Effect of Different Photoiniciers of Experimental Adhesive Systems on Adhesive Interface Union Resistance

ORIGINAL

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Abstract

Aim: The objective of this study was to investigate the performance of experimental resinous adhesives containing different combinations of photoinitiators systems through the bending test.

Material and Methods: Resinous adhesive formulations were prepared with monomer mixtures consisting of 50% by mass of bisphenol dimethacrylate glycidyl (BisGMA) and 50% by mass of triethylene glycol dimethacrylate (TEGDMA). The photoinitiators were used, camphorquinone (CQ) and bis-alkyl phosphinic oxide (BAPO). The co-initiators were diphenyliodonium hexafluorophosphate (DFI) and the amine (dimethylamino methylmethacrylate - DMAEMA) in the 1:1 proportion by mass. The photopolymerizable initiator systems were dissolved in the organic matrix at 0.5% by mass concentrations, creating eight groups (G1- CQ, G2- CQ/amine, G3- CQ/DFI, G4- CQ/amine/DFI, G5- BAPO, G6- BAPO/amine, G7- BAPO/DFI, G8- BAPO/amine/DFI). Samples with 7.0 mm in length, 2.0 mm wide and 1.0 mm height were prepared (n=12). The curing light used was VALO – Ultradent and the curing time was 20 s. The samples were subjected to evaluation of bending test at three points at a speed of 1 mm/min to evaluate the flexural resistance (FR).

Results: The results were submitted to analysis of variance with one criterion ($p < 0,001$) and multiple comparisons were performed using Tukey test. Systems with the photoinitiator BAPO showed higher or

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equivalent bending values that demonstrated by the conventional system containing CQ/amine. Systems with the DFI had higher flexural values in relation to those demonstrated by systems without the DFI to CQ.

Conclusion: The use of systems with alternative photoinitiators and co-initiators allows to obtain superior properties to the conventional system, making these promising systems to act both in isolation as associated with conventional systems.

Keywords

Photoinitiators, Dental; Dentin; Adhesiveness.

Introduction

The obtaining of a strong and lasting union between the dental substrates and the restorative materials, has been a great challenge of modern dentistry [1]. The technique of enamel conditioning with phosphoric acid represented a milestone in Adhesive Dentistry [2]. Then came the concept of hybridization that over the years has drastically changed the dental practice, by modifying the generations of adhesive systems [3].

The adhesive systems available in the market are varied, which makes it difficult for the clinician to select the material [4]. One of the difficulties is related to the different clinical steps and care to be taken when using the adhesives that have different types of monomers, solvents, photoinitiators [5]. Its mechanism of action on dental substrates, the composition of the different adhesive systems and their implications for incorrect applications; are essential parameters for the success of the system [6].

There are numerous types of adhesive systems in the dental market. Simply put, they can be divided into conventional and self-etching systems [7]. The conventional ones consist of substances that completely remove the Smear Layer and result in the demineralization of the dentinal substance through

the use of acidic conditioning [8]. Among the conventional adhesive systems the odontological market presents examples of two steps (acid + primer and bond) and another three steps (acid + primer + bond) [9].

The self-etching systems can be two steps (primer acid + bond) or single step (primer acid and bond together) [10]. The self-etching adhesives are composed of acid resinous monomers that partially modify and/or remove the smear layer, partially demineralizing the surface of the enamel and dentin [11]. However, adhesive systems are photoactivated; and this photoactivation generally occurs in unfavorable environments, such as humid, in the case of conventional systems, or in acidic environments such as self-etching systems. The photoinitiator most used in the formulation of dental composites is camphorquinone (CQ), it absorbs light at the wavelength between 460 and 480 nm [12].

Diketone (CQ) is a yellowish solid compound containing in its molecular structure a chromatic grouping, which in large quantities improves its mechanical and biological characteristics; but lead to an undesirable yellowing and thus, affecting the final appearance of the polymerized material, mainly clear and translucent [13]. Despite being an efficient photoinitiator, CQ also has a high carcinogenic potential [14].

The objective of the present study was to evaluate the bond strength of the adhesive interface, through microtraction tests, of adhesive systems containing different photoinitiator systems.

Materials and Methods

Preparation of the Tooth Sample

In this study, 48 third molars ($n = 8$), newly extracted, free of caries, cracks or fractures were used. The teeth were kept in chloramine solution (0.5%) at 4 °C for 48h for disinfection. Afterwards, they were cleaned using pumice paste and water with Robinson type brushes (Microdont®, Socorro, SP, Brazil) and analyzed using a magnifying glass (Carl Zeiss®, Jena, Germany), with a 10x magnification to discard specimens that were not intact.

The teeth were included in rectangular glass slides with dimensions of 15 x 40 mm (IVM BRASIL, glazing, Mogi das Cruzes, SP, Brazil), fixed with sticky wax (ASFER, Indústria Química Ltda., São Caetanos do Sul, SP, Brazil) in such a way that the occlusal surface was facing the outer and upper surface. (**Figure 1**).

The crowns of the teeth were sectioned 2 mm below the cusps in their central region, in the lingual-lingual direction, parallel to their long axis with a double-sided diamond disc. (Meinsinger, Neuss, Germany). After the cut, the residues from the manipulation of the specimens were removed with a sequence of Lixa D'água number 600 and 1200 (3M, Sumaré, Brazil), in Politriz Aropol 2V (Arotec Ind. And Comércio São Paulo/SP/Brazil). (**Figure 2**).

The maintenance of the teeth after these procedures was in physiological serum at a temperature of 36 degrees Celsius in a bacteriological oven ECB 1.3 digital Odontobrás Ind. And Com. Equip. Med. Odont. LTDA (Ribeirão Preto, SP, Brazil).

After the polishing to standardize the smear layer, the dentin disks belonging to each of Groups 1 to 6

Figure 1: Teeth Fixed on Blade of Glass and Including with Wax, with occlusal surface with cusps facing upwards.

Figure 2: Teeth Cut Off in the Crown Region.

($n = 8$) were conditioned with 37% phosphoric acid (Cond AC 37®, FGM, Joinville, SC, Brazil) for 15s and rinsed with copious water for 30s. The excess water was removed with absorbent paper (**Figure 3**).

Each specimen received the SingleBond adhesive system (3M ESPE, St Paul, USA), which was applied for 10 seconds under constant agitation throughout the dentine surface using a microbrush (KG Sorensen®, Barueri, SP, Brazil), followed by a light jet of air for 10s. After the first application a new layer of the adhesive system was applied on the dentin for the same time and agitation condition, followed by a light jet of air also for 10s and photoactivated

for 10s with the Radii® device (SDI, São Paulo, SP, Brazil), with irradiance of 450 mW/cm². (**Figure 4**).

After application of the adhesive system, restoration of composite resin (Z250®, 3M ESPE, St Paul, Minnesota, USA) was done to close the pulp chamber, (**Figure 5**), using resin increments until all cavity closure, which were photopolymerized for 20s each, with a photopolymerizer used in VALO (Ultradent Products, Inc. - Salt Lake City, Utah, USA) (**Figure 6**).

Figure 3: Conditioned Teeth.

Figure 4: Application of Adhesive System to Close Pulp Chamber.

Figure 5: Pulp Cavity Closure with Composite Resin.

Figure 6: Light Curing Unit VALO-Ultradent.

Sample Preparation of Experimental Adhesive Systems

For this study, the following experimental adhesive formulations were prepared with mixtures of monomers consisting of 50 wt% BisGMA - Bisphenol Glycidyl Dimethacrylate and 50 wt% in TEGDMA - Triethylene Glycol Dimethacrylate.

The photoinitiators used were: camphorquinone (CQ) and bis-alkyl phosphinic oxide (BAPO) and co-initiators, diphenyliodonium (DFI) and amine (dimethylamine methylmethacrylate - DMAEMA) in a 1: 1 mass ratio. The photopolymerizable initiator systems were each completely dissolved in the monomer matrix in concentrations of 0.5% by mass to give the groups:

1. CQ/Amine
2. CQ/Amine/DFI
3. BAPO

4. BAPO/Amine
5. BAPO/DFI
6. BAPO/Amine/DFI (**Figure 7**).

In addition, the butylated hydroxytoluene inhibitor (BHT) was added to the system in a concentration of 0.1% by mass to avoid spontaneous polymerization of the monomers. The manipulation of the experimental adhesives was performed in orange filtered light. The formulations of the experimental adhesives used in this study were selected based on the studies of Park et al. (1999), Atai, Watts (2006) and Moin et al. (2001). All reagents were from Sigma-Aldrich Inc., (St. Louis, MO, USA).

Each experimental adhesive containing different photoinitiator systems was applied for 10 seconds under constant agitation on all dentin surfaces with the aid of a microbrush (KG Sorensen®, Barueri, SP, Brazil), followed by a light air jet for 10s. After the first application a new layer of the adhesive system was applied on the dentin for the same time and agitation condition, followed by a light jet of air also for 10s and photoactivated for 10s with the Radii® device (SDI, São Paulo, SP, Brazil), with irradiance of 450 mW/cm².

After application of the adhesive system, a composite resin restoration (Z250®, 3M ESPE, St Paul, Minnesota, USA) was made in block form (4mm x 4mm x 8mm) with the aid of addition silicone matrix in the dimensions of each specimen using two resin increments of 2 mm thickness which will be photopolymerized for 20 s for each specimen. (**Figures 8 & 9**).

After 24 h of restorations, the specimens were cut longitudinally with a double - sided diamond disk (Buehler, model 11 - 4253, 15 LC series, Lake Bluff, ILL 6004, USA) on Isomet 1000 precision metallographic cutter (Buehler, Lake Forest, IL, USA) under constant cooling. Each specimen was cut resin - wise in 1 mm thick sticks in the mesio - distal direction perpendicular to the adhesive interface. Subsequently, the specimens were positioned in the vestibulo-lingual direction (rotated 90°) and

Figure 7: Experimental Adhesive Systems.

Figure 8: Restored Teeth in Resin and Groups of adhesive systems, digital caliper.

Figure 9: Restored Teeth in Resin.

sectioned perpendicular to the adhesive interface giving sticks of 1mm². The results of the cuttings were obtained with sticks of dimensions (4mmx8mmx4mm), composed of a portion of resin (Z250®, 3M ESPE, St Paul, Minnesota, USA) and the other of dentin substrate, and between these 2 structures the adhesive system (bonding interface) (**Figure 10**).

Figure 10: Formed Sticks.

Figure 11: Tooth-Rest Interface and Fixed Sticks.

Figure 12: Sticks Ready for Testing with Constant Velocity of 0.5 mm/min until toothpick rupture.

Figure 13: Fractured sticks and ready for Microscope analysis.

Microtraction Test

For the evaluation of the bond strength a digital caliper was used to verify the cross-sectional area (height and thickness) of the tooth-restoration interface and the toothpicks were attached to the micro-tensioning device in a Universal Testing Machine (EMIC Ltda., São José (Figure 10), with cyanoacrylate based adhesive (Super Bonder Gel, Loctite, Henkel Ltda., Itapevi, SP, Brazil) at their ends, in order to position the bonding area perpendicular to the long axis of the traction force. The tests were performed at a constant speed of 0.5 mm/min until the toothpick rupture. (Figure 11 & 12).

EK3ST Eikonal Optical and Analytical Equipment (São Paulo, SP, Brazil), the pattern of micro-fractures that correlated with the percentages of fracture types in each experimental group, the obtained values of bond strength. (Figure 13)

The values obtained in Kgf were transformed into MPa using the area of each palito evaluated after being measured with the aid of a digital caliper. The union resistance means were analyzed by statistical method ANOVA 01 (one) factor (factor: union of the adhesive interface) and then by the most appropriate post hoc test.

Statistical analysis

Prior to the analyzes, union resistance data were assessed for normality by the kolmogorov-smirnov test. They were then subjected to analysis of variance to one criterion. Multiple comparisons were made by the Tukey test. Statistical calculations were performed using the 5% ($\alpha = 0.05$) level of significance in the SigmaStat 3.5 program (Systat Software Inc., San Jose, California, USA).

Results

Table 1 shows the mean values and the standard deviation of the bond strength of the different dentin adhesives.

Means followed by distinct letters indicate significant difference between materials.

Table 1. Mean and standard deviation of union strength values in Mega Pascal (MPa).

Adhesive	Union Resistance	MPa
BAPO	32.0	13.3 A
BAPO/DFI	31.0	9.7 A
BAPO/Amine/DFI	25.7	9.3 A
BAPO/Amine	8.6	10.4 B
CQ/Amine	6.0	3.1 B
CQ/Amine/DFI	5.7	3.8 B

Graph 1: Types of failure (%).

The analysis of variance at one factor showed that there was a statistically significant difference in bond strength values between the different dentin adhesives used ($p < 0.01$).

According to Tukey's test, the adhesives containing the BAPO photoinitiator systems; BAPO/DFI; BAPO/Amine/DFI demonstrated the highest bond strength values, not differing from each other. While the adhesives containing the BAPO/Amine photoinitiator systems; CQ/Amine; CQ/Amine/DFI showed the lowest union strength values similar to each other.

Graph 1 shows the percentage of types of failure that occurred in the different techniques.

The predominant failure pattern for all the evaluated adhesives was adhesive type failure. Since

CQ/Amine/DFI obtained the lowest percentage of adhesive failures (89%) and adhesives B and CQ/Amine the largest (100%).

Discussion

In search of the success of clinical dental treatments, the quality of the adhesive interface between the composite resins and the dental remnant has been the target of different studies to improve its action-fu [15]. Within this theme, the enamel conditioning with phosphoric acid represented a major milestone in adhesive dentistry [16]. Since then, several researchers have been highlighting the use of dedication to the development of new concepts in the area of adhesiveness [17]. In order to continue the discussion on this topic, the purpose of this study was to test different experimental adhesive systems containing different photoinitiator and coinitiator systems, evaluating the bond strength of the adhesive interface to the microtension [18].

Photoinitiators are organic molecules, generally, that can be used alone or as part of a chemical system, which has the capacity to absorb light [19-21]. The main characteristics of photoinitiators are photochemistry and photophysics, which trigger the reaction process [22-24]. The requirements fulfilled by these substances are: high molar extinction coefficient in the activation region (application dependent and FL); high capacity to generate active species or high quantum yield of free radical formation; solubility in the reaction medium; low chemical degradation before and after the reaction; be odorless; do not cause yellowing of the photocurable resins; be non-toxic and easy to handle [25-30].

The co-initiators are part of a chemical system that does not absorb light but participates in the production of the reactive species [31-33]. The following characteristics were presented: a high oxidation or reduction potential; high reactivity in the addition of the radical to the double bond; does not absorb light at the same wavelength of irradiation

of the photoinitiator and does not react or interact with the photoinitiator and with the monomers in the ground state [34-37].

The photoinitiator most used in the formulation of dental composites is camphorquinone (CQ) and as belonging to type II, it needs a co-initiator, to finish its polymerization, usually the most used is a tertiary amine [38-40]. One of the commonly used amines is dimethylamine methacrylate (DMAEMA). Another photoinitiator is the bisexual phosphinic oxide derivative (BAPO) [41-43]. It has qualities as good efficiency and does not cause dimming [45]. The BAPO does not need co-initiators in its reaction, because it generates radicals by fragmentation of the molecule after absorption of light in a direct process of photofragmentation, belonging to type I [44-46].

The use of co-initiators, also known as reducing agents, increases the rate or kinetics of the reaction [47]. Therefore, the use of iodonium salt (DFI) could aid the polymerization reaction where there is little availability of light [48]. For this study, therefore, photoinitiators were used: camphorquinone (CQ) and bisexual phosphinic oxide (BAPO); associated or not to different combinations of the co-initiators: iodonium salt (DPI) and amine (DMAEMA) [49-51].

The analysis of variance at one factor showed that there was a statistically significant difference in the bond strength values between the different dentin adhesives used ($p < 0.01$) [52-54]. According to Tukey's test, the adhesives containing the BAPO photoinitiator systems; BAPO/DFI; BAPO/Amine/DFI demonstrated the highest bond strength values, not differing from each other [55]. While the adhesives containing the BAPO/Amine photoinitiator systems; CQ/Amine; CQ/Amine/DFI showed the lowest union strength values similar to each other [56].

The results demonstrate that BAPO photoinitiator offers a good combination of the main characteristics of the photoinitiator, as high molar extinction coefficient in the activation region; high capacity

to generate free radicals; low chemical degradation before and after the reaction; besides not causing yellowing of the photocurable resins [57]. Although the CQ/amine system has been the gold standard in dental restorations, there are parameters that affect the photopolymerization of this material [58]. The low concentration of this photoinitiator leads to unsatisfactory polymerization results [59].

In addition to camphorquinone (CQ), it has the ability to absorb blue light and enter a stage of molecular instability; there is also the use of a tertiary amine as a co-initiator [60]. Which is able to accelerate the polymerization reaction by means of an effective exchange of electrons with the CQ [61]. The choice for the tertiary amine occurs because it has some properties such as: a high oxidation potential, does not absorb light at the same wavelength of the photoinitiating substance and does not react with it [62]. Its limitation is that in large quantity can lead to a darkening of the final composite [63].

Due to these several factors, some alternative photoinitiators have been included in the organic matrix of the composites to act alone or synergistically (as co-initiators) with the CQ [64]. Derivatives of aquiline phosphoric oxides (TPO) and -diketones are used in the formulation of composites to improve polymerization kinetics and decrease the yellowing effect [65]. It is worth noting that another photoinitiator studied is the bisexual phosphinic oxide derivative (BAPO) [66]. As a consequence of their lighter color, these photoinitiators absorb light with wavelength less than camphorquinone (CQ), approximately 400 nm, closer to ultraviolet [67-72]. This photoinitiator showed good efficiency in the formation of four free radicals, and the photoreaction was accompanied by the destruction of the chromophore responsible for the absorption near the ultraviolet, causing the photocleaning of the molecule, which prevents the photoinitiator causes yellowing of the polymer [73-78].

The use of co-initiators, also known as reducing agents, increases the rate or kinetics of the reaction [79-82]. Studies have shown that the incorporation of an iodonium salt (DPI) increases the polymerization kinetics through a ternary reaction system (photoinitiator + Amine + Diphenyliodonium Hexa Fluorophosphate - (DPIHFP), without compromising the appearance of the reaction. of iodonium could aid the polymerization reaction where there is little light availability [83-85].

As for the failure pattern, the predominant for all the adhesives evaluated was adhesive type failure. Since CQ/Amine/DFI had the lowest percentage of adhesive failures (89%) and adhesives B and CQ/Amine the highest (100%) [86-88]. Even though CQ/amine initiator system is bound to a high exposure time, and that the use of DFI increases the rate of conversion and polymerization of the compound, the use of DFI associated with the CQ/Amine system was not able to aid in the faults, producing more unfavorable failures [89-91].

Conclusion

It can be concluded from this study that

With the exception of the groups containing CQ and CQ/DFI, all others increased the microtensile strength (RM) of the adhesives relative to the CQ/amine group. The systems containing the BAPO photoinitiator presented values of mechanical resistance superior to those demonstrated by the conventional system containing CQ. However, the systems containing the co-initiator AMINA may negatively interfere with the bond strength values. And those that contained the DFI showed values of mechanical resistance superior or equivalent to those demonstrated by the systems without DFI.

Interest Conflicts

The authors declare that there are no conflicts of interest.

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