Brazilian Dental Journal (2013) 24(5): 522-526
http://dx.doi.org/10.1590/0103-6440201302037
ISSN 0103-6440

Influence of Different Mechanisms of Fluoride Release from Adhesive Systems

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The objective of this study was to evaluate *in vitro* the time-dependent fluoride (F) release from three adhesive systems: Clearfil Protect Bond (CPB - Kuraray), FL Bond II (FLB- Shofu) and Adper Single Bond 2 (SB2 - 3M ESPE) (negative control). CPB and FLB are fluoride containing adhesives that use different F releasing mechanisms. The tested hypothesis was that the F releasing mechanism influences the amount of released F in water. Disc-shaped specimens (5 mm x 3 mm) were fabricated using a plastic matrix (Demetron Research Corp). Three specimens were produced for each material and each period of evaluation (1, 7, 14, 21 and 28 days) (n=3). Subsequently, the specimens were stored in 10 mL distilled water at 37° C until the analyses were done using a liquid membrane for selective F ion electrode (Orion 710). Four readings were performed on the first day and the remaining evaluation times had one reading/day. Results were statistically analyzed by two-way ANOVA and Tukey's test (α=0.05). CPB released the greatest amount of fluoride in all evaluated periods with the greatest value at 6th h (0.183 ppm) thereafter decreasing gradually up to the 7th day when it significantly increased again until the 21st day. In most measurements, FLB showed similar mean fluoride release values as SB2. Therefore, the fluoride release mechanism influenced the amount of fluoride released in water, confirming the study hypothesis.

Key Words: fluoride, adhesive systems, dental materials.

Introduction

The adhesion of resin-based composite restorations and most prosthetic restorations rely on adhesive systems (1,2). The use of adhesive techniques contributes to the preservation of dental tissues by using a less invasive restorative procedures and following the principles of conservative dentistry (3). However, a few problems are still of major concern, including resin composite polymerization shrinkage, which is responsible for the formation of gaps at the adhesive interface (3,4). These gaps allow the infiltration of fluids and microorganisms that could cause secondary caries and result in restoration replacement (2,5).

Fluoride is important to the remineralization process of the tissue disorganized by caries, and it also interferes with dental plaque development and inhibits bacterial growth (6-11). Therefore, fluoride-containing dental materials have been developed aiming at the reduction of secondary caries. Among these materials are the adhesive systems, which seem to be promising fluoride-releasing vehicles because they are in direct contact with the dental structure (12).

In vitro studies have shown fluoride release from adhesive systems, suggesting that these materials have some effect in the enamel and dentin remineralization process and contribute to the control of secondary caries (2,13-17). A previous study evaluated fluoride release behavior and the demineralization inhibition capacity of two adhesive systems and the conclusion was that adhesive systems have a fluoride-releasing behavior as they were able to reduce dental tissue demineralization after acid exposure (8). Another study reported on the microtensile bond strength, *in vitro* secondary caries inhibition and degree of conversion of a fluoride-containing adhesive and two conventional adhesives (without fluoride) (2). The fluoride-containing adhesive showed a significant increase in bond strength after water storage and was also able to create an inhibition zone in dentin when the specimens were exposed to an acid challenge. In addition, an increase in the conversion degree after one month was also reported for the fluoride-containing material (2).

On the other hand, another study concluded that, despite the fluoride-releasing capacity of the investigated adhesives, no secondary caries inhibition was observed (12). Glass ionomer cement (GIC) was used as a positive control and showed the highest level of fluoride release. Three of the five adhesives also released fluoride, which suggested a cariostatic behavior not confirmed in the second part of that study. The results were partially explained by the material volume difference between the GIC and the adhesives used in the restorations and by the aggressive artificial caries regimen used in the study. Yet, the authors claimed that fluoride-containing adhesives may improve the acid-resistance at the dentinal margins of the restorations (12).

Considering the above mentioned diversity of findings and the constant development and marketing of new adhesive systems claiming innovative fluoride releasing mechanisms, the objective of the present study was to evaluate the time-dependent fluoride release behavior

of two adhesive systems containing fluoride, testing the hypothesis that the fluoride release mechanism influences the amount of released fluoride in water.

Material and Methods

The fluoride release evaluation was performed every 6 h on the first day and daily on the following 28 days. Three specimens were produced from each material for each evaluation period (n=3). Specimens were produced using a plastic mold (Demetron disposable disk; Demetron Research Corp., Danbury, CT, USA) with 5 mm in diameter and 3 mm in thickness, and a total surface area of 86.4 mm^2. The isolated mold was positioned on a polyester strip sat on a glass slab. The materials were carefully inserted in the mold to avoid the inclusion of air bubbles. After the first material layer was inserted, the end of a little string was placed into the mold, remaining completely filled with material. Another polyester strip and glass slab were positioned over the mold with digital pressure (approximately 5 N) during 1 min to level up the specimen surface. The materials used in this study are described in Table 1.

A halogen bulb unit (Optilight Plus; Gnatus, Ribeirão Preto, SP, Brazil) with a 420 mW/cm^2 light intensity was applied for 40 s on both sides of the specimens, which were allowed to rest for 20 min at room temperature before the matrix was removed.

Every specimen was attached to the lid of a plastic container by the specimen string, which allows the specimen to dip into 10 mL of reverse osmosis water without touching the lateral and bottom walls of the plastic container. All containers with specimens were stored in an incubator at 37±1 °C until the analyses were performed. The medium (reverse osmosis water) was replaced after each specimen measurement.

The measurements were performed using the direct potentiometry method with a liquid membrane for selective fluoride ion electrode. Two standard fluoride solutions with concentrations of 5 $mg.L^{-1}$ and 10 $mg.L^{-1}$ were used to calibrate the measuring device (Orion 710 digital ion-analyzer; Orion Research Inc., Beverly, MA, USA) (16). Once calibrated, the analyzer performed the analyses of the specimen media, which were transferred to new sterilized containers with 10 mL of a total ionic strength adjustment buffer solution (TISAB) under constant agitation. After each reading, the electrode was washed with osmosis water.

The fluoride release data were recorded and organized according to critical periods (every 6 h for the first day and weekly after the first day). The data were statistically analyzed using two-way ANOVA and Tukey's test (α=0.05).

Results

The mean fluoride release values (in mg/L or ppm) of all tested materials after 6 h, 12 h, 18 h, 24 h, 7 days, 14 days, 21 days and 28 days are presented in Table 2. Statistical analysis showed significant interaction between the factors material and period ($p<0.05$).

CPB released the greatest amount of fluoride in all evaluated periods. In most measurements, FLB showed similar mean fluoride release values as SB2, the negative control. Thus, considering the CPB behavior, the greatest mean fluoride release value was observed in the first 6 h (0.183 ppm) and gradually decreased until the seventh day when it significantly increased again until the 21st day (Fig. 1 and Table 2).

Discussion

The objective of fluoride-containing materials is to constrain caries disease. The fluoride released from the material is capable of interfering in the enamel demineralization process and on the oral microbiota, even under conditions of high caries risk (7,9,10,18). That was also the main purpose of introducing the fluoride-containing adhesive systems on the market (2,7).

Among the evaluated adhesives, CPB released a significantly greater amount of fluoride than others. SB2 was used as a negative control because it has no fluoride in its composition; therefore fluoride release was not expected from this material. On the other hand, FLB is marketed as a fluoride-releasing adhesive system but the amount of fluoride release level was significantly low and statistically similar to SB2 (control), suggesting that FLB is not able to release a significant amount of fluoride in water.

The fluoride-releasing rate of dental materials can be influenced by intrinsic and extrinsic factors. Among the intrinsic factors are permeability, material composition, specimen's geometry, surface treatment and finishing

Table 1. Group acronyms, commercial names, composition and manufacturers of the materials used in this study

Groups	Material	Basic Composition*	Manufacturer
CPB	Clearfil Protect Bond	MDP, HEMA, MFM, PI, colloidal silica, NaF	Kuraray Medical Inc. Osaka, Japan
FLB	FL Bond II	HEMA, S-PRG glass filler, UDMA, TEGDMA	Shofu Inc. Kyoto, Japan
SB2	Adper Single Bond 2 (negative control)	BisGMA, HEMA, dimethacrylates, MFM, PI, silica nanofiller	3M-ESPE, St. Paul, MN, USA

(9,12,18). Except for the adhesive composition, all the remaining factors were standardized in the present study. Thus, the observed differences can be partially explained by differences in the composition, since the fluoride release rate of resin-based materials could be affected by the type and size of the fluoride filling particle and the type of resin (7). In addition, the evaluated adhesive systems have different fluoride releasing mechanisms. CPB has sodium fluoride filler with a special treatment patented by the manufacturer. This filler is an inorganic compound that breaks up to facilitate its solubility in water, which greatly assists the fluoride releasing mechanism of CPB (2). FLB is marketed as a second generation fluoride-releasing giomer bonding system. It releases fluoride from a S-PRG filler (Table 1), which is formed by an acid-base reaction between fluoride-containing glass particles (fluoro-boro-alumino silicate glass filler) and polyalkenoic acid, in the presence of water prior to integration into the resin. S-PRG filler particles show a three-layer structure: (1) a glass core; (2) a layer constituted by a stable glass-ionomer hydrogel; and (3) a "reforming phase," which provides structural protection for the hydrogel. Fluoride releasing occurs as the result of the dissolution of the filler surface by the storage medium. In addition, the acidified water within the hydrogel surrounding the inner glass of S-PRG particles facilitates fluoride release by the continuing dissolution of the fluoride-containing glass core. Giomers are different from compomers because the glass ionomer hydrogel within the compomers forms only after water uptake by the resin matrix after polymerization (5,8).

The mean fluoride release values reported in the present study for CPB are in agreement with previous reports (2,13), which suggested a significant effect of this material on the formation of demineralization-inhibition zones after a cariogenic challenge (2,13).

Previous studies on S-PRG-based adhesives investigated different aspects of the fluoride releasing behavior. A study (8) compared this adhesive system to other containing a penta-methacryloxy-ethyl-cyclo-phosphazene-mono-fluoride (PEM-F). Although the S-PRG-based adhesive released less fluoride than the PEM-F-based adhesive, the former showed a high level of fluoride uptake by dentin and enamel. These findings were recently corroborated by another study (5).

The low amount of fluoride release from FLB could be related to extrinsic factors such as the storage medium, the experimental design and analytical methods used to evaluate the fluoride release behavior (5,9,19,20). The storage medium influences the fluoride release values, which vary if the storage solution is replaced daily or used cumulatively (19). In the present study, the medium was replaced after each F release measurement. Yet, dental materials release more fluoride in deionized water than in artificial saliva due to the cations present in the artificial saliva (20). In addition, another study showed a greater fluoride release in lactic acid than in water (5). This behavior indicates that these materials may show a higher capacity of providing fluoride to the tooth structure at the moments when the

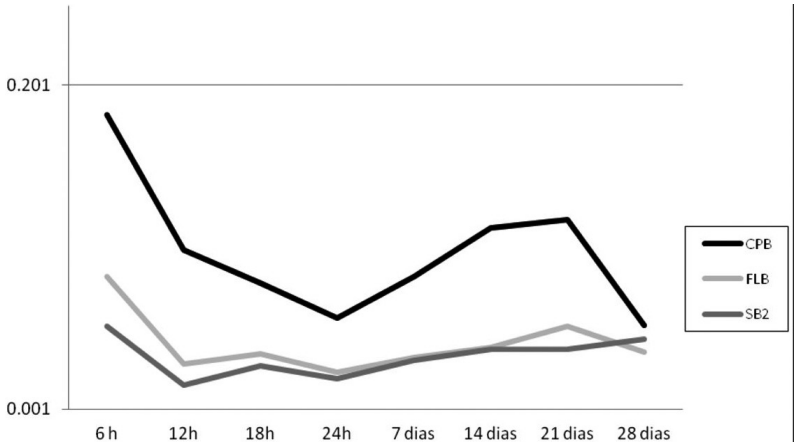

Figure 1. Fluoride release (in mg/L or ppm) curves over time for the experimental groups.

Table 2. Mean fluoride release and standard deviation values (mg/L or ppm) at the different times and the statistical groupings for the experimental groups

Time	CPB	FLB	SB2
6 h	0.183 ± 0.048 aA	0.083 ± 0.028 bA	0.053 ± 0.002 cA
12 h	0.099 ± 0.019 aBC	0.029 ± 0.009 bB	0.016 ± 0.000 cB
18 h	0.079 ± 0.010 aD	0.035 ± 0.006 bB	0.028 ± 0.000 bAB
24 h	0.057 ± 0.005 aD	0.024 ± 0.004 bB	0.020 ± 0.000 bAB
7 days	0.083 ± 0.006 aCD	0.033 ± 0.000 bB	0.031 ± 0.000 bAB
14 days	0.113 ± 0.014 aBC	0.039 ± 0.001 bB	0.038 ± 0.000 bAB
21 days	0.118 ± 0.010 aB	0.052 ± 0.002 bAB	0.038 ± 0.005 cAB
28 days	0.053 ± 0.000 aD	0.037 ± 0.003 bB	0.044 ± 0.004 bAB

Mean values with different lowercase letters in the same row (same period of time) are significantly different ($p<0.05$). Mean values followed by different uppercase letters in the same column (same material) are significantly different ($p<0.05$).

adjacent enamel is most susceptible to demineralization. Thus, when the cariogenic inhibition potential of a dental material is analyzed, the fluoride release pattern may be more important than the quantity of material (5,9). Clinically, components of saliva, acquired pellicle, pH, ion concentration and temperature may decrease the fluoride diffusion from the restorative materials. In addition, the fluoride incorporated into dentifrices and solutions could affect the amount of fluoride uptake and release from the materials (9). Thus, research protocols should focus on using a medium that simulates the oral environment. The principles of the present research protocol were based on the ASTM D 1179-10 standard (21). Nevertheless, the above-mentioned factors preclude direct comparison of fluoride release values from the present study with the values found in previous studies using the S-PRG-based adhesive (5,8).

In the present study, CPB showed the greatest mean fluoride release value at the 6th hour, followed by a significant decrease in value for the remaining hours of the first day. A new peak of fluoride release was shown at 21 days then it decreased approximately to the mean values of the other adhesive systems (FLB and SB2) (Table 2 and Fig. 1). A previous work (16) using the same methodology to evaluate the fluoride release from restorative materials also reported the greatest mean fluoride release value during the first day, followed by a significantly fast drop to reach a constant low value in the following days, irrespective of the fluoride-releasing material. This behavior has been reported elsewhere (5,9,19). Clinically, alternate episodes of remineralization and demineralization occur over time, thus a constant fluoride release behavior is desired to maximize the inhibition of secondary caries (5,9).

The fluoride release from GICs is ascribed to three different mechanisms: surface loss, diffusion through pores and cracks and bulk diffusion. It has been suggested that the high level of fluoride release on the first day is associated to the initial surface loss, while the lower and relatively constant fluoride release over time is related to the fluoride ability to diffuse through cement pores and cracks (9). As CPB is an adhesive with sodium fluoride filler using a special treatment (manufacturer patented), it is difficult to understand the releasing mechanism over time. In addition, there are only a few studies assessing CPB adhesive, which compromises the interpretation. Nevertheless, the results of the present study suggest the presence of an additional delayed fluoride releasing mechanism that could be ascribed to the special treatment applied by the manufacturer.

The present study showed that fluoride-containing adhesives that use diverse fluoride releasing mechanisms released significantly different amounts of fluoride in water, confirming the study hypothesis. Future studies should consider using fluoride-containing adhesives in cariogenic challenge designs in order to investigate the fluoride uptake by dental tissues and the effect on bond strength.

Resumo

O objetivo deste estudo foi avaliar, *in vitro*, a liberação de flúor (F), ao longo do tempo, de três sistemas adesivos: Clearfil Protect Bond (CPB-Kuraray), FL Bond II (FLB-Shofu), Adper Single Bond 2 (SB2-3M ESPE) (controle negativo). Os sistemas adesivos CPB e FLB contêm flúor em sua composição e liberam F por diferentes mecanismos. A hipótese testada foi a de que o mecanismo de liberação de F influencia a quantidade de F liberado em água. Foram confeccionados espécimes em forma de discos (5 mm x 3 mm) utilizando uma matriz de plástico (Demetron Research Corp). Foram produzidas 3 amostras para cada um dos materiais, para cada período de avaliação (n=3) (1, 7, 14, 21 e 28 dias). Subsequentemente, as amostras foram armazenadas em 10 mL de água destilada a 37 °C até o momento das leituras que foram feitas usando uma membrana líquida para eletrodo seletivo de íons F (Orion 710). Foram realizadas quatro leituras no primeiro dia; após foi feita uma leitura/dia. Os resultados foram analisados estatisticamente por ANOVA e teste de Tukey (α=0,05). O sistema adesivo CPB liberou a maior quantidade de flúor em todos os períodos avaliados, com o maior valor em 6 H (0,183 ppm), então ela diminuiu gradualmente até o sétimo dia, quando aumentou significativamente até o dia 21. Na maioria das análises realizadas, FLB mostrou valores de liberação de flúor semelhantes aos de SB2. Portanto, o mecanismo de liberação de flúor influenciou a quantidade de fluoreto de liberado em água, confirmando a hipótese do estudo.

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Received July 19, 2012
Accepted August 28, 2013