, St. Louis, MO, USA) as a co-initiator, and 0.1 mol% of hydroxybutyl toluene (BHT) as an inhibitor. From this base material, two formulations were obtained, one containing 0.5 mol% of DPI and one without the iodonium salt, used as control. The model cements were loaded with 60 w% of 0.7 μm silanated barium aluminum silicate glass filler particles (Esstech Inc.). All chemicals were used as received, without further purification. The commercial resin cement Variolink II (Ivoclar Vivadent AG, Schaan, Liechtenstein) was used in both light- and dual-cure modes as the commercial reference.

Two different light-curing units (LCUs) were used in the present study: a polywave unit (Bluephase G2®-BP; Ivoclar Vivadent AG, Schaan, Liechtenstein) and a single-peak unit (Radii-Cal-RC; SDI Limited, Victoria, Australia). Prior to the procedures, the irradiance of LCUs was measured with a power-meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel), and the energy dose was standardized at ≈14 J/cm^2.

Descriptions of the cements and LCUs are listed in Table 1.

Hardness and crosslink density evaluation

Eighty disc-shaped specimens (n=10) were made in a stainless steel mold (4.5 mm inner diameter x 1 mm thick). The resin cements were inserted into the mold in single increments and light-cured from the top, with a glass slide (0.15 mm thick) used to avoid the formation of an oxygen inhibition layer. Samples were dry-stored for 24 h in lightproof containers at 37°C, and then wet-polished with 1200-grit SiC paper. Five Knoop hardness measurements were taken on the irradiated surface by means of an indenter (HMV-2, Shimadzu, Tokyo, Japan), under a load of 50 g for 15 s. The initial Knoop hardness number (KHN) was recorded as the average of the five indentations for each specimen. Thereafter, the specimens were stored in absolute ethanol for 24 h at room temperature, and Knoop hardness was repeated with the same parameters. The crosslinking density (CLD) was estimated by the softening effect promoted by the ethanol by the decrease in Knoop hardness (13). Data were subjected to repeated-measures ANOVA followed by Tukey's test ($p<0.05$).

Table 1. Descriptions of the cements and LCUs used in the present study

Material	Description
Negative control	Bis-GMA, TEGDMA, 60wt% of filler particles with mean size of 0.7 μm.
Experimental cement	0.5 mol% of DPI, Bis-GMA, TEGDMA, 60wt% of filler particles with mean size of 0.7 μm.
Variolink II	Base: Bis-GMA, UDMA, TEGDMA, 73.4wt% of filler particles with mean size of 0.7 μm (Batch- N64549)
	Catalyst: Bis-GMA, UDMA, TEGDMA, dibenzoyl peroxide, 77.2wt% of filler particles with mean size of 0.7 μm (Batch-N72921)
Bluephase	Polywave LED source with 800 mW/cm^2 (18 s)
Radii-Cal	Single-peak LED source with 645 mW/cm^2 (22 s)

Flexural strength and flexural modulus

One hundred and 60 bar-shaped specimens (n=20) were prepared for a three-point bending test in a bipartite stainless steel matrix with internal dimensions of 25±2 mm (length) × 2±0.1 mm (width) × 2±0.1 mm (height). The specimens were irradiated on the top and bottom surfaces, with five light exposures overlapping the previously irradiated section with half the diameter of the light guide, according to ISO 4049-2000, and stored at 37ºC (±1ºC) for 24 h. The specimens were wet-polished with 1200-grit SiC paper and their dimensions were measured with a digital caliper (Mitutoyo Co., Kawasaki, Japan). Prior to the flexural strength test, the specimens of each group were randomly divided. Half were simultaneously subjected to 2,000 thermal cycles with distilled water varying in temperature from 5±2ºC to 55±2ºC and 100,000 mechanical cycles with a frequency of 2 Hz and vertical load of 48 N at the center of the specimen (thermomechanical cycling machine ER 37000, ERIOS, São Paulo, SP, Brazil) while others were stores in distilled water at 37ºC (±1ºC). Three-point bending tests were performed in a universal testing machine (Instron 4411, Instron Corp., Canton, MA, USA) with a crosshead speed of 1 mm/min until failure. The flexural strength (MPa) and flexural modulus (GPa) were provided by the materials testing software Bluehill 2® (Instron Corp.) installed on a computer connected to the universal testing machine and supplying the values for flexural strength and flexural modulus at the end of each test sample. The flexural strength and modulus data were subjected to three-way ANOVA and Tukey's post-hoc test, and the analysis of KHN before ethanol immersion was done by two-way ANOVA and Tukey's test. All statistical analyses were performed at a 5% level of significance.

RESULTS

Knoop hardness and crosslink density

The light-curing unit promoted statistically significant differences in KHN for all resin cements, except the dual form of Variolink II (Table 2). When the cements were compared, the same pattern was observed for the LCUs, with the highest value for dual-cured Variolink, followed by light-cured Variolink and Exp 0.5% DPI, with Exp 0% DPI having the lowest value.

In terms of the CLD, when the LCUs were compared, a significant difference was observed only for Exp 0% DPI (Table 3). When the resin cements were evaluated, light-cured Variolink showed a greater hardness decrease after ethanol immersion. Dual Variolink and Exp 05% DPI showed intermediate reduction, while the experimental cement without DPI had the least reduction in hardness after ethanol immersion.

Flexural strength and flexural modulus

The results of three-way analysis of variance (ANOVA) for the experimental conditions presented significant differences for thermomechanical fatigue and resin cement factors (Table 4). The factor LCU and other interactions between factors (fatigue and cement) were not statistically significant ($p>0.05$). Thermomechanical fatigue conditions decreased the flexural strength results significantly for both LCUs and for all cements. The commercial resin cement, both light- and dual-cured, showed higher flexural strength compared with that of the experimental cements.

A statistically significant interaction among cements, light sources, and fatigue was detected for flexural modulus (Table 5; $p=0.00003$). Thus, the interaction of each factor with the levels of the others was demonstrated, and this interaction was examined by the Tukey test.

Table 2. Basic demographic information among the study groups

Cements	Radii-Cal	Bluephase
Light-cured Variolink II	37.35 (2.49) Bb	43.26 (2.64) Ab
Dual-cured Variolink II	59.04 (2.64) Aa	62.37 (2.11) Aa
Exp 0% DPI	14.21 (0.96) Ad	11.79 (0.88) Bd
Exp 0.5% DPI	32.18 (2.37) Ac	29.73 (1.34) Bc

Different capital letters in the same line and small letters in the same column indicate statistically significant differences ($p<0.05$).

Table 3. Mean values for the percentage of hardness decrease after ethanol storage

Cements	Radii-Cal	Bluephase
Light-cured Variolink II	62.0 (5.4)% Aa	63.3 (3.3)% Aa
Dual-cured Variolink II	42.4 (5.3)% Ab	48.2 (3.5)% Ab
Exp 0% DPI	32.9 (9.1)% Ac	22.7 (5.9)% Bc
Exp 0.5% DPI	48.3 (3.95) %Ab	45.0 (2.49)% Ab

Different capital letters in the same line and small letters in the same column indicate statistically significant differences ($p<0.05$).

Flexural modulus decreased after fatigue only for experimental cements containing 0.5 mol% DPI photoactivated by Radii. When light-cured with BP, both experimental resins had reduced flexural modulus (Table 5). Without fatigue, Exp 0% DPI had the lowest modulus for specimens irradiated by Radii. When BP was used, light-cured Variolink had the lowest modulus.

After fatigue, a significant reduction in the flexural modulus of experimental resins was observed for specimens cured by Radii as well as BP, except for Exp 0% DPI with Radii, with flexural modulus of experimental resins being statistically significantly lower than that of the commercial references.

DISCUSSION

The hypothesis investigated in this study was partially rejected, because DPI showed a positive influence on the properties of the model resin cements evaluated. However, the influence of LCUs was limited to Knoop hardness, flexural modulus, and ethanol softening, causing no effects on the flexural strength of the resin cements tested.

Hardness can be used as an indirect assessment of degree of conversion (DC), as has been demonstrated in several studies (17, 18). According to previous studies, a higher DC of dual-cured cements is expected compared with that of light-cured cements, especially when both cements are properly photoactivated (19), with the results of the present study corroborating previous findings. Similarly, the presence of DPI in experimental cement confirms the results of previous studies (6-8), showing higher polymerization for the cement with onium salt. Generally, Variolink II presented higher hardness than the model cements evaluated. The better performance of the commercial cement can be credited to higher filler load content (73.4 to 77.2 wt%) vs the 60 wt% contained in the model cements, as well as to the good performance of the dual activation system of the commercial reference in both forms.

Softening after ethanol storage was observed for all resin cements activated for both LCUs. This behavior occurred as a consequence of ethanol penetration into the polymeric network, causing expansion of the polymer network, releasing unreacted monomers and causing the breakup of linear chains of the polymer (14, 20). This expansion is facilitated when the crosslink density is low, because solvent can break the secondary links of structure, but not the crosslink itself (13). The significant presence of crosslink reduces the free volume between

Table 4. Means (SD) for flexural strength in MPa

Light sources	Cements	Fatigue		NO
		–	+	
Radii-Cal	Light-cured Variolink II	128.83 (20.74)	111.52 (24.49)	a
	Dual-cured Variolink II	123.76 (19.15)	104.77 (16.74)	a
	Exp 0% DPI	95.92 (5.19)	92.56 (9.43)	b
	Exp 0.5% DPI	104.30 (17.61)	70.65 (24.78)	b
		A	B	
Bluephase	Light-cured Variolink II	118.01 (24.07)	125.00 (10.14)	a
	Dual-cured Variolink II	111.47 (16.74)	96.62 (32.85)	a
	Exp 0% DPI	103.43 (14.53)	60.74 (12.33)	b
	Exp 0.5% DPI	114.03 (12.96)	71.54 (15.81)	b
		A	B	

Different capital letters compare fatigue, while lower-case letters compare cements. + – performed. – – not performed.

Table 5. Means (SD) of flexural modulus in GPa

Light Sources	Cements	Fatigue	
		–	+
Radii-Cal	Light-cured Variolink II	6.32 (0.54) Ba	6.33 (0.37) Ba
	Dual-cured Variolink II	7.5 (0.29) Aa	7.51 (0.46) Aa
	Exp 0% DPI	5.00 (0.18) Ca	5.36 (0.23) Ca
	Exp 0.5% DPI	6.84 (0.21) ABa	5.36 (0.23) Cb
Bluephase	Light-cured Variolink II	6.2 (0.42) Ca	6.66 (0.33) Aa
	Dual-cured Variolink II	7.54 (0.85) ABa	7.31 (0.21) Aa
	Exp 0% DPI	7.32 (0.57) Ba*	4.87 (0.19) Bb
	Exp 0.5% DPI	8.38 (0.53) Aa*	5.4 (0.23) Bb

Means followed by the same letters are not statistically significantly different (3-way ANOVA/ Tukey test. α=5%). Capital letters compare cements under each light source/fatigue condition. Lower-case letters compare fatigue levels within each light source/cement condition. * (asterisks) represent significant differences between light sources within each level of cement/fatigue.

polymer chains and decreases polymer plasticizing. The lowest softening of the commercial cement possibly indicates higher CLD compared with that in experimental materials. The better performance of Variolink II can be attributed to the more complex polymer structure, due to the presence of UDMA added to Bis-GMA and TEGDMA.

Studies have shown the cyclization of TEGDMA molecules in methacrylate networks (21). Although the presence of the pendant double bonds results in higher DC, it causes the inhibition in the formation of crosslinks, resulting in a heterogeneous polymer with more linear chains and greater porosity in the network (22, 23). High concentrations of TEGDMA, such as that contained in the experimental cements studied, tend to accentuate this effect (24), making these cements more susceptible to softening in ethanol. However, the greater number of free-radicals produced by DPI in Exp 0.5% DPI produced higher initial KHN and CLD compared with those of the group without DPI, even in this adverse condition.

For flexural strength, the same behavior was observed for both LCUs. The commercial reference had the best values, probably due to its different composition and the factors related to cyclization, cited above. DPI had a positive influence on the flexural strength of the model cement, corroborating the results of a previous study (6). In the analysis of all tests, this influence appeared to result from higher DC, as demonstrated in previous studies that used cements with the same composition (6, 25), and confirmed the hardness results found in this study, as well as the higher CLD obtained by the cement containing DPI.

The flexural moduli of the commercial cements were not influenced by the thermomechanical cycles for both LCUs, contrary to those of the model cements, which were negatively influenced and presented different behaviors depending on the LCU type. The wavelength spectrum of Bluephase (385-515 nm) compared with that of Radii-Cal (440-480 nm) resulted in a stiffer polymer for the model cements. However, this effect on the flexural modulus of the experimental cement was not capable of avoiding the post-fatigue reduction in this property. The results for the Exp0%DPI group compared with those for the same non-cycled material were not significant and did not represent an improvement in the material properties, especially when the flexural strength values of this group were considered, because although cycled Exp0%DPI presented a higher flexural modulus, its flexural strength was significantly lower than that of the non-cycled group.

One objective of this study was to verify whether the LCUs would influence the polymerization of the resin cements. Although the polywave LED emits light with a wavelength spectrum between 385 and 515 nm, in general it did not improve the properties of the resin cements compared with the single-peak LED, with a narrow spectrum of wavelength (440-480 nm). Despite the broad spectrum of wavelength of the polywave LED, the single-peak LED had similar efficacy, probably due to the coincident peak with the camphorquinone activation, optimizing the results.

The results of the present study showed a negative influence of thermomechanical cycles and ethanol dilution on the properties of the resin cements. In contrast, a positive influence of DPI on the reactivity of the model resin cements was observed.

CONCLUSIONS

Based on the findings of this study, we can conclude that:

- DPI had a positive influence on the properties of the model resin cements and worked with camphorquinone as a co-initiator.
- The commercial cements presented better performance than did the experimental materials tested.
- The light source had no influence on the flexural strength of the resin cements.

CONFLICT OF INTEREST

The authors state no conflict of interest.

ACKNOWLEDGEMENTS

First author is grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the grant of the scholarship.

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Received: 04 10 2017
Accepted for publishing: 25 12 2018