Bonding orthodontics brackets to enamel using experimental composites with an iodonium salt


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SUMMARY
OBJECTIVES: This study investigated whether the addition of diphenyliodonium chloride (DPC) to experimental resin bonding agents would allow fixation of brackets to enamel using shorter light exposure times.

METHODS: Photoactivated dimethacrylate-based composites were prepared containing DPC molar concentrations of 0 (control), 0.5 (R05), or 1 per cent (R1). Metallic brackets were bonded to bovine incisors and the bond strengths were evaluated using a shear test. In total, 18 groups were tested (n = 15 per group) defined by three bonding materials (control, R05, or R1), three light-activation time (8, 20, or 40 seconds), and two storage periods (10 minutes or 24 hours). The adhesive remnant index (ARI) was scored under magnification. Data were statistically analysed at a 5 per cent significance level.

RESULTS: At 10 minutes, the control composite showed lower bond strengths than the DPC-modified bonding agents for all light-activation times. Differences in bond strengths between both DPC-modified agents were not significant. Lower bond strengths at 10 minutes were generally observed for groups light activated for 8 seconds compared with groups light activated for 20 and 40 seconds. At 24 hours, no significant differences were observed among the light-activation times. The bond strengths at 24 hours were higher than the bond strengths at 10 minutes for all groups. A predominance of ARI scores 2 and 3 was generally observed.

CONCLUSION: The use of a ternary photoactivation system containing an iodonium salt in bonding composites may allow bonding brackets to enamel using reduced light exposure times.

Introduction

Light-cured materials are routinely used for bonding orthodontic brackets. The main advantage of light-cured materials is the set on demand, which offers to the clinician sufficient time to position the brackets accurately before photoactivation. Complete polymerization may not be feasible when considering the light exposure times used clinically unless extremely high light irradiance is used (Staudt et al., 2006); however, adequate early polymerization is necessary for the bonding material to resist debonding when the initial archwire is placed.

The polymerization of methacrylate-based resin materials requires sufficient light irradiance and a suitable wavelength (between 400–500 nm) to activate the photosensitizer camphorquinone (CQ), which reacts with a reducing agent (amine, co-initiator) to trigger the curing mechanism (Rueggeberg, 1999; Stansbury, 2000). A major clinical drawback of light-cured materials is that light exposure times between 20 and 40 second are required to bond each bracket, according to the manufacturers’ instructions. Long curing times are uncomfortable for patients, impractical with children, and have disadvantages for the clinician.

Methods used in an endeavour to reduce the light-curing time necessary for bonding orthodontic brackets are reported in the literature (Lalani et al., 2000; Oesterle et al., 2001; Sfondrini et al., 2001; Staudt et al., 2005). Among these, the most popular method is the use of light-curing units with high irradiance levels (e.g. xenon plasma arc and argon lasers), which may provide sufficient light energy within reduced exposure times. However, these units are usually not cost-effective. An alternative is the development of more effective photoinitiator systems for orthodontic bonding agents. The use of an iodonium salt has shown satisfactory results for dental adhesives (Ogliari et al., 2007) when used with CQ. The theory is that the CQ, after excited by light...
irradiation, can promote decomposition of the iodonium salt, enhancing the polymerization kinetics by allowing generation of free radicals suitable for polymerization (Odian, 2004; Ogliari et al., 2007).

Another variable is the time for placement of the orthodontic archwire. Bond strength tests are usually carried out 24 hours after the bonding procedures. This time period, however, does not reflect what occurs in the clinical practice, when the archwire is generally placed minutes after the bracket is bonded. Some studies have shown that the bracket bond strength may increase over a short time period of 24 hours compared with times such as 5, 10, and 30 minutes after the bonding procedure (Bishara et al., 1999; Correr Sobrinho et al., 2002; Yamamoto et al., 2006; Oesterle and Shellhart, 2008). The initial bond strength of brackets is important because orthodontists insert the archwire into the slot of the brackets from 10 to 15 minutes after bonding. There is no consensus, however, about the minimum time required to wait before loading the bracket; times from 5 minutes to 24 hours have been suggested (Oen et al., 1991; Millett and Gordon, 1994; Oesterle et al., 1995; Ching et al., 2000).

The purpose of this study was to investigate whether the addition of an iodonium salt to experimental bonding composites would allow bonding orthodontic brackets to enamel using shorter light exposure times. Two storage periods after bonding were tested: 10 minutes and 24 hours. The hypotheses tested were as follows: 1. higher bond strengths would be observed for materials containing the iodonium salt; 2. higher bond strengths would be detected for specimens light activated for longer periods; and 3. the bond strengths would be higher for groups tested after 24 hours.

Materials and methods

Experimental design

This in vitro study involved a 3 × 3 × 2 factorial design (n = 15). The factors under evaluation were: bonding material [experimental composites with 0 (control), 0.5, or 1 per cent molar of iodonium salt], light-activation time (8, 20, or 40 seconds), and storage period (10 minutes or 24 hours). The response variable was shear bond strength of orthodontic brackets to enamel. Secondary response variable was adhesive remnant index (ARI) of the debonded specimens.

Formulation of the experimental bonding composites

A model dimethacrylate comonomer blend was obtained by mixing the monomers bisphenol-A glycidyl dimethacrylate (Esstech, Essington, Pennsylvania, USA) and triethylene glycol dimethacrylate (Esstech) at a 3:1 mass ratio. The photoinitiating system consisted of CQ (Esstech) and ethyl-4 dimethylamino benzoate (Sigma-Aldrich, Milwaukee, Wisconsin, USA), each added at a molar concentration of 1 per cent. Butylated hydroxytoluene (0.1 mol per cent) was added as radical scavenger (Moraes et al., 2010). In order to obtain three different experimental bonding materials, diphenyliodonium chloride (DPC; Sigma-Aldrich) was added at molar concentrations of 0 (control), 0.5 (R05), or 1 per cent (R1). The blends were loaded with a 20 per cent mass of silanated silica nanofillers with 7 nm average particle size.

Bonding procedures

Two-hundred seventy bovine incisors were used. The teeth were embedded in polyvinyl chloride tubes leaving the vestibular face perpendicular to the horizontal axis. The teeth were cleaned using a rotational brush with non-fluoridated pumice–water slurry and divided into 18 groups (n = 15) according to the bonding material, light-activation time, and storage period tested, as shown in Table 1. The middle third of the vestibular face of each tooth was etched with 35 per cent phosphoric acid gel (Dentsply Caulk, Milford, Delaware, USA) for 30 seconds, rinsed with air–water spray for 30 seconds, and dried with air for 30 seconds. A layer of a two-step, etch-and-rinse adhesive (Single Bond 2; 3M ESPE, Saint Paul, Minnesota, USA) was applied, dried with air for 5 seconds, and photoactivated for 20 seconds using a light-emitting diode curing unit (UltraLume 5; Ultradent, South Jordan, Utah, USA) with 1100 mW/cm² irradiance. Stainless standard maxillary incisor metallic brackets (Morelli; Sorocaba, Sao Paulo, Brazil) were bonded to the teeth. The brackets were positioned, seated firmly on the tooth surface, and excess resin was removed using a microbrush. Light activation was carried out with one exposure on each of the four sides of the bracket. Total exposure times of 8, 20, or 40 seconds were tested.

Table 1  Description of the groups tested in the study (n = 15). DPC, diphenyliodonium chloride.

<table>
<thead>
<tr>
<th>Bonding material</th>
<th>Light-activation time (s)</th>
<th>Storage time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no DPC)</td>
<td>8</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24 h</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10 min</td>
</tr>
<tr>
<td>R05 (0.5% molar of DPC)</td>
<td>8</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24 h</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10 min</td>
</tr>
<tr>
<td>R1 (1% molar of DPC)</td>
<td>8</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24 h</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h</td>
</tr>
</tbody>
</table>
**Shear bond strength test and failure analysis**

The shear testing was performed 10 minutes or 24 hours after the bonding procedures using a mechanical testing machine (model 4411; Instron, Canton, Massachusetts, USA). A mounting jig was used to align the tooth-bracket interface parallel to the testing device. The shear load was applied using a knife-edged rod at a crosshead speed of 1 mm/minute. Shear bond strength values were calculated in megapascal. After debonding, the tooth and bracket surfaces were examined with a stereomicroscope under magnification (×8). The ARI was used to classify the failure modes: Score 0, no bonding resin remained on the tooth; Score 1, less than half of the bonding resin remained on the tooth; Score 2, more than half of the bonding resin remained on the tooth; Score 3, all bonding resin remained on the tooth, along with a distinct impression of the bracket mesh.

An additional set of 10 specimens for materials control, R05, and R1 photoactivated for 20 seconds and tested after 24 hours was obtained in order to compare their bond strengths with a commercially available orthodontic bonding composite tested as a reference (Transbond XT; 3M Unitek, Monrovia, California, USA), which was used according to the manufacturer’s directions.

**Statistical analysis**

Bond strength data for each storage time were separately submitted to two-way analysis of variance (ANOVA) (bonding material × light-activation time) followed by the Student–Newman–Keuls’ method for pairwise multiple comparisons. Comparisons between 10 minutes and 24 hours for each bonding material–light-activation time combination were carried out using the Student’s t-test when homoscedasticity was achieved; otherwise, the Mann–Whitney rank sum test was used. Comparison between Transbond XT and the experimental materials (additional set of specimens) was carried out using one-way ANOVA and Student–Newman–Keuls’ test. ARI scores were analysed by ANOVA on Ranks and Dunn’s test. A 5 per cent significance level was set for all analyses.

**Results**

Results for shear bond strength are shown in Table 2. For the analysis at 10 minutes, the factors ‘bonding material’ and ‘light-activation time’ were both significant (P < 0.001), whereas the interaction between the factors was not significant (P = 0.355). At 24 hours, the factor bonding material was significant (P = 0.001), whereas the factor light-activation time (P = 0.108) and the interaction between the factors (P = 0.928) were not significant.

At 10 minutes, the control composite showed significantly lower bond strengths than the other bonding agents for all light-activation times (P ≤ 0.05). At 24 hours, R1 yielded significantly higher bond strength than the control composite when light activated for 20 seconds (P = 0.036), whereas no other significant differences were detected (P ≥ 0.059). Differences in bond strengths between both DPC-modified agents (R05 and R1) were not significant, irrespective of the light-activation time or storage period (P ≥ 0.268).

Comparing the light-activation times, significant lower bond strengths at 10 minutes were observed for groups light activated for 8 seconds compared with groups light activated for 20 (P ≤ 0.014) and 40 seconds (P ≤ 0.004), except for R05 (P ≥ 0.137). At 24 hours, no significant differences were observed among the light-activation times, irrespective of the bonding material (P ≥ 0.124). The bond strengths at 24 hours were significantly higher than the bond strengths at 10 minutes for all groups, irrespective of the bonding material or the light-activation time (P ≤ 0.031).

Results for failure analysis (ARI scores) are shown in Figure 1. Significant differences were detected between groups (P < 0.001). A predominance of scores 2 and 3 was generally observed for all groups, with a predominance of score 3 at 10 minutes shifting to a predominance of score 2 after 24 hours. Figure 2 shows the comparison of the commercial reference Transbond XT with the experimental composites. The control composite showed significantly lower bond strength than the other materials (P < 0.001), which showed similar results (P ≥ 0.076).

**Discussion**

The control composite generally showed lower bond strengths compared with DPC-modified agents. Therefore, the hypothesis that higher bond strengths would be observed for materials containing the iodonium salt is accepted. The higher bond strength of DPC-modified agents, especially when the specimens were tested at 10 minutes, is explained by the higher polymerization reactivity caused by the salt. Although DPC cannot absorb light in the 400–500 nm
wavelength range, the iodonium salt as a third component of the initiator system may react with inactive CQ radicals formed during polymerization (the salt acts as electron acceptor) to decrease the termination rate and enhance the initiation rate by generation of new radicals from fragmentation of the salt, leading to faster polymerization compared with two-component initiator systems (Padon and Scranton, 2000; Odian, 2004; Kim and Stansbury, 2009).

Differences in bond strengths between the two concentrations of DPC (R05 and R1) were not significant. This indicates that within the conditions of this study, increase in iodonium salt fraction may have not increased the curing reactivity of the bonding composite. This finding corroborates a previous study showing a minor effect for the concentration of iodonium salts on the polymerization rate (Ogliari et al., 2007); the authors hypothesized that the iodonium salt acts as a true catalyst, being regenerated at the end of reaction. Thus, even low DPC concentrations may have a positive effect in increasing the rate of polymerization. Another explanation is that the increased amount of DPC and the resulting increased light-curing rate may have increased the generation of polymerization stress. It is known that polymerization rate and stress are well related for polymers light-cured under confined and isothermal conditions (Braga and Ferracane, 2002). The increased stress at the bonded interface could affect the bonding ability of the cement as a slower curing process allows more resin to flow from the unbounded surface, reducing the shrinkage from the bonded area and, in turn, reducing the stress at the bonding interface.
The bond strength of groups light activated for 8 seconds was generally lower at 10 minutes compared with longer light exposure times. Polymerization of resin-based materials relies upon the radiant exposure it receives, i.e. the product light-activation time × irradiance level of the curing unit. In this study, a high-irradiance curing unit was used, delivering approximately 9, 22, and 44 J/cm² energy doses for specimens cured for 8, 20, and 40 seconds. These differences in energy dose may explain the differences among the light-activation times. At 24 hours, in contrast, no significant differences were observed among the light-activation times. Therefore, the hypothesis that higher bond strengths would be detected for specimens light activated for longer periods is rejected.

The hypothesis that the bond strengths would be higher for groups tested after 24 hours is accepted. This result is in line with previous studies, showing an increase in bond strength of brackets tested after 24 hours compared to early bond strengths (Bishara et al., 1999; Correr Sobrinho et al., 2002; Yamamoto et al., 2006; Oesterle and Shellhart, 2008). This increase in shear bond strength might be attributed to a phenomenon known as ‘post-polymerization’ that takes place mainly in the first 24 hours of free-radical polymerization (Leung et al., 1983). Polymer vitrification causes free radicals and remaining C=C to be entrapped in the polymeric matrix (polymer $T_g$ is above 37°C), thus no appreciable monomer or oligomer movements may occur (Truffier-Boutry et al., 2006). Polymer relaxation during water storage, however, might cause remaining reactive species to approach, leading to slight improvement of polymerization (Truffier-Boutry et al., 2006; Mohamad et al., 2007). Even minor changes in conversion in the latter curing stages can improve polymer properties, mainly by increasing polymer crosslinking (Burtscher, 1993; Mohamad et al., 2007).

The failure results showed a predominance of score 3 (all bonding resin left on the tooth) at 10 minutes shifting to a predominance of score 2 (more than half of the bonding resin left on the tooth) after 24 hours. This finding is most likely related to the post-polymerization effect described before. As the polymer gets slightly stronger during water storage for 24 hours, the mechanical keying with the bracket mesh is enhanced, leading failures to involve fracture of the bonding agent. This is also true when comparing failures of control composites with R05 and R1. Failures of DPC-modified materials tended to include fracture of the bonding material, indicating a better mechanical interlocking of the composite with the bracket mesh, which is attributed to improvement of the photopolymerization due to the addition of the salt.

Proper bond strength between the brackets and tooth structure is required to minimize bond failure during orthodontic treatment. The focus of this study was to present a possible way for manufacturers to improve the reactivity of their bonding materials and, as a consequence, to reduce the light exposure times required to bond brackets. However, it should be borne in mind that the adhesive agents formulated here are experimental materials, with simpler formulations as compared with commercially available proprietary adhesives. The fact that similar bond strengths were observed between the experimental materials and the commercial reference only when DPC was added to the composite ratifies the positive results of using a three-component initiator system in orthodontic bonding composites. Although discretion should be taken when extrapolating results of in vitro studies to the clinical setting, reduction in light activation might lead to beneficial aspects to both clinicians and patients. Therefore, further investigations on that respect should be carried out.

**Conclusion**

The use of a ternary photoactivation system containing an iodonium salt may allow bonding brackets to enamel using reduced light exposure times.

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