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Influence of diphenyliodonium hexafluorophosphate on the bond strength and mechanical properties of model resin cements

Murilo Baena Lopes [a,*], Angelo Marcelo Tirado dos Santos [a], Diogo Coelho [a], Alcides Gonini Júnior [a], Fabrício Aulo Ogliari [b], Rafael Ratto de Moraes [b]

[a] University of North Parana, Jd. Piza, Londrina, PR 86046-230, Brazil
[b] Federal University of Pelotas, Centro, Pelotas, RS 96010-560, Brazil

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ABSTRACT

The influence of diphenyliodonium hexafluorophosphate (DPI) on the mechanical properties and bond strength of resin cement to the intraradicular dentin was evaluated. A model BisGMA/TEGDMA-based luting composite containing camphorquinone and ethyl 4-(dimethylamino)benzoate was modified by incorporating DPI at 0 (control), 0.5, 1, or 2 mol%. Flexural strength (FS) and modulus (E_f) were evaluated by a 3-point bending test. The bond strength to dentin was evaluated by push-out testing of glass-fiber posts luted into bovine roots, which were sectioned into cervical, middle, and apical thirds. Polymerization stress (PS) was analyzed using photoelastic analysis. Data were statistically analyzed at $p<0.05$. No significant differences in FS were observed. The 2 mol% group showed higher E_f than the control and 0.5 mol% groups. The control group showed higher PS than the 1 and 2 mol% groups. The control group showed higher bond strength in the cervical region than the other groups. The use of cements with DPI might be promising for the luting of fiber posts due to lower stress generation at the bonding interface.
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1. Introduction

Endodontic posts are commonly used in dentistry to support the restoration of teeth with great loss of structure, but there are some controversies about the actual role of the posts [1]. Although it had been believed that metallic cast posts could reinforce pulpless teeth [2], it is known that the purpose of endodontic posts is to support the crown restoration [3,4]. The use of glass-fiber posts associated with resin cement is an effective restorative procedure that can be used even when the root canal is wide and fragilized [5,6].

The polymerization of dental resin cements can occur by light and/or redox mechanisms [7]. Light-activated materials have a disadvantage during post luting, because it is difficult for light to reach the deeper regions of the root canal. Even with prolonged light exposure, adequate activation of the luting material in the root medium and apical thirds cannot be guaranteed, due to the distance from the tip of the curing unit and the reduction in light irradiance owing to scattering and absorption effects [8].

To improve light activation, the reactivity of the resin cement can be increased by using a more effective photoinitiator system to improve the polymerization potential. From this perspective, onium salts such as the diphenyliodonium hexafluorophosphate (DPI) have shown a good response when used as coinitiators in dental adhesives [9,10]. When associated with a coinitiator, camphorquinone (CQ) produces a synergic effect that can improve polymer conversion [11]. DPI is inactive without a photosensitizer [12]; however, as a complex metallic halide, DPI may act as counter ion improving the free-radical polymerization of dimethacrylates [9]. During light exposure, the low bond energy between the iodine and the carbon allows decomposition of the excited iodonium to an aryliodo radical cation, a reactive aryl radical, and an anion [13]. Iodonium salt is activated at a wavelength below 300 nm; however, its combination with CQ, which absorbs light between 400 and 500 nm [14], could promote iodonium decomposition, allowing the iodonium-CQ system to generate free radicals [9,15].

The purpose of the present study was to evaluate the influence of the incorporation of DPI salt on the mechanical properties and bond strength of experimental resin cements to intraradicular dentin. The polymerization stress (PS) generated between the root canal and the cement was also predicted through photoelastic stress analysis.

2. Materials and methods

2.1. Formulation of the resin cements

A base comonomer blend was prepared with a 1:1 mixture of bisphenol-A glycidyl dimethacrylate and triethyleneglycol dimethacrylate (Esstech Inc., Essington, PA, USA). The monomers were used

* Correspondence to: University of North Parana, School of Dentistry, Rua Marselha, 183-Jd. Piza, Londrina, PR 86041-100, Brazil. Tel.: +55 43 3371 7820; fax: +55 43 3371 7834.
E-mail address: baenalopes@gmail.com (M. Baena Lopes).

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without additional purification. An initiator system was added that contained 1 mol% of CQ (Esstech Inc., Essington, PA, USA) and 2 mol% of ethyl 4-(dimethylamino)benzoate (Sigma-Aldrich, St. Louis, MO, USA). As an inhibitor, 0.1 mol% of butylated hydroxytoluene (Sigma-Aldrich, St. Louis, MO, USA) was added to minimize or prevent spontaneous polymerization of the cements. The DPI salt (Sigma-Aldrich, St. Louis, MO, USA) was added in the following concentrations according to each group: 0 (control group), 0.5, 1, or 2 mol%. Silanized 4 μm barium silicate filler particles (Esstech Inc., Essington, PA, USA) were added at 60 wt% load. The cements were stored in amber flasks and homogenized at low rotation in a mechanical mixer.

2.2. Flexural strength (FS) and modulus (E_f)

Ten bar-shaped specimens (12 × 2 × 2 mm) were prepared for each group using a metallic mold. The cement was inserted into the mold, and a Mylar strip was positioned over and under the specimen. The upper surface of the specimen was photoactivated twice for 40 s at 600 mw/cm^2 irradiance using a quartz-tungsten-halogen curing unit (Vip; Bisco, Schaumburg, IL, USA) to assure the light reach the whole specimen, as the light guide tip had a 10 mm diameter. Specimens were stored in at 37 °C. A 3-point bending test was carried out after 24 h until fracture in a mechanical testing machine (DL2000; Emic, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/min, with a distance of 10 mm between the supports. E_f (GPa) was calculated by the software of the testing machine from 20 to 50% of the linear portion of the load-displacement trace.

2.3. Bond strength by push-out test

Forty bovine incisors were cleaned with a periodontal curette, and their crowns were removed at the cervical limit. Endodontic treatment was carried out and the root was filled with gutta-percha (Dentsply, Petrópolis, RJ, Brazil) and endodontic sealer (Endofill; Dentsply-Caulk, Milford, DE, USA). A sequence of 2–5 largo drills (Dentsply Maillefer, Ballaiges, Switzerland) was used to enlarge the root canal, according to post manufacturer's instructions (Reforpost, Angelus, Londrina, PR, Brazil), which left 4 mm unprepared near the apex. A 37% phosphoric acid solution (3 M Espe, St Paul, MN, USA) was applied to the root canal for 30 s. The canal was rinsed and dried, and one layer of adhesive was applied (Adper Single Bond 2; 3 M Espe, St Paul, MN, USA). The solvent was gently evaporated using compressed air and the adhesive was photoactivated for 20 s. Silane (Silano, Angelus, Londrina, PR, Brazil) was applied to the post and left undisturbed for 1 min.

The cement was inserted into the root canal with a lentulo spiral drill (Dentsply Maillefer, Ballaiges, Switzerland), and the post was positioned into the prepared root. Photoactivation was performed for 40 s. After 24 h of storage in distilled water at 37 °C, the root was sectioned into three slices of 4 mm in length (cervical, medium, and apical thirds), and the unprepared part of the root was removed. The slices were positioned in the mechanical testing machine and the push-out test was conducted at a crosshead speed of 5 mm/min until dislodgment of the post from the root canal. Ten teeth were tested for each group. Push out bond strength values were calculated (MPa) by dividing the load need to dislodge the post (N) by the bonded area (trunk cone shape – mm^2).

2.4. Polymerization stress (PS) by photoelastic analysis

Photoelastic resin rings (PL2; Vishay Measurements, Raleigh, NC, USA) were prepared using a cylindrical mold (2 mm thickness), with 20 mm diameter for the rings and 5 mm diameter for the internal orifice. The inner surface was sandblasted with 50 μm-alumina particles. The cement was inserted using a lentulo spiral drill into the photoelastic resin-extensor system. An 8-mm-high extensor was placed on the photoelastic ring to increase the distance from the curing unit used to activate the cement to simulate the apical area of the root. The specimens were light activated for 40 s (n=10 per group). Analysis was performed in a polariscope (PhotoStress LF/Z-2; Vishay Measurements, Raleigh, NC, USA). Two diametrically opposed points with 1 mm distance from the cement were marked in the photoelastic ring. The material properties of the photoelastic resin and the test specimen were inserted into the PhotoStress PSCalc software (Vishay Measurements, Raleigh, NC, USA). With the model 832 Electric Compensator (Vishay Measurements, Raleigh, NC, USA) and the PSCalc computer software, measurement and calculation of stress/strain values were acquired. At the point of measurement, an initial no load reading was made with the compensator. A second reading was then made after the cement polymerization. After this, null balance readings were made and the numerical information was electronically transferred to a computer configured with PhotoStress PSCalc software, which made all the calculation and the PS data (MPa) based on the information provided by the manufacturer [16].

2.5. Statistical analysis

Data from each test were separately analyzed using the Kolmogorov-Smirnov normality test, followed by one-way Analysis of Variance and Tukey's *post hoc* test. The root thirds were analyzed separately in the push out test. The 5% significance level was set for all analyses.

3. Results

Results FS, E_f and PS are presented in Table 1. For FS, no significant differences were observed among the groups. The 2 mol% group showed a significantly higher E_f than the control and 0.5 mol% groups, which did not differ between each other. The E_f results in the 1 mol% group did not differ from those in the 2 and 0.5 mol% groups. For PS, the control group showed significantly higher values than the 1 and 2 mol% groups. The 0.5% group did not differ from any group.

Results for bond strength to dentin are presented in Table 2. The control group showed a significantly higher bond strength in the cervical area than the other groups, which did not differ

Table 1
Means (standard deviations) for flexural strength (FS), flexural modulus (E_f) and polymerization stress (PS).

	DPI molar concentration			
	0 (control)	0.5%	1%	2%
FS (MPa)	94 (11)^a	95 (16)^a	95 (17)^a	108 (14)^a
E_f (GPa)	4.2 (0.2)^c	4.9 (0.5)^{bc}	5.3 (0.3)^{ab}	5.4 (0.2)^a
PS (MPa)	5.1 (2.9)^a	3.4 (3.1)^{ab}	2.3 (2.6)^b	2.5 (3.10)^b

In each line, distinct letters indicate significant differences ($p < 0.05$).

Table 2
Means (standard deviations) for push out bond strength, MPa.

Root third	DPI molar concentration			
	0 (control)	0.5%	1%	2%
Cervical	158 (74)^a	79 (42)^b	63 (30)^b	72 (45)^b
Middle	75 (41)^a	71 (57)^a	41 (15)^a	69 (22)^a
Apical	49 (16)^a	47 (25)^a	31 (8)^a	76 (37)^a

In each line, distinct letters indicate significant differences ($p < 0.05$).

between each other. For the middle and apical thirds, there were no statistically significant differences between the groups.

4. Discussion

The most common photoinitiator used in dental resin is CQ associated with coinitiators. CQ is an α-dicarbonyl compound that becomes a reactive species after light absorption and photolysis [17]. CQ is a Norrish Type-II photoinitiator, which means that a second component (coinitiator, usually an amine) must be used for effective radical generation [18]. The binary CQ-amine system exhibits two main limitations for use in dentin adhesive formulations [19]. First, a certain level of phase separation exists [12] due to the water trapped within the hybrid layer [20]. Because CQ exhibits hydrophobic behavior, it tends to migrate to the hydrophobic domain sometimes without effectively activating the hydrophilic phase [21]. Second, this system tends to be influenced by the acidity of the reaction medium, which may interfere with the polymerization of self-etch adhesives.

The solubility of the iodonium salt is relatively unaffected by changes in the hydrophobicity of the medium. DPI is expected to be distributed approximately equally in both the hydrophobic and hydrophilic phases. The inclusion of iodonium salt as a third component in photoinitiator systems is generally associated with improvements in the polymerization potential and mechanical properties of dimethacrylate-based polymers [9,12,17]. As an electron acceptor, iodonium salt regenerates the photosensitizer molecules by replacing inactive terminating radicals with active phenyl-initiating radicals, and also generates additional active phenyl radicals [22].

Water present in the tooth, saliva, and oral cavity greatly hinders adhesion in the oral environment. Dentin is composed of approximately 10 wt% water and 20 wt% organic components [23]. Although water inhibits the polymerization of methacrylates, the use of iodonium salt increases the compatibility of these monomers with the aqueous oral environment [15]. The improvement of adhesion by iodonium salt may be explained by the production of an active phenyl radical from the regeneration of the original CQ, which could increase the compatibility between the monomers and the initiators in the presence of water [9]. Although no significant differences were found among the groups in terms of the FS, the E_f of the cements with 1 and 2 mol% DPI was higher, indicating improvement in the polymer properties by addition of the salt. Incorporation of DPI above 2 mol% was not tested, because these samples showed deficient behavior in pilot tests in terms of other properties.

Dental resin cements include self-activated, photoactivated, and dual-activated versions. Self-cured materials may show higher bond strength to intraradicular dentin compared to photoactivated cements [1]. However, this advantage usually appears in the apical region [11], because it is difficult for the light to reach the lower regions of the root canal. Control of the rapid polymerization of self-curing composites is difficult to obtain, as is the correct application of adhesive systems within the canal space [24]. The use of a dual-cured adhesives might improve the bond strength between the root canal and the cement by improving the monomer conversion in the apical region where the light barely reaches [25].

The polymerization shrinkage of the cement is an inherent function of methacrylates [26]. Shrinkage of the cement in contact with the canal walls generates stress at the bonded interface. In the present study, this stress, which was analyzed by PS analysis, indicated that the presence of DPI interfered with the degree of C=C conversion without affecting the other mechanical properties. In the pus-out test, the incorporation of DPI decreased the bond strength in the cervical region compared to the control group; however, the bond strength values were consistent among all the other thirds. This result could be an advantage, because the masticatory forces would be distributed in a more uniform manner along the entire root. Finite analysis could be used to reveal this important aspect of the adhesion in that respect.

Evaluation of the PS analysis revealed that the 1 and 2 mol% DPI groups showed less stress than the control material. This reduced stress could be due to lower C=C conversion in the bottom area. The presence of DPI may have affected the light transmission to the bottom of the specimen due to the faster polymerization in the upper area, increasing light absorption and scattering effects, and restricting the monomer mobility in the reaction environment. This could also explain the higher bond strength at the cervical area observed for the control material, which probably had a less active early stage polymerization [27] and less PS generated at the upper area than the modified materials. However, the overall stress state for DPI-containing materials was lower compared with the control group. Although the DPI did not appear to affect the strength of the materials or their bond strength to root canals, the lower and probably more evenly distributed PS may be mentioned as an advantage for DPI-containing materials over the non-modified cement. Further investigation on DPI-modified resin luting agents is, however, necessary.

5. Conclusion

Judicious incorporation of DPI to resin luting agents reduced the polymerization stress without affecting the other evaluated properties. The use of cements with DPI might be promising for the luting of fiber posts.

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