Facultad de Odontología
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Evaluación de la unión entre cementos resinosos auto-adhesivos y la dentina

(Evaluation of the bonding potential of self-adhesive resin cements to dentin)

Tesis de Doctorado de
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I. RESUMEN

Debido a la variabilidad de los sustratos a los que nos enfrentamos durante las técnicas de adhesión (diente, medio cementante y material de restauración), no resulta tan fácil alcanzar una unión duradera en Odontología. Hoy en día, todavía no se puede recomendar el uso clínico de un material con respecto a otro y que este pueda ser eficaz en todas las situaciones clínicas, a pesar del continuo desarrollo de materiales y técnicas.

Las diferencias estructurales entre la dentina coronal, la dentina radicular y el esmalte, hacen que estos sustratos se comporten de manera diferente aún utilizando el mismo material de restauración. Todos los materiales presentes en el mercado dental presentan ventajas y desventajas y el odontólogo debe ser capaz de elegir el más apropiado para utilizarlo en las diferentes situaciones clínicas. El deseo de poseer un material "universal" que pueda actuar de la misma manera sobre todos los sustratos dentales (dentina coronal, dentina radicular y esmalte) y con todos los tipos de restauraciones (directas, incrustaciones o coronas de cerámica integral, postes de fibra) está latente.

Al mismo tiempo, la demanda de poder contar con materiales que reduzcan la sensibilidad post-operatoria y que requieran el menor número posible de etapas clínicas se hace más frecuente, también en el caso del cementado de restauraciones indirectas. Para limitar los problemas relacionados con la aplicación de los cementos que prevén el uso de sistemas adhesivos de tres pasos (i.e. discrepancia entre el grado de grabado y la penetración de la resina en el sustrato dental), se desarrollaron nuevos productos limitando el uso de adhesivos de grabado total que, en su formulación tradicional, prevén tres fases consecutivas (grabado, imprimación y aplicación del adhesivo). Los sistemas de cementado que se componen de sistemas adhesivos auto-grabadores permiten reducir las fases clínicas a 2 etapas, incluyendo en un único paso la solución de ácido grabador y *primer*, seguido por la aplicación del adhesivo (*bonding*). En la actualidad, estos adhesivos auto-grabadores se pueden encontrar en una solución única *(one bottle)*, donde las etapas de grabado, imprimación y *bonding* se realizan en una sola aplicación.

La simplificación clínica de estos adhesivos puede llevar a una disminuida capacidad adhesiva, y la durabilidad de las interfases adhesivas puede ser cuestionada.

Recientemente, los cementos auto-adhesivos han sido introducidos para el cementado de todos tipos de restauraciones. Estos cementos pertenecen al grupo de los cementos resinosos, e incorporan todas las ventajas de los cementos hasta ahora presentes en el mercado en un único producto: el fácil manejo de los

cementos convencionales (ya que su aplicación se resuelve en un único paso clínico sin prever ningún pre-tratamiento de los sustratos a adherir, sean estos dentales o materiales de restauración), la auto-adhesión y la liberación de flúor de los cementos de ionómero de vidrio pero con mejoradas propiedades mecánicas, la estabilidad dimensional y la retención micro-mecánica de los cementos resinosos adhesivos.

Contrariamente a lo esperado, estos cementos todavía no pueden sustituir completamente a los cementos resinosos que utilizan adhesivos de grabado total, debido a la limitada interacción entre cementos y sustratos dentales. A pesar de estar compuestos por monómeros ácidos, los cementos auto-adhesivos poseen una limitada capacidad de infiltrar el barrillo dentinario y desmineralizar la dentina subyacente para poder penetrar en los túbulos dentinarios y formar los *tags* de resina necesarios para una efectiva adhesión, así como se ha evidenciado utilizando la coloración de Masson y microscopía óptica y electrónica de barrido (MEB) para el análisis de la interfase adhesiva (Anexo VIII.1).

En el caso de que sea necesario rehabilitar un diente vital mediante una restauración indirecta, es importante tener en cuenta que la dentina es un sustrato dinámico que se caracteriza por un movimiento del fluido dentinal a través de los túbulos dentinarios. Esta transudación de fluidos puede llegar hasta la interfase adhesiva, pudiendo afectar la adhesión. De los cementos auto-adhesivos investigados en el presente trabajo, algunos de ellos se benefician de la presencia de la hidratación del sustrato, dando como resultado valores de fuerza de unión más elevados que en ausencia de transudación (Anexo VIII.2). Este asunto nos lleva a teorizar que algunos cementos necesitan de agua para ionizarse y facilitar el proceso de neutralización de los monómeros ácidos y así reforzar su capacidad adhesiva.

A pesar de los resultados obtenidos en esta investigación, permanecen algunas dudas sobre la capacidad de estos cementos de desmineralizar la dentina a través del barrillo dentinario: si por un lado puede funcionar como una barrera capaz de reducir la transudación de fluidos, por otro puede representar un obstáculo limitando la interacción entre la dentina y los cementos. La aplicación previa de agentes quelantes y/o grabadores (como EDTA y ácido poliacrílico), ha tenido efectos diferentes sobre la fuerza de unión de los diferentes cementos auto-adhesivos (Anexo VIII.3). A pesar de la parcial eliminación del barrillo dentinario, que debería favorecer la interacción entre los cementos y la dentina, los valores de fuerza de unión adhesiva obtenidos son contradictorios y parecen ser más bien debidos al diferente comportamiento mecánico de estos cementos, que depende de sus composiciones químicas. De manera general, estos cementos se clasifican como auto-adhesivos, pero esto no significa que sean iguales, sino que el pertenecer al mismo grupo depende del concepto común de auto-

adhesión. Los diferentes componentes químicos de cada cemento hacen que el material se parezca más al grupo de los cementos convencionales que al de los cementos de ionómero de vidrio o resinosos.

Debido a sus recientes introducciones y a sus escasas interacciones con los sustratos dentales, muy poco se sabe acerca de la durabilidad de la adhesión de los cementos auto-adhesivos, y estudios futuros son necesarios para aclarar este mecanismo.

Siendo materiales de uso universal, los cementos auto-adhesivos pueden ser elegidos para el cementado de los postes de fibra. Los postes de fibra representan una válida alternativa clínica a los postes metálicos y anatómicos para restaurar los dientes endodonciados con reducida estructura coronal. Debido a la incompatibilidad química entre la matriz de resina epóxica, de la que se componen la mayoría de los postes, y el componente metacrílico de los cementos resinosos, algunos tratamientos químico-mecánicos de la superficie de los postes han sido propuestos para poder exponer las subyacentes fibras de vidrio que, efectivamente, puedan interactuar con el cemento creando también rugosidades de superficie que permitan aumentar la retención micro-mecánica de los cementos resinosos. Algunos de estos pre-tratamientos (como el uso de ácido fluorhídrico) pueden dañar en exceso las fibras de vidrio, según el análisis realizado mediante microscopía de fuerza atómica (AFM) y confocal y descrito en esta tesis (Anexo VIII.4). La interacción entre la solución grabadora y el poste, no se limita solamente a la matriz resinosa, y por eso este tratamiento no debería ser recomendado. Al contrario, como se ha propuesto con anterioridad, el grabado con peroxido de hidrógeno y el arenado de las superficies de los postes, actúan específicamente con la matriz resinosa sin modificar las fibras de vidrio, creando además rugosidades para facilitar la retención mecánica. Estos tratamientos han sido considerados ventajosos para mejorar la adhesión a los materiales resinosos de restauración y cementado y por lo tanto se teoriza que puedan ser válidos para mejorar la retención de postes cementados con cementos auto-adhesivos.

El poder disponer de postes de fibra pre-tratados, sin la necesidad de aplicar agentes silanos o adhesivos durante las etapas de cementado y de cementos universales, representa sin duda una estrategia deseable para simplificar las técnicas adhesivas indirectas.

I.1 Summary

In dentistry, an effective adhesion may be hampered by the structural differences and variabilities of the adhesive substrates (tooth, luting agent and restoration). The search for better materials has since inspired many developments, even though actually it is not possible recommend a single product suitable to be used for all the clinical requirements.

The structural differences between coronal dentin, radicular dentin and enamel may influence the bonding effectiveness. The materials available into dental market show some vantages and disadvantages. Clinicians should be consciensous on selecting the proper material to be used with its technique and the restoration. Clinician's demands for a material that can similarly interact with all dental substrates (coronal dentin, radicular dentin and enamel) and with all type of restorations (i.e. direct, indirect or ceramic crown, fiber posts) is increasing over time.

The practical demand reflect a time saving and economical request as well. All these requests are also addressed to reduce the operative phases. Manufacturers are actually move to meet requirements of the dentists and overpass some problems related to traditional adhesives (i.e. discrepancies between the degree of demineralization and the depth of resin penetration), and after etch-and-rinse adhesives (that require the etching, priming and bonding steps). For these reasons, self-etch products have been introduced. These adhesives allow the reduction of the operative steps up to two, as the etchant and the primer are included in a single bottle, followed by the adhesive application. More recently, it is possible to find *one bottle* self-etch adhesives, where the acid, primer and bonding are fournished in one single solution. However, the adhesive simplification seems to reflect a decrease in bond strengths, thus the durability of a restoration could be doubtefully.

Recently, self-adhesive resin cements have been introduced and they have been marketed to be used with all kind of restorations. These cements are a subgroup of the resin cements and they have been designed to join in a single product the advanced handling properties of conventional cements (as the application procedure rely on a single clinical step), the self-adhesion and fluoride release of glass-ionomer cements with the improved mechanical properties, dimensional stability and micro-mechanical retention of adhesive resin cements.

Despite the attractive expectations, it seems that the new cements can not completely substitute cements relying on etch-and-rinse or self-etch systems, due to their incomplete interactions with dental substrates. Although the high

acidity of their monomers, self-adhesive cements demonstrated to be unable to interact with smear layer and demineralize the underneath dentin as to penetrate onto dentinal tubules and form resin tags. This mechanism was observed in the present study that used the Masson's staining technique and scanning electron microscope evaluations for interfaces evaluations (Chapter VIII.1).

Moreover, it should be taken into consideration that vital dentin is characterized by a fluid movement through dentinal tubules. The transudating water can reach the bonding interface and hamper the adhesion. Some of the self-adhesive cements tested in this thesis took benefit from the presence of a positive pulpal pressure, and higher bond strength values were obtained when compared to the no pulpal pressure group (Chapter VIII.2). It was supposed that these cements need water to ionize and help the neutralization of the acidic monomers as to improve the adhesion.

Some concerns remain on the ability of the simplified resin cements to demineralize through the smear layer. A clinically relevant smear layer from one side could act as a barrer against an excessive water transudation; from the other side, it could jeopardize the direct interaction between cement and dentin. A study has been conducted evaluating the effect of mild acidic agents (EDTA and Polyacrylic acid) on the bond strengths of different self-adhesive cements to dentin (Chapter VIII.3). It was thought that the partial removal of the smear layer should enhance the cement/dentin interaction; however, different cement responsiveness have been recorded and it was more likely related to their different chemical compositions that influence their mechanical behaviours. In general, these cements have been marketed with the common name of "self-adhesives", but we can not think that they are equal to each other as their accorporation under the same group is more likely due to the general concept of self-adhesion. For this reason, due to their relative recent introduction, additional studies are required.

As self-adhesive cements have been introduced as universal products, they have been proposed to be used to lute fiber post as well. Fiber posts are an effective alternative to metal and anatomic posts used to restore endodontically treated teeth with an excessive loss of coronal structure. Due to the chemical incompatibility between the epoxy-based matrix of the posts and the methacrlyte-based resin cements, some post surface pre-treatments have been proposed. The idea was that of exposing a large number of the glass fibers of the posts that can bond to the cement and even of creating superficial roughness that rely on increased micro-retentive spaces. According to the confocal and atomic force microscopy (AFM) analysis of this study, some of these treatments (i.e. hidrofluoric acid) seem to produce excessive damages of the glass fibers (Chapter VIII.4). As these chemical solutions do not selectively interacted with

the matrix but comprehend also the fibers, these treatments should not be recommended. On the contrary, sandblasting and etching with hydrogen peroxide have been indicated as more reliable pre-treatments. These conditioning approaches have been previously considered efficacies for bonding to resin materials.

II. INTRODUCCIÓN

II.1 Introducción general

El éxito clínico de una restauración indirecta está, en parte, relacionado con la técnica de cementado utilizada para crear una unión entre la restauración y el sustrato dental. La investigación en el área de los materiales odontológicos ha favorecido el desarrollo de nuevos productos para la mejora de las técnicas clínicas. La realización de una duradera unión, restauración-cemento-diente, está relacionada también con factores de tipo económico. Lo ideal es que una restauración perdurase al menos 10 años, pero los pacientes piensan que debería durar toda la vida.

Hasta ahora, una restauración indirecta adhesiva se mantiene en buenas condiciones clínicas durante 3-5 años (1) y entre los factores responsables de una posible reducción de su integridad, se considera una inadecuada adaptación marginal del cemento a nivel de las interfases adhesivas y una disminución de la retención de la restauración (2,3).

El mecanismo de adhesión se considera eficaz cuando se realiza una íntima relación entre cemento y dentina. Cuando el sistema de cementado prevé el uso de un adhesivo de grabado total, esta unión se basa en la remoción del componente mineral de la dentina para crear una zona desmineralizada de 1,5 µm, sin dañar las fibras de colágeno que permanecen formando una red. Este objetivo se logra a través de soluciones ácidas. El grabado ácido permite, además de lo anterior expuesto, eliminar el barrillo dentinario, que ha sido considerado uno de los factores que pueden limitar la infiltración de la resina en los túbulos dentinarios abiertos (4). La interacción directa entre la resina con la dentina, presupone que el material resinoso pueda rellenar los espacios dejados por la remoción de las componentes minerales, infiltrando los túbulos dentinarios y estabilizando la matriz de colágeno para formar una capa híbrida entre resina y dentina (5,6,7,8). Desde que los sistemas adhesivos se desarrollaron, la formación de la capa híbrida ha sido considerada el mecanismo clave del proceso de adhesión, ya que determina una retención micro mecánica entre la resina y la dentina grabada (9).

El éxito clínico de una restauración indirecta puede estar influenciado por cinco factores principales: el operador, el diseño de la restauración, el material, las condiciones intra-orales y la tipología de paciente (10). Los primeros dos factores están directamente relacionados con la habilidad del odontólogo. Con respecto a la elección del material, el conocimiento de todas sus características,

incluyendo las propiedades de laboratorio y clínicas se hace imprescindible. Los dos últimos factores están relacionados con el paciente (10).

Los sistemas de cementado se pueden catalogar en cinco tipologías, según una primera clasificación que toma como referencia sus composiciones químicas: cementos al fosfato de zinc, cementos policarboxilatos, cementos de ionómeros de vidrio, cementos híbridos (cementos de ionómero de vidrio modificados y compomeros) y cementos resinosos (11). A pesar del gran número de cementos actualmente disponibles en el mercado dental, ninguno de estos materiales puede ser universalmente utilizado para todos los tipos de restauraciones. Seguramente es fundamental que el clínico conozca las ventajas y desventajas de cada producto, en referencia a su composición química y propiedades mecánicas, al tipo de sustrato a adherir y de preparación dental realizada (11). Además, la elección del material debe tener en cuenta criterios de tipo funcional y biológico.

La introducción de los cementos resinosos, ha hecho indispensable el uso de sistemas adhesivos que pudieran tratar la dentina para alcanzar retenciones micro-mecánicas normalmente ausentes. Los sistemas y las técnicas adhesivas han sufrido varias modificaciones a partir de su introducción en 1955 (12). Desde entonces, se ha pasado de cementos que no necesitaban del uso de sistemas adhesivos previos, a aquellos que requerían una adhesión separada al esmalte o a la dentina, hasta llegar a combinar sistemas adhesivos esmalte/dentina (13). Actualmente, la investigación en el área de los materiales odontológicos tiene como objetivo optimizar el mecanismo de unión a la dentina de estos sistemas adhesivos.

Este mecanismo se basa en el principio de hibridización entre sustrato y material. El barrillo dentinario formado durante las preparaciones dentales (14) puede ser completamente eliminado o solamente modificado y por lo tanto considerado como sustrato de adhesión intermedio. Una vez tratado/grabado el sustrato a adherir, los túbulos dentinarios resultarán abiertos, la dentina superficial descalcificada y las fibras de colágeno expuestas. Esta red de fibras no colapsada debería favorecer la difusión de la resina fluida para formar la capa híbrida (5). Es posible hacer una clasificación de los sistemas adhesivos según el número de componentes del sistema y el tipo de ácido utilizado (9).

Los sistemas de cementado que incluyen adhesivos de tres pasos se componen de una etapa grabado ácido, con consecuente imprimación y aplicación de la resina adhesiva (por ejemplo: Variolink y Variolink II, Ivoclar-Vivadent; Calibra, Dentsply Caulk; Nexus, Kerr). El grabado ácido del sustrato es necesario para la eliminación del barrillo dentinario y la desmineralización de la dentina ínter tubular o de los prismas del esmalte. Para eso, se utilizan ácidos fuertes que puedan cumplir con su acción en un periodo de tiempo limitado. Una vez tratado el sustrato dental, se aplica un *primer* para mejorar la humectabilidad

y optimizar las características de superficie de los sustratos. Estas soluciones son altamente hidrofilitas y con baja viscosidad. Luego se recurre a la utilización de un agente adhesivo que pueda unir el sustrato tratado con el material de restauración (15). Debido a la susceptibilidad de la dentina grabada a los cambios físicos, un mojado o secado excesivo de las fibras de colágeno (durante la eliminación del ácido mediante lavado o la evaporación del agente imprimador) puede afectar a la difusión de la resina, aumentando el riesgo de fallos adhesivos (16) con la consecuente incorporación de defectos en la capa híbrida que pueden determinar fenómenos de micro infiltración (17).

A partir del concepto inicial de grabado de los tejidos dentales, nuevos sistemas adhesivos caracterizados por una reducción de las etapas clínicas se desarrollaron para satisfacer el ideal de facilidad técnica y ahorro de tiempo. En 1990, los sistemas adhesivos se han simplificado mediante la incorporación de monómeros ácidos al *primer* para formar una solución única (Panavia 21, Panavia F y Panavia F 2.0, Kuraray; Multilink, Ivoclar-Vivadent). La idea en la que se basa esta técnica de adhesión prevé que los monómeros ácidos modifiquen el barrillo dentinario y consecuentemente a la dentina ínter-tubular y que simultáneamente infiltren las fibras de colágeno para producir un estrato híbrido efectivo (9). Las etapas clínicas se reducen y se limitan los errores relacionados con el uso de los sistemas adhesivos de pasos múltiples (18,19).

Recientemente se han introducido los adhesivos auto-grabadores de paso único (Adper Prompt L Pop, 3M ESPE) (20,21). A pesar del interés mostrado por estos nuevos adhesivos, se ha evidenciado, por algunos de ellos, una incompatibilidad química cuando son utilizados en combinación con cementos resinosos químiopolimerizables o duales (22,23). Además, estos adhesivos simplificados pueden estar negativamente afectados por la presencia de fluido procedente de los túbulos dentinarios en los dientes vitales, que puede incorporarse a los monómeros hidrofílicos del adhesivo y afectar la polimerización del material, aportando una reducción de la durabilidad de la restauración (24,25,26). Estos adhesivos presentan valores inferiores de unión si son comparados con los adhesivos de grabado total (19).

Existe un consenso general de que la unión resina/dentina creada por los adhesivos dentinarios hidrofílicos puede sufrir un deterioro en el tiempo (27,28). En el caso de los adhesivos de grabado total, se ha notado una incompleta difusión de los monómeros resinosos en la dentina grabada (29), resultando zonas no infiltradas a nivel de la base de la capa híbrida (27,30). Los adhesivos auto-grabadores condicionan e infiltran el sustrato dental simultáneamente, eliminando la diferencia entre el grado de desmineralización y de difusión de la resina aunque los túbulos dentinarios resultasen infiltrados sólo de manera parcial (31).

Algunos estudios de micro-infiltración han evidenciado la deposición del agente colorante no sólo en las zonas de la capa híbrida no infiltrada sino también en el grosor del adhesivo (32,33).

II.2 General Introduction

The clinical success of an indirect restoration is partially related to the technique used for the luting procedure. New products are continually developed to improve clinical techniques. The economic aspect should be also taken into consideration during the planification a dental restoration. Ideally, a restoration should survive for 10 years, despite patient expectations for which it should last all life long.

Until recent, an indirect adhesive restoration preserve good clinical condition for 3-5 years (1). The factors mainly involved in the failure are an inadequate marginal adaptation of the cement on the adhesive interfaces and a decreased retention (2,3).

An effective adhesion is obtained when an intimate relation exists between cement and dentin. When using cements based on total-etch technology, the adhesive mechanism is based on the removal of the mineral component of dentin as to create a demineralized area of 1,5 µm, without damaging collagen fibrils. The objective is achieved thtough acidic solutions. Acid etching promote the removal of smear layer, that may hamper resin infiltration into the opened dentinal tubules (4). It has been supposed that the resin fullfill the voids left by the removal of the mineral content, infiltrate dentinal tubules and stabilize the collagen matrix, as to form an hybrid layer between dentin and resin (5,6,7,8). Hybrid layer has been considered necessary for an effective adhesion when using cements based on adhesive systems since micromechanical retentions between resin and dentin could be favoured (9).

Some variables are supposed to influence the clinical outcome of a restoration: the operator, the design of the restoration, the material, the intra-oral conditions and the patient (10). The first two factors are directly related to the dentist hability. Regarding the material, it is indispensable know its characteristics as well as the laboratory and clinical properties. The last two variables are related to the patient per se (10).

The cements that are actually available to the dentist have been catecorized into five main classes: zinc phosphate cements, polycarboxilate cements, glass ionomer cements, hybrid cements (resin-modified glass ionomer and compomers) and resin cements (11). Despite the large number of product nowadays available, no one could be generally recommended for all type of restorative procedures. It is important for clinicians to know the advantages and disadvantages of each single product, its chemical composition and mechanical properties, the adhesive mechanism to dental substrate and the type of dental

preparation (11). Other considerations should be made based on functional and biologic concepts.

Once introduced resin cements, it has been necessary develop adhesive systems that could interact with dentin as to achieve mechanical retention usually absent. Adhesive systems and techniques have been modified over the years since their first introduction in 1955 (12). Originally, cements did not needed for adhesive systems; recently, the cements have required separate steps for enamel or dentin conditionings as to arrive to products that utilize combined enamel/dentin adhesive systems (13). All these adhesive systems have been adjusted to enhance the adhesion to dentin.

The adhesive mechanism to dentin is based on the hibridization of the hard dental tissue and the material. During prosthetic preparation, smear layer is formed (14). This layer could be completely removed or modified and in that case it is considered as intermediate adhesive substrate. After dental tissue conditioning, dentinal tubules are opened up, superficial dentin results descalcified and the collagen fibrils exposed. In these conditions, the resin should be encouraged to infiltrate dentin and form the hybrid layer (5). The adhesive systems employed for tissue conditioning could be classified according to the operative steps and the type of etchant used (9).

The cements that utilize three step adhesives are composed by an acid etchant, a primer and a bonding agent (i.e. Variolink and Variolink II, Ivoclar-Vivadent; Calibra, Dentsply Caulk; Nexus, Kerr). Acid etching is necessary for smear layer removal and intertubular dentin or enamel prisms demineralization. Strong acidic solutions are used to achieve that goal in a short period of time. After the conditioning step, a priming solution is applied to increase the wettability and improve the characteristics of the substrates. Primer solutions are tipically very hydrophilic with a low viscosity. The adhesive layer is used as a physical link between conditioned dental substrate and restorative material (15). As dentin is susceptible to physical changes, an excessive overwetting or overdrying of collagen fibrils (during acid wash-out or primer evaporation) may hamper resin infiltration. This situation may favour the occurrence of adhesive failures (16) and formation of defects into hybrid layer (17).

New adhesive systems have been developed to reduced operative steps and satisfy clinician’s demands of technique simplification and time saving. In 1990, simplified adhesives have been introduced. The acidic monomer and the primer, or the primer and the bonding, have been combined in a single solution, (Panavia 21, Panavia F and Panavia 2.0, Kuraray; Multilink, Ivoclar-Vivadent). The rationale is based on procuring a modification of smear layer and simultaneous dentin infiltration, as to form an effective hybrid layer (9). In that way, clinical

phases are reduced and the problems related to multistep systems are overpassed (18,19).

Recently, self-etch adhesive systems have been introduced in one solution (Adper Prompt L Pop, 3M ESPE) (20,21). A part the interest deserved to these new products, a problem has been individuated on the chemical incompatibility between these adhesives and auto/dual polimerizable resin cements (22,23). Moreover, these adhesive could be influenced by the water trasudation through dentinal tubules, typical of vital dentin. These fluids may incorporate to the hydrophilic monomers of the adhesive and affect the polimerization reaction of the material, thus decreasing the longevity of the restoration (24,25,26). The simplified adhesives have registered inferior bond strength values when compared to total-etch systems (19).

There is a common thougth for which the resin/dentin union can deteriorate over time (27,28). As for total-etch adhesives, it has been noted an incomplete resin diffusion into treated dentin (29), resulting in non-infiltrated areas at the bottom of the hybrid layer (27,30). Self-etch adhesives are supposed to simultaneously demineralize and infiltrate dentin, and the discrepancy between the degree of demineralization and depth of resin infiltration should be reduced. Anyway, an uncomplete resin diffusion into dentinal tubulos could be also identified for these adhesives (31).

Some microleakage studies have evidenced stained areas on the non infiltrated hybrid layer and on the adhesive layer as well (32,33).

II.3 Propriedades de la dentina como sustrato adhesivo

La dentina representa uno de los principales sustratos adhesivos en la Odontología adhesiva. Muchos tratamientos de superficie y el desarrollo de nuevos materiales se han propuesto para mejorar la adhesión a este sustrato altamente variable y heterogéneo. Mientras que el esmalte representa un tejido bastante favorable debido a sus características más homogéneas, la dentina sigue siendo el principal punto de interrogación para los científicos. Desde el punto de vista clínico, los dentistas se enfrentan a este sustrato con incertidumbres.

Conocer los principales componentes de la dentina y sus propiedades mecánicas puede ayudar a desarrollar nuevos materiales que mejor puedan sustituir el tejido dental perdido e integrarse fisiológicamente con la restante estructura, para que los efectos de micro o nano infiltración, responsables del fracaso prematuro de la restauración, se reduzcan. Además, las modificaciones estructurales y físicas de la dentina aportadas por el envejecimiento o los tratamientos químicos, se reflejan en los procesos cariosos, en la progresión de lesiones de V clase, en la sensibilidad dental y en algunos casos la fractura del diente (34).

Se pueden distinguir varios tipos de dentina: primaria, segundaria, reparativa, terciaria, transparente, cariada, desmineralizada, remineralizada o hipermineralizada (35). De hecho, la dentina es una estructura altamente compleja y heterogénea distinta de los demás tejidos dentales y formada por un 50% de su volumen de componentes minerales, por un 30% de matriz orgánica (especialmente fibras I de colágeno) y por un 20% de fluidos (36).

La dentina representa un sustrato elástico por el esmalte, y contemporáneamente tiene la función de proteger el tejido pulpar subyacente. Entre la dentina superficial y la profunda se pueden encontrar diferencias morfológicas, químicas y estructurales, por ejemplo el número de túbulos dentinarios y sus dimensiones, el tipo de dentina peri tubular y el área ocupada por la dentina inter-tubular (37,38,39). Los túbulos dentinarios tienen una orientación de tipo radial a partir de la parte central del tejido pulpar. Tanto la densidad de los túbulos como sus diámetros, disminuyen a la vez que los túbulos se alejan de la pulpa. La orientación de los túbulos influencia las propiedades mecánicas de la dentina, ya que una disposición perpendicular resulta en una resistencia disminuida a la carga oclusal (40). El componente mineral se encuentra en la dentina inter-tubular y en la dentina peri tubular (34). Los cristales de hidroxiapatita se diferencian de los del esmalte en ser más pequeños, con un contenido inferior de calcio y un porcentaje de carbonates de 4-5% (41,42). Los cristales de apatita se unen con los túbulos dentinarios (43), y esta unión puede favorecer las propiedades mecánicas de la dentina (34,35,37).

Para completar este cuadro estructural participan algunas proteínas cuya función es una incógnita (44).

A diferencia del esmalte, la dentina es una estructura altamente hidratada, caracterizada por un continuo movimiento de fluidos a través de los túbulos dentinarios (25,26,45,46,47) en los que se encuentran los procesos odontoblasticos.

El movimiento de fluidos es mayor a nivel de la dentina profunda que en la dentina superficial (48,49). El grado de perfusión diferente entre la dentina superficial y profunda depende del mayor diámetro de los túbulos más cercanos al tejido pulpar, con una diferencia que va desde los 2.5 µm de los túbulos profundos hasta las 0.8 µm de los superficiales (48,50). Las dos áreas se diferencian por el número de túbulos por área (22% a nivel de la dentina profunda a 1% en la superficial) (48). Algunos investigadores revelaron que el movimiento de fluido se realiza gracias a la presencia de una ligera presión pulpar de 15-20 mmHg (46,51).

Hoy en día es posible simular las condiciones del diente vital en laboratorio. Desde el punto de vista de la adhesión, el grado de hidratación de la dentina puede influenciar la capacidad adhesiva de algunos materiales resinosos y limitar la longevidad de la unión. Este mecanismo puede tener efectos negativos en algunos sistemas adhesivos que se componen de un alto porcentaje de monómeros hidrofílicos (25,52,53), especialmente durante las primeras fases de polimerización (54).

En general, los mecanismos de adhesión a la dentina se pueden clasificar en dos tipos: químicos y mecánico-retentivos. La adhesión química se realiza entre el material y el componente mineral del sustrato, las fibras de colágeno de la dentina o las precipitaciones derivantes de los pre-tratamientos ácidos (55). Por otro lado, la formación de *tags* de resina en los túbulos dentinarios abiertos y las modificaciones a nivel de la componente ínter-tubular, permiten lograr una retención óptima (56) que debe finalizarse con la completa polimerización del material resinoso (57). En realidad, la situación no es tan clara como podría parecer y la adhesión a la dentina y la longevidad de esta unión representan uno de los principales desafíos de la Odontología restauradora moderna (58).

La desmineralización de la dentina provoca modificaciones en su estructura y determina un aumento de la permeabilidad dentinaria debido a la remoción del barrillo dentinario y al apertura de los túbulos dentinarios (24.59). Hoy en día, son varios los agentes utilizados para este objetivo y cada solución es capaz de aportar diferentes alteraciones morfológicas a la superficie dentinaria (60,61,62).

El grabado ácido de la dentina provoca la remoción de la componente peri tubular, desmineralización de la dentina inter-tubular, y crea una superficie porosa que puede ser infiltrada por los agentes adhesivos. Los cambios estructurales han sido investigados con diferentes metodologías (8,37,59,61,63,64).

II.4 Cementos auto-adhesivos

Los cementos auto-adhesivos han sido introducidos recientemente en la práctica clínica y han sido presentados como una alternativa innovadora a los cementos resinosos tradicionales. Estos cementos reúnen en un solo producto el fácil manejo de los cementos convencionales, la capacidad de auto-adhesión y de liberación de fluor de los cementos de ionómero de vidrio y las propiedades mecánicas, estabilidad dimensional y retención micro-mecánica alcanzadas por los cementos resinosos.

La reducida sensibilidad a la técnica de aplicación ha representado unas de las razones fundamentales para el uso de los cementos auto-adhesivos cuya aplicación se resuelve en un único paso clínico: tras la mezcla de las pastas base y catalizadora o la activación de las capsulas monouso, el material se aplica directamente sobre la superficie a adherir. Se limitan por lo tanto los errores relacionados con su manejo.

Se supone que los cementos auto-adhesivos ofrecen una buena tolerancia a la humedad (Informaciones del fabricante, 3M ESPE).

Se limita también la incompatibilidad reconocida entre los adhesivos auto-grabadores simplificados y los cementos resinosos químiopolimerizables o de tipo dual (23,65,66) porque la polimerización radicálica está asegurada de acuerdo con el concepto de los cementos de ionómero de vidrio, permitiendo una extensiva cadena entrecruzada del cemento y la creación de polímeros de alto peso molecular. Según las informaciones adquiridas por los fabricantes, se debería llegar a una reducción de la sensibilidad post-operatoria, ya que estos cementos se aplican sobre la dentina cubierta con barrillo dentinario. Gracias a la buena estética, a las propiedades mecánicas y a la interacción micro-mecánica con los sustratos dentales, estos cementos se acercan a los cementos resinosos convencionales.

Los cementos auto-adhesivos disponibles en el mercado dental se diferencian por la modalidad de aplicación, el tiempo de trabajo y de polimerización y la composición química. A parte las informaciones obtenidas por los fabricantes, muy poco se sabe acerca de sus composiciones químicas exactas, del grado de polimerización y de las propiedades adhesivas.

Además no se encuentran estudios *in vivo* que puedan validar las escasas investigaciones *in vitro* realizadas hasta ahora.

A pesar de que el mecanismo de adhesión debería ser igual para todos los cementos auto-adhesivos, las principales propiedades de RelyX Unicem (3M

ESPE) son hasta ahora la más explicadas por su fabricante (3M ESPE, Seefeld, Alemania), mientras que actualmente muy poco se sabe acerca de otros productos como por ejemplo el Max-Cem y G-Cem (67,68,69,70). El mecanismo de adhesión consta de una retención micro-mecánica e interacción química entre los monómeros ácidos del cemento y el componente mineral (hidroxiapatita) de la dentina. Como consecuencia de la simplificación de su aplicación, el cemento debería ser capaz de desmineralizar y simultáneamente infiltrar el sustrato dental actuando aún en presencia del barrillo dentinario.

Por otro lado, el mecanismo de polimerización se realiza tras la exposición a la luz polimerizadle o según un mecanismo de químiopolimerización, ya que estos cementos pertenecen a la clase de los cementos de tipo dual (71). La reacción entre los grupos ácidos y el relleno alcalino asegura la neutralización de los monómeros ácidos. Esta reacción ácido-base libera agua, que debería favorecer al comportamiento hidrofilito del cemento en las fases iníciales de su aplicación, permitiendo así una mejor adaptación a la dentina y limitando la influencia de la humedad típica de este sustrato. Posteriormente, la función del agua es la de comportarse como un tampón necesario para que el cemento desarrolle unas propiedades más hidrofóbicas y no incorpore el agua resultante de la transudación de fluidos a través de los túbulos dentinarios.

Estudios *in vitro* han evidenciado que los cementos auto-adhesivos desarrollan una fuerza de adhesión inferior cuando se utilizan sobre el esmalte (68,72,73), por esta razón los autores recomendaron omitir el uso de estos cementos para el cementado de *inlays* o coronas parciales en presencia de cantidades relevantes de esmalte a nivel de la preparación, así como para el cementado de *bracketts* ortodónticos (67,74,75). Una mejoría de los valores de fuerza de adhesión se registró con solo grabar la superficie del esmalte con una solución de ácido fosfórico al 35% (73,76).

A pesar de que los autores coincidan con la evaluación del comportamiento de los cementos auto-adhesivos sobre el esmalte, todavía siguen muchas dudas en las valoraciones realizadas a nivel de la dentina. Algunos artículos científicos han comparado la fuerza de adhesión de los cementos auto-adhesivos *in vitro* a la de sistemas adhesivos auto-.grabadores (68,73,77,78,79), mientras que otros autores han descrito una fuerza adhesiva inferior (80).

Estudios morfológicos de la interfase entre cementos auto-adhesivos y dentina demostraron que a pesar de la elevada acidez de los monómeros hidrofílicos, estos no determinan la formación de una capa híbrida ni de *tags* de resina (68,73,80,81). Este aspecto se evidenció especialmente comparando los cementos auto-adhesivos con cementos resinosos convencionales que utilizan adhesivos de grabado total o auto-grabadores. De Munck y col (2004), afirmaron

que la interposición del barrillo dentinario que podría funcionar como una barrera, podría ser la causa de la escasa interacción y penetración de la dentina, tal y como se suele observar utilizando los cementos de ionómero de vidrio (73).

Por otra parte, el grabado ácido de la dentina, realizado mediante una solución al 35% de ácido fosfórico, determinó una remoción completa del barrillo dentinario, pero no aseguró la adecuada infiltración de la resina en la dentina subyacente. La explicación posible está en la elevada viscosidad del cemento investigado en el estudio (RelyX Unicem) que no le ha permitido fluir a través de los túbulos dentinarios abiertos (73).

En estudios de laboratorio recientes, se demostró que la aplicación de una presión estática durante la fase de cementado de las muestras, mejoró la difusión del material y sus propiedades tixotrópicas. Goracci y col. (2006) hallaron una mejoría de la fuerza de adhesión de RelyX Unicem aplicando una presión estática durante las primeras fases de la polimerización del material. No se han encontrado los mismos resultados positivos utilizando el Max-Cem (68).

Estudios de laboratorio sobre la micro infiltración de diferentes materiales utilizados para el cementado de coronas completas, demostraron que RelyX Unicem tiene valores de micro infiltración inferiores a los sistemas de cementado convencionales tanto en esmalte como en dentina (82,83). Este comportamiento puede depender de la presencia en el cemento auto-adhesivo de monómeros metacrílicos ácidos multifuncionales que puedan reaccionar con el componente mineral de los diferentes sustratos dentales, asegurando así un sellado eficaz. La interacción química a través de la formación de puentes hidrógenos favorece posteriormente la calidad adhesiva (82).

De manera similar, la fuerza de adhesión de RelyX Unicem, utilizado para el cementado de coronas en zirconio, fue similar a la de otros cementos convencionales, especulando que los cementos auto-adhesivos puedan representar una alternativa para el cementado de restauraciones indirectas (84,85), aunque se quedan algunas dudas cerca la durabilidad de esta unión.

Como consecuencia de la promoción de los cementos auto-adhesivos como sistemas de cementado universal, también se han utilizado para el cementado de postes de fibra de vidrio. A pesar de que la dentina radicular tiene diferencias morfológicas con la dentina coronal (86), las investigaciones realizadas han encontrado resultados similares caracterizados por la ausencia de una capa híbrida y la limitada capacidad del cemento de desmineralizar la dentina subyacente a través del barrillo dentinario (69,87,88). Desde el punto de vista de la fuerza de adhesión, los valores registrados por los cementos resinosos auto-adhesivos a nivel de la dentina radicular, fueron similares a los valores de

cementos convencionales cuando han sido utilizados para la cementación de postes de fibra de vidrio y de titanio (87,89,90,91).

RelyX Unicem presenta propiedades mecánicas superiores, como la resistencia a la compresión y la dureza superficial si se compara a cementos convencionales (77,92). Por otro lado, el porcentaje de conversión de los monómeros registrado en dicho estudio ha sido inferior, despejando algunas dudas acerca su estabilidad clínica a largo plazo y sobre la biocompatibilidad del material (92). De Souza Costa y col (71), no han hallado fenómenos de inflamación pulpar después de 60 días en dientes cementados con RelyX Unicem, probablemente debido a la baja solubilidad del material y al mecanismo de neutralización durante la fase de polimerización del cemento. En este estudio se ha asistido también a una leve respuesta pulpar tras 7 días desde el cementado, hecho justificado con el bajo valor inicial de pH presentado por el material (71). Se hacen necesarios estudios futuros para aclarar las propiedades físicas y mecánicas de estos cementos aún relativamente nuevos.

II.5. Postes de fibra de vidrio y pre-tratamientos

La utilización de postes de fibra de vidrio representa hoy la técnica de elección para la restauración de dientes endodonciados con escasa estructura coronal (93,94,95).

Los postes de fibra de vidrio han sido originariamente introducidos en el 1990, como alternativa a los postes metálicos (96,97,98). A pesar de las superiores propiedades físicas de los postes de metal, estos postes se han propuesto como alternativa para satisfacer las demandas estéticas clínicas (99,100). Junto a una mejorada calidad estética, los postes de fibra de vidrio permiten una uniforme distribución de los estreses a nivel de la raíz del diente (101,102) gracias al módulo elástico similar al de la dentina (103). Las ventajas relacionadas con la utilización de los postes de fibra de vidrio se reflejan también en el ahorro de tiempo durante los tratamientos (104), en la posibilidad de transmitir la luz polimerizable a través del poste, permitiendo la polimerización del cemento (105), en la posibilidad de remoción de los postes en caso de que sea necesario un re-tratamiento (106) y en una reducida probabilidad de producir hipersensibilidad alérgica.

Los postes de fibra de vidrio están formados por una matriz de resina epoxíca que durante la fabricación se inyecta entre las fibras y un agente de acoplamiento silano que se utiliza para mantener la adhesión entre las fibras y la matriz resinosa. Grandini y col. (2005) evaluaron la resistencia a la fatiga y las características estructurales de diferentes postes de fibra, concluyendo que el diámetro y la densidad de las fibras y sus uniones con la matriz resinosa afectan las propiedades mecánicas (107).

Los cementos resinosos se utilizan a menudo para el cementado de postes de fibra de vidrio, ya que ambos poseen un módulo elástico similar al de la dentina permitiendo una disminución de la concentración de estreses y del riesgo de fractura radicular (108). Se observó una mayor retención de los postes y resistencia a la fractura de los dientes endodonciados cuando se cementaron los postes con materiales resinosos en lugar de con cementos convencionales (109,110). A pesar del desarrollo de nuevos materiales para mejorar la adhesión en el conducto radicular, en la mayoría de los casos el fracaso de las restauraciones con postes de fibra depende de la pérdida de retención a nivel de la interfase cemento/dentina (111,112), llevando a presumir que la dentina radicular es un sustrato adhesivo poco favorable si se compara con la dentina coronal (113). Algunos autores han informado que el fracaso de las restauraciones con postes de fibra cementados adhesivamente, puede ocurrir también por el fallo de la unión entre postes y cementos (96,114).

Mayores fuerzas de adhesión entre poste-cemento-dentina son deseables para que los tres sustratos se unan para formar un monobloque y así poder garantizar la longevidad de la restauración (115). Sin embargo, el concepto de monobloque es poco predecible, debido a las diferentes propiedades de los sustratos (69,116).

Recientemente, se propusieron diferentes tratamientos de la superficie de los postes de fibra con la intención de aumentar la retención de los materiales de restauración resinosos (117,118). Según la naturaleza del tratamiento, hay tres clases de procedimientos: químicos (a través de la aplicación de agentes de acoplamiento silano o sistemas adhesivos), mecánicos (como el arenado o la grabación ácida) y químico-mecánicos (a través del uso combinado de los dos tratamientos anteriores) (119).

La adhesión entre cementos resinosos de tipo metacrílico y los postes con matriz de resina epóxica, sólo se realiza a través de una interacción entre los grupos metacrílicos del cemento y las fibras de vidrio de los postes. Debido a esta limitada interacción, los tratamientos de la superficie de los postes tiene la finalidad de eliminar la matriz resinosa epóxica superficial, exponer el mayor número posible de fibras que puedan reaccionar con el material. Además, la formación de rugosidades superficiales debida a los varios tratamientos, debería favorecer la retención micro-mecánica del material (117,118,120,121,122).

De los tratamientos químicos propuestos, el uso de silano como agente intermedio para optimizar la adhesión, ha sido seguramente el más investigado, y su utilización ha sido reconocida y recomendada por varios autores (90,123,124). La justificación es la mejoría en la fuerza de adhesión como consecuencia de un aumento de la humectabilidad de la superficie, pudiendo el silano ejercer una función de mediador entre material y superficie. La fuerza lograda a nivel de la interfase cemento/poste, no es comparable con aquella alcanzada entre silano y dentina, y esto se supone que es debido a una incompatibilidad química entre los grupos metacrílicos de los cementos resinosos y la matriz resinosa de los postes, que en la mayoría de los casos es de tipo epóxica (125). Ya que el silano puede ser eficaz solamente cuando la interacción ocurre entre el cemento y las fibras, los tratamientos combinados silano y ácido o pre-calentamiento de la solución pueden ayudar en alcanzar el objetivo final (126). Para aumentar el mecanismo de adhesión química y favorecer la unión, se propuso el uso combinado de silano y agentes adhesivos y actualmente algunos fabricantes presentan soluciones en dos etapas con un silano/*primer* seguido de la aplicación del adhesivo. Los resultados descritos en la literatura dental son muy variados, y la eficacia de este tipo de tratamiento está relacionada con el tipo de adhesivo. (127,128).

Se supone que el tratamiento químico combinado con la retención mecánica debería ayudar a mejorar esta unión. La idea de grabar los sustratos adhesivos ha sido inicialmente propuesta por los tejidos dentales (12,129), con la intención de crear sitios adicionales en las superficies para favorecer la retención micro mecánica. En la rea de los materiales dentales, este concepto ha sido adaptado a materiales diferentes como la cerámica, y recientemente ha sido experimentado también en los postes de fibra de vidrio. Las evaluaciones realizadas con microscopía electrónica de barrido, han permitido observar los efectos aportados por los varios tratamientos, evidenciando respuestas diferentes a nivel de las fibras y la matriz resinosa. Se ha comprobado que la eficacia del tratamiento con ácido fluorhídrico depende del tiempo de aplicación. Este tratamiento se ha revelado muy agresivo, determinando la corrosión de las fibras de vidrio. Se supone que las alteraciones provocadas pueden afectar la integridad de los postes, y por eso no se aconseja como tratamiento superficial (118,130).

Resultados similares caracterizados por modificaciones de la morfología de los postes, se han observado en caso de algunos tratamientos mecánicos, como el arenado con partículas de alúmina. El tiempo de aplicación del chorro y el tamaño de las partículas pueden afectar al resultado final dañando la estructura del poste (131). La utilización combinada del arenado para aportar rugosidad superficial y de agentes de acoplamiento silano para facilitar la interacción química, ha determinado valores de fuerza de adhesión más elevados (118). En la actualidad están disponibles en el mercado postes de fibras de vidrio preliminarmente tratados (i.e. DT Light SL post, VDW) para simplificar las fases clínicas.

Otros tratamientos químicos han sido propuestos con la misma intención, como el tratamiento con peróxido de hidrógeno, permanganato de potasio o etóxido de sodio (119,120). La elección de estos tratamientos se realiza para remover de forma selectiva la matriz de resina epóxica superficial dejando las fibras de vidrio expuestas para la posterior aplicación del silano.

Estos tratamientos han sido considerados ventajosos para mejorar la adhesión a los materiales resinosos de restauración y cementado y por lo tanto se teoriza que pueden ser válidos para mejorar la retención de postes cementados con cementos auto-adhesivos. El poder disponer de postes de fibra pre-tratados, sin la necesidad de aplicar agentes silanos o adhesivos durante las etapas de cementado y de cementos universales, representa sin duda una estrategia deseable para simplificar las técnicas adhesivas indirectas. Son todavía necesarios estudios a largo plazo para así poder realmente recomendar su utilización clínica.

III. JUSTIFICACIÓN Y OBJETIVOS

Debido a la reciente introducción en el mercado dental, muy poco se sabe acerca del potencial de los cementos auto-adhesivos. Al pertenecer al grupo de los cementos resinosos, se supone que estos materiales promueven una retención micro-mecánica a los sustratos dentales, acompañada por la simultánea interacción química. Utilizando los cementos resinosos convencionales, es posible lograr una unión más predecible gracias al grabado ácido de los tejidos dentales y a la aplicación de un sistema adhesivo.

Los cementos auto-adhesivos resultan innovadores ya que incorporan en un único producto los componentes necesarios para modificar e infiltrar el sustrato dental.

De los pocos estudios actualmente presentes en la literatura dental, todos se han centrado en comparar la capacidad de cementado de los sistemas auto-adhesivos, con la de cementos convencionales o cementos resinosos que utilizan adhesivos de grabado total o auto-grabadores. De manera particular, tras la introducción del primer cemento auto-adhesivo en el 2002 (RelyX Unicem, 3M ESPE, Seefeld, Alemania) se ha desarrollado un gran número de cementos auto-adhesivos. No obstante, desde un punto de vista científico, RelyX Unicem sigue siendo el material más investigado. Un número limitado de investigaciones tuvieron como objetivo evaluar la capacidad de unión de otros cementos auto-adhesivos, sin aclarar el mecanismo de adhesión de estos productos.

El comportamiento de los cementos auto-adhesivos utilizados para el cementado de restauraciones indirectas, no está claro todavía. La presente tesis doctoral se propone investigar la interacción entre cementos auto-adhesivos y la dentina coronal evaluando el potencial adhesivo de estos materiales y por ello nos hemos planteado cuatro objetivos principales.

1. Todos los autores afirman que el mayor problema relacionado con estos cementos es su interacción verdadera con la dentina, que resulta ser bastante débil teniendo en cuenta los valores de fuerza de adhesión obtenidos, y dejando dudas sobre la longevidad de la unión. Estas investigaciones se han realizado a través de evaluaciones de la interfase adhesiva cemento-dentina utilizando la microscopía electrónica de barrido. Dicha metodología puede no llegar a darnos una idea exacta de la interacción a nivel de la interfase. En la primera parte de esta tesis doctoral, se evaluó la capacidad de desmineralización y la consecuente infiltración de los cementos auto-adhesivos de la dentina coronal mediante microscopía óptica y coloración de Masson acompañada por microscopía electrónica de barrido.

2. No existen enfoques previos que establezcan la capacidad adhesiva de estos cementos simplificados en la dentina vital donde la presencia de presión pulpar positiva determina un movimiento de fluidos a través de los túbulos dentinarios. Estudios precedentes han afirmado que la presencia de presión pulpar puede limitar la capacidad de unión de adhesivos de grabado total y auto-grabadores. No hay informaciones sobre el comportamiento de los cementos auto-adhesivos en las mismas condiciones experimentales. El segundo objetivo de esta tesis doctoral ha sido evaluar la influencia de la presión pulpar sobre la capacidad adhesiva de estos cementos a través de un ensayo de microtensión y una evaluación con microscopía electrónica de barrido.

3. En la literatura científica se afirma que el grabado ácido de la dentina, a pesar de la eliminación del barrillo dentinario, no favorece una superior interacción de RelyX Unicem con el sustrato. Otros tratamientos de la dentina han sido investigados en la presente tesis, como EDTA y ácido poli acrílico con el objetivo de eliminar el barrillo dentinario, cuya influencia como sustrato intermedio, puede no favorecer el mecanismo de unión. El tercer objetivo planteado en esta tesis ha sido evaluar el efecto de EDTA y ácido poli acrílico para eliminar el barrillo dentinario sobre la capacidad adhesiva de diferentes cementos auto-adhesivos. Se ha podido valorar sí efectivamente la eliminación del barrillo dentinario puede facilitar la interacción directa con la subyacente dentina.

4. Los tratamientos químico-mecánicos de las superficies de los postes de fibra con matriz de resina epoxíca, han sido originariamente propuestos para mejorar la adhesión de materiales de restauración con matriz de resina metacrílica. La mayoría de las evaluaciones realizadas, suelen utilizar microscopía electrónica de barrido para observar los cambios estructurales aportados por los diferentes tratamientos. La microscopía de fuerza atómica (AFM) y confocal han sido utilizadas muy a menudo para evaluar morfológicamente diferentes sustratos. Este tipo de análisis puede ser utilizado para visualizar y medir el grado de rugosidad de la superficie de los postes de manera predecible. El objetivo planteado en el cuarto estudio ha sido determinar a través de un análisis combinado mediante AFM y microscopía confocal, el grado de rugosidad de la superficie de los postes de fibra con matriz de resina epóxica, tras realizar unos tratamientos químico-mecánicos, y el de evaluar la influencia de estos tratamientos a nivel de la matriz resinosa y de las fibras de vidrio. Una vez aclarado el mecanismo de adhesión de los cementos auto-adhesivos a los sustratos dentales, se podría teorizar sus utilizaciones en combinación con postes de fibra pre-tratados. El beneficio de los tratamientos de superficie de los postes de fibra y la simplicidad de uso de los cementos auto-adhesivos, podrían contribuir a optimizar el cementado de los postes de fibra consiguiendo resultados predecibles a largo plazo.

IV. DISCUSIÓN

Los estudios realizados en la presente tesis doctoral han permitido aclarar el mecanismo de adhesión de los cementos auto-adhesivos. Se ha decido evaluar el potencial adhesivo de estos materiales desde puntos de vista diferentes.

Investigaciones anteriores han evaluado las propiedades mecánicas y físicas de estos cementos (79,92,132) o la unión a la dentina radicular (91,133). En esta tesis, la adhesión a la dentina coronal ha sido el principal tema de discusión ya que se ha evidenciado una escasa adaptación marginal, y débil interacción con el sustrato a adherir (80,81). De hecho, la optimización de la adhesión a la dentina representa uno de los principales desafíos de la Odontología adhesiva, debido a la complejidad morfológica de este sustrato (80,81).

Diferentes cementos auto-adhesivos han sido analizados en esta tesis doctoral y comparados en diferentes condiciones de laboratorio.

Como recoge la literatura, la capacidad de "auto-adhesión" de estos productos depende de la incorporación de monómeros ácidos que reaccionan con el componente mineral de la dentina, permitiendo una simultánea desmineralización y penetración de la resina en el sustrato dental (68,73). Este mecanismo consta de dos etapas principales. En primer lugar, los monómeros ácidos interactúan con la hidroxiapatita de la dentina según una reacción de tipo ácido-base. Al mismo tiempo, los monómeros metacrílicos, reaccionan con el relleno básico del cemento, en un proceso de neutralización que lleva a la formación de agua. El agua es necesaria para equilibrar la reacción ácido-base entre cemento e hidroxiapatita, para que los monómeros ácidos sean neutralizados en un tiempo reducido, favoreciendo así la reacción de polimerización del material. El barrillo dentinario representa el sustrato intermedio de adhesión. El uso de estos cementos permite una simplificación de las fases clínicas, ya que el tratamiento de la dentina no se hace necesario, aunque haya dudas sobre su efectiva capacidad de unión (68,73,81). Diferentes variables pueden influenciar la unión: el tipo de cemento, su composición química, sus propiedades mecánicas y físicas (134), la presencia de dentina cubierta con el barrillo dentinario, débilmente anclado al sustrato dental (135,136), la dentina, un sustrato heterogéneo y complejo (9).

Las investigaciones realizadas hasta ahora, han evaluado la interfase cemento auto-adhesivo/dentina a través de la microscopía electrónica de barrido (68,81,137). Los resultados obtenidos han evidenciado una buena adaptación marginal del cemento al sustrato dental, sin formación de una capa híbrida que pueda presuponer una efectiva interacción con la dentina (81). La utilización de

la coloración de Masson en microscopía óptica, junto al análisis con microscopía electrónica de barrido, ha permitido evaluar el grado de desmineralización de la dentina, la profundidad de penetración de la resina y la cantidad y calidad de la capa híbrida (138,139).

Los resultados alcanzados en el primer estudio de esta tesis doctoral (Anexo VIII.1) han evidenciado cómo la interfase entre los cementos auto-adhesivos y la dentina se caracteriza por una buena adaptación marginal para todos los cementos (RelyX Unicem, Bis-Cem, G-Cem y Multilink Sprint); sólo Multilink Sprint presentó una escasa penetración de la resina en las fibras de colágeno parcialmente expuestas (7,11). En el caso de los otros cementos no ha sido posible encontrar síñales de infiltración de la dentina ni de formación de capa híbrida. La elevada viscosidad del cemento o la inadecuada neutralización de la reacción ácido-base durante la fase de polimerización, han podido afectar a la reacción química entre el cemento y el sustrato dental (73,77). La escasa interacción con la dentina deja suponer que a pesar de la elevada acidez de los monómeros, son necesarios otros mecanismos para completar la interacción química (140). Diferentes resultados se podían esperar por G-Cem, ya que según el fabricante, el mecanismo de adhesión debería ser similar al de los cementos de ionómero de vidrio. El agua, ya presente en su formulación, debería favorecer la neutralización de los monómeros ácidos reduciendo así el tiempo requerido para la interacción con el sustrato dental (140). Pero también en este caso, la elevada viscosidad del material ha podido afectar la difusión de la resina. En estos tres casos, la coloración de Masson no ha evidenciado ninguna área teñida de rojo, que debería reflejar la desmineralización de la dentina. Sólo en el caso de Multilink Sprint, se evidenció una débil desmineralización, seguida de una escasa infiltración por parte de la resina.

Los resultados de la investigación no han detectado un claro equilibrio entre el grado de desmineralización e infiltración de la resina como sí han sido observado por los sistemas adhesivos auto-grabadores. Si de un lado la elevada acidez de los monómeros puede favorecer la infiltración del sustrato dental, desde otro la inadecuada neutralización de estos monómeros ha podido afectar a la fase de polimerización del material. Los monómeros ácidos no completamente polimerizados, pueden mantener activo su potencial y afectar la longevidad de la unión (32,141). La diferente interacción de los cementos auto-adhesivos con la dentina es relevante si la comparamos con el mecanismo de unión de los cementos que utilizan sistemas adhesivos de grabado total (Calibra y Prime&Bond NT). Según las imágenes obtenidas, a pesar de que el grabado ácido previo determinó una desmineralización de la dentina, no se han evidenciado signos de infiltración de la resina.

La dentina vital es un tejido altamente hidratado, caracterizado por un continuo movimiento de fluido a través de los túbulos dentinarios (25,46).

La fuerza de microtensión de los cementos investigados previamente, utilizados para el cementado de *onlays*, ha sido evaluada en presencia de presión pulpar (Anexo VIII.2). Según se ha descrito en investigaciones anteriores, el pasaje de fluidos a través de los túbulos dentinarios puede influenciar de forma negativa el potencial adhesivo de sistemas auto-grabadores y de paso único (25,26). La rápida evaporación del solvente y el alto contenido de monómeros hidrofílicos, son los principales responsables del pasaje de fluidos en la capa de adhesivo (23,24). Eso determina una alteración del proceso de polimerización, que puede no ser completo, y altera la longevidad de la unión. Hasta ahora, ninguna investigación había evaluado la influencia de la hidratación de la dentina sobre la capacidad adhesiva de estos cementos. Los resultados obtenidos en el estudio han demostrado que algunos cementos (RelyX Unicem y Bis-Cem) se benefician de la presencia de agua. Estos resultados han confirmado en parte algunas de las conclusiones logradas en el previo estudio y han evidenciado cómo algunos cementos auto-adhesivos tienen un comportamiento similar al de los cementos silicato. El agua presente a nivel del sustrato, pudo haber facilitado la ionización de los monómeros ácidos, permitiendo una adecuada interacción con el sustrato dental (20). Según los resultados obtenidos mediante microscopía de barrido, G-Cem no llegó a infiltrar la dentina subyacente, probablemente debido al elevado peso molecular de los monómeros funcionales. Utilizando Multilink Sprint se alcanzó una interacción más evidente con la dentina y la formación de algunos *tags* de resina, aunque la fuerza de adhesión de Multilink Sprint fue la más baja. Esto puede confirmar que una interacción más íntima con el sustrato, no necesariamente, puede garantizar una fuerza de adhesión mayor (53,142). Calibra ha sido el único sistema de cementado de grabado total investigado en este estudio: los valores de fuerza de adhesión han sido más elevados en ausencia de presión pulpar. Las imágenes de microscopía electrónica de barrido y los valores de microtensión, han confirmado los resultados de estudios precedentes (127).

Al-Assaf y col. (2007) han obtenido resultados similares analizando la fuerza de adhesión a la dentina coronal de RelyX Unicem (81). Según estos autores, la presencia del barrillo dentinario limita el poder alcanzar una efectiva adhesión, ya que se pensaba que los cementos auto-adhesivos no tenían la capacidad necesaria para modificar el barrillo dentinario, desmineralizar la subyacente dentina e infiltrarla a la vez. Estudios recientes han demostrado el efecto negativo del grabado ácido de la dentina sobre la capacidad adhesiva de estos cementos (73,76). A pesar de la completa eliminación del barrillo dentinario y de la abertura de los túbulos dentinarios, la penetración de la resina puede ser insuficiente debido a la viscosidad, al peso molecular, a escasa afinidad de los

monómeros con el sustrato orgánico y al tiempo necesario para la difusión (81). En la tercera investigación descrita en esta tesis doctoral (Anexo VIII.3), se ha determinado la fuerza de adhesión de diferentes cementos auto-adhesivos a la dentina tratada con un agente quelante y una solución ácida débil (0.1 M EDTA y 10% ácido poli acrílico).

Para la realización de este protocolo de investigación se han testado RelyX Unicem, Bis-Cem y G-Cem. Multilink Sprint no se ha utilizado. Durante el desarrollo de la tesis doctoral, este material ha sido retirado del mercado debido a la prematura degeneración a la que se enfrentaba el producto.

Los tres cementos se han comportado de manera distinta en las mismas condiciones de laboratorio. RelyX Unicem no ha registrado ningún cambio en la fuerza de unión, Bis-Cem se ha caracterizado por una fuerte disminución de estos valores cuando se ha aplicado sobre dentina pre-tratada con EDTA o ácido poli acrílico. La fuerza de unión de G-Cem ha mejorado cuando se ha utilizado sobre dentina grabada con ácido poli acrílico, sin registrar ninguna diferencia entre el grupo de EDTA y el grupo sin tratamiento. La eliminación del componente mineral de la dentina puede suscitar incertidumbre si se quiere utilizar los cementos auto-adhesivos.

Como se ha descrito anteriormente, los monómeros ácidos de estos materiales tienen la capacidad de reaccionar selectivamente con el componente mineral de la dentina y así favorecer la interacción química. La retención mecánica que se puede realizar grabando anteriormente el sustrato puede consolidar la adhesión. Según ha sido sugerido por el fabricante, los monómeros ácidos reaccionan con el calcio de la hidroxiapatita. La eliminación del componente mineral de la dentina con EDTA o con el grabado con ácido poli acrílico limita inevitablemente la interacción química de estos cementos.

Hoy en día la utilización de postes de fibra de vidrio para la rehabilitación de dientes endodonciados con reducida estructura coronal es una práctica clínica diaria. La posibilidad de realizar un monobloque entre poste-cemento-estructura coronal residual, es objeto de continuo interés por parte de los investigadores (116,117). Algunos autores han afirmado que la mayoría de los fracasos de estas restauraciones depende del fallo de la unión entre poste y cemento (123,143). Diferentes tratamientos de la superficie de los postes han sido propuestos hasta ahora, con la intención de mejorar la longevidad de la unión (118,121,144). Estos se pueden clasificar en tratamientos químicos, mecánicos, o químico-mecánicos (145). Estudios de laboratorio han evidenciado la capacidad de mejorar la fuerza de unión a la resina compuesta de estos tratamientos (119,121). Se ha constatado también que algunos de estos tratamientos pueden dañar las fibras de vidrio (121,146).

En la actualidad la microscopía de fuerza atómica y la microscopía confocal se han utilizado para el análisis de sustratos dentales tras los diferentes tratamientos de superficie (147,148,149). Por primera vez, se ha utilizado este tipo de microscopía para el análisis de la superficie de los postes de fibra de vidrio tras realizar diferentes tratamientos químico-mecánicos, para evaluar cualitativamente la rugosidad superficial y las modificaciones aportadas por cada tratamiento.

Esta análisis ha permitido evaluar hasta qué nivel, el tipo de pre-tratamiento ha alterado la integridad de las fibras de vidrio y de la matriz de resina epóxica. Los resultados obtenidos, han convalidado algunos datos precedentemente reportados por otros autores. El grabado con ácido fluorhídrico ha determinado la exposición de las fibras de vidrio y también un daño de las últimas (121). De acuerdo con previas investigaciones, este tipo de tratamiento no se considera apropiado para los postes de fibra de vidrio. El arenado es un tratamiento mecánico y se utiliza a menudo en Odontología restauradora. Una correcta elección del tipo de partículas de alumina y de la distancia de operación, hace que el arenado pueda ser utilizado para el tratamiento de los postes de fibra (144,150). En la actualidad están disponibles en el mercado postes de fibra tratados por el mismo fabricante (arenado más silanización): el análisis microscópico ha revelado una superficie plana, con las fibras de vidrio completamente hundidas en la matriz de resina epóxica, recubiertas por la capa de agente de acoplamiento superficial. Estos resultados han sido comparables a aquellos alcanzados por el permanganato de potasio. El peroxido de hidrógeno y el etóxido de sodio, no han demostrado poseer una rugosidad diferente al grupo sin tratamiento.

V. CONCLUSIONES

La reciente introducción de los cementos auto-adhesivos universales, ha supuesto una innovación en la Odontología de tipo adhesivo. La idea de utilizar un solo cemento para todos los tipos de restauraciones, y el ahorro de tiempo relacionado con su utilización, es una razón que facilita el trabajo de los dentistas. Desde el punto de vista de la eficacia adhesiva, la disminuida sensibilidad al operador, relacionada con la aplicación de estos cementos en una única fase clínica, es su punto más relevante.

En la mayoría de los casos las preparaciones protésicas determinan la remoción del esmalte dental y la exposición de la subyacente dentina. En este sentido, el mecanismo de acción de los cementos auto-adhesivos debería tener en cuenta dos sustratos diferentes de adhesión: al barrillo dentinario formado durante las preparaciones, así como descrito por los adhesivos auto-grabadores, y la dentina coronal. Ambos sustratos resultan complejos, heterogéneos y escasamente uniformes, y el mecanismo de adhesión es, aún hoy en día, uno de los principales objetos de investigación.

Según las instrucciones aportadas por los fabricantes para lograr una perfecta adhesión, los cementos auto-adhesivos, gracias a sus monómeros ácidos, deberían infiltrar el barrillo dentinario, desmineralizar parcialmente la dentina, difundir en los túbulos dentinarios abiertos y polimerizar lo suficientemente rápido. A pesar de sus pH ácidos iniciales, recientes estudios han demostrado que estos cementos se caracterizan por una escasa capacidad adhesiva a las estructuras dentarias. Muchas investigaciones son necesarias todavía para establecer sus mecanismos de adhesión y hacer que la simplificada tecnología de estos cementos se refleje, igualmente, en una eficacia clínica.

Las conclusiones que se pueden deducir de la presente tesis doctoral son:

1. Una escasa interacción química y retención mecánica parece caracterizar la interfase entre los cementos auto-adhesivos y la dentina coronal. La dentina es un tejido complejo, y una óptima adhesión puede ser comprometida por su variabilidad estructural. En general, el mecanismo de adhesión entre sistemas de cementado que prevén el uso de adhesivos de grabado total y la dentina está basado en la hibridazación del tejido dental, donde el grado de desmineralización de la dentina y la infiltración de la resina juegan un papel fundamental. Si se comparan los cementos auto-adhesivos con los cementos basados en sistemas adhesivos de paso múltiple, se evidencian diferencias a nivel de la interfase y una escasa adaptación marginal. La elevada viscosidad de estos materiales y la inadecuada neutralización del mecanismo ácido-base con consecuencias directas sobre el proceso de polimerización de los mismos, han

sido considerados los factores que mayormente pudieron afectar la interacción con la dentina.

2. En un diente vital, la dentina se caracteriza por una transudación de fluidos a través de los túbulos dentinarios. Después de una preparación cavitaria o protésica, el sustrato dental se encuentra recubierto por una capa de barrillo dentinario. Su presencia debería limitar la excesiva transudación de fluidos a nivel dentinal. La aplicación en laboratorio de perfusión dentinaria simulada, ha influenciado la capacidad adhesiva de los cementos auto-adhesivos investigados de manera diferente. La composición química y el porcentaje de relleno han podido influenciar los resultados obtenidos.

3. Si por un lado el barrillo dentinario sirve como barrera para limitar los efectos del movimiento de fluidos a través de los túbulos dentinarios, por otra parte puede representar el principal obstáculo para la unión entre cementos auto-adhesivos y la dentina. El grabado de la dentina con soluciones de ácidos fuertes, determina una modificación excesiva estructural del tejido dental y evidencia cómo la exposición de las fibras de colágeno no representa un medio para optimizar la unión del cemento al sustrato. El uso de soluciones consideradas "*mild"* (desmineralización con solución 0.1 M de EDTA y grabado con 10% de ácido poli acrílico) no ha dado el mismo resultado para los cementos testados. La distinta composición química de los cementos auto-adhesivos puede explicar los diferentes resultados alcanzados en las situaciones investigadas. A pesar de la pertenencia al mismo grupo de cementos resinosos auto-adhesivos, algunos de ellos se parecen más a los cementos convencionales, mientras que otros son más similares a los cementos de ionómero de vidrio.

4. El tratamiento superficial de los postes de fibra de vidrio con matriz de resina epóxica ha sido investigado por primera vez con una metodología alternativa, a través de evaluaciones con microscopía de fuerza atómica (AFM) y microscopía confocal. El análisis ha permitido averiguar el grado de rugosidad aportado por los diferentes tratamientos químicos y mecánicos, y evaluar la influencia de dicho tratamientos sobre la matriz resinosa y las fibras de vidrio. Algunos tratamientos de superficie (ácido fluorhídrico) han producido daños en las fibras; por lo tanto, no es recomendable. El arenado, el grabado con peroxido de hidrógeno seguido por la aplicación de silano son los pre-tratamientos de elección.

V.1 Conclusions

Self-adhesive cements have represented a pioneer aproach in adhesive and restorative dentistry. The fascinating technology based on a universal concept and saving time have encountered clinician's desire. The gold point of these simplified cements, rely on the inferior technique sensitivity related to them and to the reduced clinical steps, that enhance for a simultaneous demineralization/infiltration of dental substrates.

During prosthetic preparation, a large removal on enamel may occur leaving exposed the underlying dentin. Thus, self-adhesive cements have two possibility to bond to the substrate: interposing the smear layer formed during the restorative procedures as it was proposed for self-etching adhesives, or directly to dentin. Both smear layer and dentin are complexes, heterogeneous and uniform substrates. Due to their complexity, their adhesion mechanism remain still complicate. However, as all prosthetic preparation form smear layer covered dentin, it is natural that with this simplified cement, smear layer represent the intermediate adhesive substrate.

According to manufacturer's instructions, the acidic monomers contained into their compositions should help the material to intercat with smear layer, demineralize the underlying dentin, penetrate into the exposed dentinal tubules where it should polymerize in a short period of time in order to achieve an effective adhesion.

Despite the advertized high acidity of their monomers, a poor interaction with dentin has been reported for self-adhesive cements. For this reason, further studies are necessary for determine the adhesive mechanism and improve their bonding effectiveness.

The following conclusions can be drawn from the present doctoral thesis:

1. A poor chemical interaction and questionable mechanical retention characterize the cement-dentin interfaces. Dentin is a complex substrate, and the structural variabilities may influence the adhesive hability of a material. Generally, the tissue hybridization fix the basis for a perfect adhesion, where the degree of dentin demineralization and the depth of resin infiltration play an important role. Similarly, resin infiltration onto dentin is directly related to the dental substrate conditioning. When compared to conventional cements based on the previous application of multi-step adhesives, self-adhesive cements did not showed an effective dentin hibridization but the interface was characterized by a poor marginal adaptation. The high viscosity and the inadequate neutralization

of the acid-base reaction have been recognized has the main factors influencing the obtained results.

2. The vital dentin is characterized by an otward fluid flow through dentinal tubules. In that scenario, the smear layer should form a barrer against an excessive water transudatioin, so it can not affect the quality of the adhesion. In the second study performed during this doctoral thesis, the presence of a simulated positive pulpal pressure influenced differently the luting materials investigated. It has been postulated that the different chemical compositions and the percentages of fillers of each cement influenced their mechanical properties so resulting in different responsiveness in the same laboratory conditions.

3. If from one side, the presence of smear layer serve as barrer for limiting the deleterious effect of water, from the other side it may represent a weak link that represent an obstacle affecting the quality of the bond between self-adhesive cement and dentin. Dentin etching with strong acidic solutions imply huge structural modifications of the dental substrate. However, dentin conditionings with mild solutions (demineralization with 0.1 M EDTA or etching with 10% polyacrylic acid) did not have the same effects on the bonding potential of the self-adhesive cements investigated. Probably, the obtained results can be referred to the different chemical compositions of the tested materials, that characterize their clinical behaviour. Even if grouped in the same self-adhesive family, some of them showed conventional cements typical characteristics, meanwhile others behave in a glass ionomer cmeent way.

4. For the first time, surface conditionings of epoxy resin-based fiber posts have been investigated with alternative methodologies as an evaluation with atomic force microscopy (AFM) and confocal microscopy. These observations allowed to assess the surface roughness after post surface conditionings with chemical solutions and mechanical approaches and evaluate how these pre-treatments can affect the components of the fiber post: epoxy matrix and glass fibers. Of the conditioning approaches investigated, hydrofluoric acid and potassium permanganate affected the glass fibers, thus they should not be recommended for post surface pre-treatments. On the other hand, etching with hydrogen eproxide still represent the pre-treatment of election.

VI. PERSPECTIVAS FUTURAS

Los cementos auto-adhesivos representan una innovación en la Odontología de tipo adhesivo. A pesar de su "universalidad", estos cementos no se pueden recomendar todavía de manera absoluta, y futuros estudios deberían desarrollarse para que la simplificación de los pasos clínicos se refleje en la calidad de la unión.

No todos los cementos auto-adhesivos hasta ahora presentes en el mercado se comportan de la misma manera. Estos cementos se diferencian principalmente por sus composiciones químicas. En la actualidad, el cemento más investigado ha sido RelyX Unicem (3 M ESPE). Futuros estudios deberían realizarse para aclarar las propiedades físicas y mecánicas y la capacidad de adhesión de otros productos.

Hay escasas informaciones acerca de la unión entre cementos auto-adhesivos y postes de fibra de vidrio. A pesar de que la interacción entre cementos auto-adhesivos y la dentina radicular lleva la mayoría de las incertidumbres, fallos de la restauración a nivel de la interfase cemento/poste también pueden ocurrir. Ha sido aceptada la idea de que algunos tratamientos de superficie de los postes de fibra favorecen la retención mecánica de los cementos resinosos sin dañar las fibras. La eficacia de estos tratamientos de superficie para mejorar la unión a la resina compuesta para la reconstrucción coronal ya ha sido evaluada. Sería interesante plantear futuros estudios sobre la unión entre cementos auto-adhesivos y postes de fibra de vidrio pre-tratados.

Un número limitado de estudios se han centrado en evaluar la eficacia adhesiva de los cementos auto-adhesivos a largo plazo, a través del envejecimiento en laboratorio que pudieran simular las condiciones clínicas reales. Investigaciones posteriores a esta tesis se realizarán para evaluar la longevidad de los cementos auto-adhesivos.

Hoy en día el conocimiento de estos cementos está basado principalmente en estudios *in vitro*. Si de un lado los ensayos de laboratorio pueden anticipar el comportamiento clínico de los materiales, por otra parte los estudios *in vivo* son necesarios para convalidar los resultados obtenidos en laboratorio. Actualmente, no existen en la literatura dental estudios clínicos basados en el uso de cementos auto-adhesivos.

VI. 1 Future directions

Self-adhesive resin cements are innovative materials of the adhesive dentistry. Despite the interest deserved, these cements can not universally be recommended, and future studies should be addressed in order to combine the simplified self-adhesive technology with the clinical excellence.

As it has been previously reported, the self-adhesive cements already available in the market do not behave in the same manner. The main difference is related to their chemical composition. Actually, the most investigated material has been RelyX Unicem (3M ESPE). Further studies are necessary to clarify the mechanical and physical properties of all the contemporary self-adhesive products.

Scarce information is present regard the self-adhesive cement/fiber post interaction. Although the cement/dentin bonding mechanism seems to be uncertain and it requires additional investigations, adhesive failure at the post/cement interface may occurr. Some post surface pre-treatments have been recognize to improve mechanical retention of resin material while maintaining glass fiber integrity. The effective retention of the treated post/resin material complex has been assessed for resin composite used for coronal restorations. No information is available about the efficacy of these pre-treatments on resin cements. It could be of interest to evaluate the effect of post surface pre-treatments on self-adhesive cement retention.

Little information is present regard the longevity of self-adhesive cements bonds. Laboratory investigations, that can reproduce clinical conditions, are necessary to predict their behaviour *in vitro*.

Actually, the information regards self-adhesive cements is mainly based on laboratory studies. From one side, these investigations are necessary to reproduce *in vitro* the clinical behaviour; on the other hand, *in vivo* clinical studies are necessary to validate the experimental results. Until recent, there is no information in literature based on clinical studies conducted on self-adhesive cements.

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VIII Anexo de trabajos publicados

Anexo VIII.1 (Chapter VIII.1)

Descalcificación limitada y difusión de cementos auto-adhesivos en la dentina
(*Limited decalcification/diffusion of self-adhesive cements into dentin).*

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Limited decalcification/diffusion of Self-Adhesive Cements into Dentin.

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Short title: Limited infiltration of self-adhesive cements

KEY WORDS: Self-adhesive cement; Masson's trichrome; smear layer; demineralization; exposed collagen.

ABSTRACT

Resin cement diffusion into dentin may differ as a function of the pre-treatment regimen. As self-adhesive cements do not require substrate pre-treatment for luting, penetration and interaction with the underlying dentin is questioned. Differences in the resin cement diffusion into dentin may exist between current commercial adhesive cements. Composite cylinders were luted on mid-coronal dentinal surfaces using an etch-and-rinse cement (Calibra), a self-etching system (Panavia F 2.0) and four self-adhesive cements (Multilink Sprint; Rely X Unicem; G-Cem; Bis-Cem). Dentin/cement interfacial characteristics were analyzed using a staining technique (Masson's trichrome) and with scanning electron microscopy. Conventional acid etching resulted in partially-infiltrated adhesive interfaces differing from the application of self-etching primer. No hybrid layer and/or resin tags formation were detectable at the interfaces bonded with self-adhesive cements. Limited decalcification/infiltration was observed for self-adhesive cements into the underlying dentin. Self-adhesive cements were not able to completely demineralise/dissolve the smear-layer.

INTRODUCTION

Resin-based dental luting agents, which are routinely used for luting gold, composite crowns and all-ceramic restorations have traditionally required a separate etching step to allow subsequent adhesive infiltration (Diaz-Arnold *et al.*, 1999). Incomplete adhesive diffusion throughout the demineralized dentin has been reported for conventional dentin bonding agents (Spencer and Swafford, 1999). The discrepancy between etching depth and adhesive penetration led to a large area of exposed collagen at the interface between the adhesive and prepared dentin surfaces. If this discrepancy occurs with luting agents that require a separate etching step, it is conceivable that there may be post-operative sensitivity as a result of the exposed collagen (Walshaw and Mc Comb, 1996).

To overcome some of the limitations associated with dentin etching, resin cements that include self-etching primers have been proposed (Watanabe *et al.*, 1994). This approach has reintroduced the concept of employing smear layer as bonding substrate, but with novel formulations that should etch beyond the smear layer into the underlying dentin (Reis *et al.*, 2005).

A growing interest has been focused on the use of self-adhesive cements. These systems were designed with the purpose of combining the favorable characteristics of different cements in a single product. Trying to satisfy demands for simplification of luting procedures and supposedly leaving little room for application mistakes induced by technique-sensitivity (De Munck *et al.*, 2004) (Ibarra *et al.*, 2007).

Self-adhesive cements do not require any tooth surface pretreatment and their application is accomplished through a single clinical step, similarly to more conventional zinc-phosphate and polycarboxylate cements (Diaz-Arnold *et al.*, 1999).

Based on recent *in vitro* data, the behavior of the most investigated self-adhesive cement to dentin (Rely X Unicem) and different restorative materials should not differ from

multi-step resinous cements (Fabianelli *et al.,* 2005) (Bitter *et al.,* 2006) (Piwowarczyk *et al.,* 2004). However, concerns emerged regarding the bonding potential of these materials to enamel and dentin (Behr *et al.,* 2004) (Gerth *et al.,* 2006). Although the basic adhesion mechanism appears similar for all self-adhesive cements, these materials are still relatively new and detailed information on their composition and adhesive properties is limited.

The purpose of this study was to qualitatively compare the dentin/cement interfacial characteristics of six current commercial adhesive cements that differ as a function of pre-treatment regimen. Scanning electron microscopy (SEM) and a staining technique for optical microscopy, that specifically identifies depth of decalcification/infiltration or exposed collagen at the dentin/cement interface, were employed. This study tested the hypothesis that resin cement diffusion into the prepared dentin surfaces would differ as a function of the pre-treatment regimen.

MATERIALS & METHODS

Thirty extracted human third molars, stored at 4°C in 0.1% wt/vol Chloramine T solution were decoronated (Isomet 4000, Buehler, Lake Bluff, IL) obtaining mid-coronal dentin surfaces that were grinded with 600-grit wet silicon carbide papers creating a uniform thin smear layer. The use of human specimens was obtained following a protocol that was approved by the institutional review board (IRB) and with the informed consent of the donors.

Composite cylinders were made by layering 2 mm-thick increments of a micro-filled hybrid composite (Gradia Direct Anterior, GC Corp., Tokyo, Japan, shade A3) in a split aluminium mold (8 mm diameter/4 mm height). Each increment was light-cured for 40s (VIP, Bisco Inc., Schaumburg, IL, USA, output: 600 mW/cm^2). The specimen was

removed from the mold, additionally light-cured from five aspects for 40s each on the portions previously in contact with the metallic surface of the mold.

The prepared dentin surfaces (n=5 each group) were luted with: 1. Calibra dual-cured etch-and-rinse cement (Dentsply DeTrey GmbH, Konstanz, Germany); 2. Panavia F 2.0 dual-cured self-etch cement (Kuraray Co. Ltd, Osaka, Japan); 3. Multilink Sprint (Ivoclar-Vivadent, Schaan, Liechtenstein); 4. Rely X Unicem (3M ESPE, St. Paul, MN, USA); 5. G-Cem (GC Corporation, Tokyo, Japan) 6. Bis-Cem (Bisco, Schaumburg IL, USA) dual-cured self-adhesive cements.

pH measurements were performed for all tested luting agents. After mixing, they were dispensed on pH acid indicator strips with narrow ranges (0.0-1.8; 1.8-3.8; 3.8-5.5; Panreac Química, Barcelona, Spain). The composition, pH and application mode of the tested resin cement systems are reported in Table 1.

The luting procedure of composite cylinders on dentinal substrates was performed exerting a constant pressure of 40 g/mm^2 during the initial 5-min self-curing period (Goracci *et al.,* 2006).

Trichromic stain and microscopic observation

After 24h storage (37°C at 100% humidity), three samples from each group were sectioned perpendicularly to the bonded surface into 1-mm thick slabs using a water-cooled, low-speed diamond saw (Isomet 4000). A total of 12 sections were analyzed for each dentin treatment. Slabs were glued on methacrylate supports with photo-curing adhesive (Technovit 7200 VLC, Kulzer, Norderstedt, Germany) and grinded with an Exakt polishing machine (EXAKT Technologies, Inc., Oklahoma City, OK, USA) using SiC abrasive wet papers (800; 1200; 2500; 4000 grit) until getting a thickness of 5-6µm. Differential staining was accomplished with Masson's trichrome, a classic bone stain

(Erhardt *et al.*, 2008). After cover-slipping with mounting media, they were examined using a light microscope (BH2, Olympus, Tokyo, Japan) at 100x magnification.

Scanning Electron Microscopy

Two additional specimens for each group were prepared for SEM evaluation. Samples were sectioned perpendicularly to the bonded surface (Isomet 4000). Each section was polished with wet abrasive SiC papers, gently decalcified (37% phosphoric acid/10s) and deproteinized (2% NaOCl solution/1 min) ultrasonicated in 96% ethanol for 2 min and air-dried. Samples were mounted in stubs, sputter-coated with gold (Polaron Range SC7620; Quorum Technology, Newhaven, UK) and observed under a scanning electron microscope (SEM; JSM-6060 LV, JEOL, Tokyo, Japan) at different magnifications to evaluate for resin tags and hybrid layer formation. Impressions of the restored teeth and positive impression replicas were fabricated (Chersoni *et al.*, 2004) and observed by SEM to control for artefact formation.

Table 1. Chemical composition and application mode of the resin cements tested in the study

Material	Composition	Application
Calibra (H_3PO_4) pH= 0.4	**Caulk 34% Tooth Conditioner Gel** (34% phosphoric acid). **Prime&Bond NT:** Acetone; Di- and Tri methacrylate resins; Urethane Dimethacrylate; PENTA; Nanofiller- amorphous silicone dioxide; Photoinitiators; Stabilizers; Cetylamine hydrofluoride **Calibra:** Base: Barium boron fluoroalumino silicate glass; Bis-phenol A diglydidylmethacrylate;Polymerizable dimethacrylate resin; Hydrophobic amorphous fumed silica; Titanium dioxide; dl-camphoroquinone. Catalyst: Barium boron fluoroalumino silicate glass; Bis-phenol A diglydidylmethacrylate; Polymerizable dimethacrylate resin; Hydrophobic amorphous fumed silica; Titanium dioxide; Benzoyl peroxide.	Apply etchant (30s). Water rinse (20s). Air-drying. Apply adhesive in a single coat. Gently air-drying after 5s. Light cure for 20s. Mix Base and Catalyst (1:1). Apply and self-cure (5 min) Light-cure (40s).
Panavia F 2.0 pH= 2.4	**ED Primer II:** Liquid A: 10- methacryloloxydecyl dihydrogenphosphate; 2-hydroxyethyl methacrylate; N,N-diethanol-p-toluidine; N-methacryloyl 5-aminosalicylic acid; water. Liquid B: N,N-diethanol-p-toluidine; Sodium benzen sulphinate; N-methacryloyl 5-aminosalicylic acid; water. **Panavia F:** Paste A: Silanated barium glass; colloidal silica; Bisphenol A Polyethoxy Dimethacrylate; 10- methacryloloxydecyl dihydrogenphosphate; Hydrophilic dimethacrylate; Hydrophobic dimethacrylate; benzoil peroxide; dl-camphoroquinone. Paste B: Silanated barium glass; Silanated titanium oxide; Sodium fluoride colloidal silica; Bisphenol A Polyethoxy Dimethacrylate; Hydrophilic dimethacrylate;Hydrophobic dimethacrylate; N,N-diethanol-p-toluidine; Sodium 2,4,6-Triisopropyl benzene sulfinate.	Mix ED Primer A+B (1:1). Apply on the tooth. Gently air-blow after 30s. Mix Paste A+B (1:1) for 20 s. Apply and self-cure (5 min) Light-cure (40s)
Rely X Unicem pH= 2.1	Powder: glass fillers, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators. Liquid: methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing initiators, light-curing initiators	Mix cement. Apply, self-cure (5 min) and light-cure (40s)
Multilink Sprint pH= 4.2	Dimethacrylates; adhesive monomer; Fillers; initiators / stabilizers	Mix cement. Apply, self-cure (5 min) and light-cure (40s)
G-Cem pH= 2.7	UDMA; phosphoric acid ester monomer; 4-META; water; dimethacrylates; silica powder; initiators/stabilizers; fluoro-amino-silicate glass	Mix cement. Apply, self-cure (5 min) and light-cure (40s)
Bis-Cem	Bis (Hydroxyethyl methacrylate) phosphate (Base); Tetraethylene glycol dimethacrylate;	Mix cement. Apply, self-cure

pH=2.1	dental glass	(5 min) and light-cure (40s)

RESULTS

According to the Masson's trichrome-staining technique, the mineralized dentin stains green, whereas the resin cement is clear with filler particles. The staining reaction of proteins is non-specific and some non-collagenous proteins may have been marked. Type I collagen represents the 90% of dentin organic matrix. Thus, it is likely that the protein staining (red) resulted from dentin collagen unprotected by mineral and/or resin.

Using the conventional etch & rinse luting agent (Calibra) a distinct red zone of denuded collagen at the basis of the bonded interface was observed. Tubules were opened (Fig. 1A), and hybrid layer with resin tags formation were identified by SEM (Fig. 2 A). At the dentin/cement interface of teeth luted with the self-etching cement (Panavia) a narrow purple line representing mild collagen demineralization is detectable at the intact dentin surface (Figs. 1B). After Multilink Sprint application, dentin surface appeared in red (decalcified), but not resin infiltrated (Fig. 1C).

No demineralization/infiltration of dentin was evident for the self-adhesive cements Rely X Unicem (Fig. 1D), G-Cem (Fig. 1E) or Bis-Cem (Fig. 1F), that produced similar interfacial patterns. All light microscopy sections from Bis-Cem group debonded at the cement/dentin interfacial level during laboratory preparation procedures (Fig. 1F).

A scanning electron micrograph of a Bis-Cem bonded to dentin revealed an intimate adaptation with the substrate. However, no signs of hybrid layer formation with the underlying dentin could be noticed; no resin tags were observed (Fig. 2 B). All the tested auto-adhesive luting cements recorded an acidic pH ranging from 2.1 and 4.2 after mixing (Table 1).

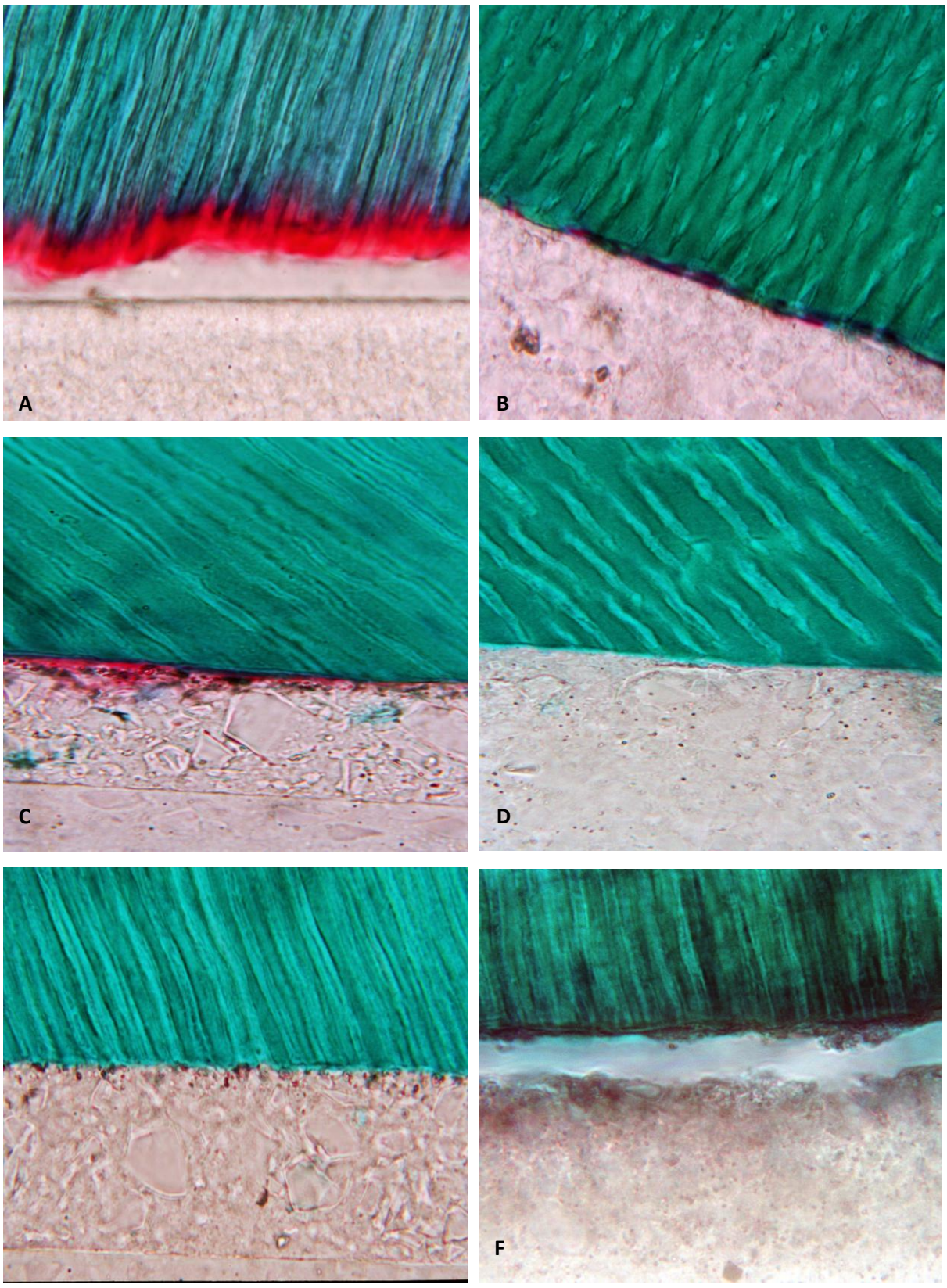
A
B
C
D
F

Figure 1. Representative light micrographs of cement/dentin interfaces stained with Masson's trichrome: mineralized dentin (green), resin cement (clear with filler particles), exposed protein (red). **A.** A distinct red zone of exposed protein was identified in the sections recovered from specimens etched with phosphoric acid (Calibra). **B-C.** A slight purple line representing collagen partially reacted with resin cement is detectable at the interface between dentin and the self-etching primer (B; Panavia F 2.0) or Multilink Sprint (C). **D-E-F.** No signs of demineralization and/or exposed protein (red stain) are detectable at the cement/dentin interface of Rely X Unicem (D), G-Cem (E) and Bis-Cem (F). (Original magnification 100x, bar 10 μm).

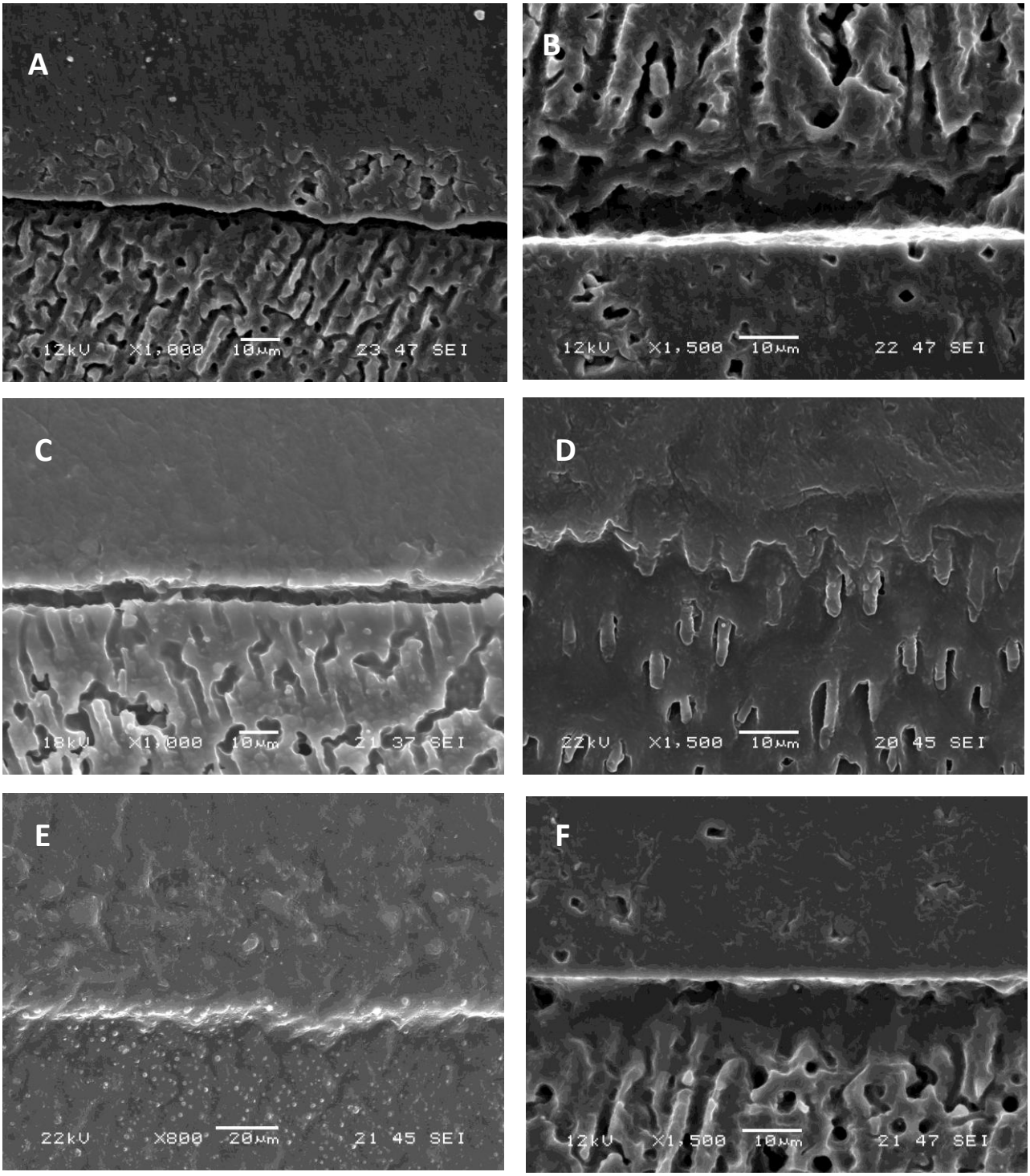

Figure 2. Scanning electron micrographs of G-Cem (A), Rely X Unicem (B), Multilink Sprint (C), Calibra (D), Panavia F 2.0 (E) and Bis-Cem (F). When using the multi-step resin cement (Calibra), dentin was demineralized and consecutively infiltrated by resin.

Resin tags and resin cement/ hybrid zone are identified. When luting with self-adhesive cements, tubules were not infiltrated by resin, but intimate adaptation is patent, no distinct morphological manifestation of interaction with dentin may be observe

DISCUSSION

Within the limitations of this study, the combined application of trichromic technique and SEM examination provided information about the demineralized dentin depth, extent of adhesive diffusion and hybrid layer formation (Spencer and Swafford, 1999). Differences in resin cement diffusion into the prepared dentin surfaces as a function of the pre-treatment regimen were evidenced. The interfacial pattern of the tested simplified self-adhesive cements was not comparable to that of conventional resin-based systems. Thus, the null hypothesis has to be rejected.

The substantial zone of demineralization produced by the etch-and-rinse pre-treatment facilitates resin penetration, but infiltration of Prime&Bond NT was not complete, as it was encountered when compared to other etch&rinse systems (Spencer et al., 2004). It seems that the solvent (acetone) is not able to generate interfibrillar spaces wide enough to accommodate the infiltrating adhesive (Pashley *et al.*, 2002). This adhesive does not contain monomers capable of enhancing diffusion and lowering the initial viscosity of the mixture (HEMA or TEGDMA) (Toledano *et al.*, 2006).

Differing from the application of the etch & rinse system, the mild etching-priming blend (Panavia; pH=2.4) produced minimal dentin demineralization, but resin penetration is identified. It contains ambiphilic monomers (HEMA, 10-MDP, 5-NMSA), with low molecular weight, that may have selectively diffused into dentin (Al-Assaf *et al.*, 2006), forming the hybridized complex (Walker *et al.*, 2002) (Reis *et al.*, 2005).

Similarly to self-etching primer formulations, self-adhesive cements contain multifunctional phosphoric acid methacrylates that are claimed to react with the hydroxyapatite of the hard tooth tissue (Moszner *et al.*, 2005) (Fu et al., 2005) (Hikita *et al.*, 2007). However, no evidences of decalcification/infiltration into dentin are found in any of the tested self-adhesive cements. To achieve a correct infiltration pattern, these cements should be able to etch the substrate in a relatively short time, requiring optimal wetting properties to ensure a fast interaction with dental

hard tissues (Moszner *et al.*, 2005). Ideally, the thin smear layer evaluated in this study should allow acidic monomers to freely reach the mineralized tissue underneath (Reis *et al.*, 2005), but it did not occur. Despite of the initial acidic pH, Rely X Unicem and Bis-Cem did not produce any evidence of dentin demineralization and/or hybridization in a micrometer scale (Al-Assaf *et al.*, 2004) (Yang *et al.*, 2006). The adhesive joint appeared essentially similar to that of some conventional luting agents (silicate cements or zinc-phosphate) (Beher *et al.*, 2004).

Some reasons may be advocated regarding the limited capacity of these cements to effectively diffuse up and decalcify the underlying dentin: 1) high viscosity (De Munck *et al.*, 2004), that may rapidly increase as an acid-base reaction (ionic bond formation and setting), that is reminiscent of conventional cements (i.e. silicate or glass-ionomers), is supposed to occur (Fukuda *et al.*, 2003); 2) a neutralization effect during setting, as these chemical reactions involve water releasing and alkaline filler that may raise the pH level (Behr *et al.*, 2004) (Al-Assaf *et al.*, 2006); this neutralization effect may also be exerted by dentin buffering components contained in the smear layer (Reis *et al*., 2005) (Olivera *et al*., 2003).

In the attempt of improving diffusivity, a reduction in the initial pH of the cement formulations may be proposed, but it would impair the hydrolytic stability of acidic methacrylates phosphates (Moszner *et al.*, 2005), may reduce polymerization efficacy (Nunes *et al;* 2006) and should leave an unprotected interface prone to degradation.

The presence of smear layer has been recognized as the "weak" link in bonding of glass ionomers to dentin, and may also be the case of self-adhesive cements (Al- Assaf *et al.*, 2004). Phosphoric acid etching, prior to the application of the self-adhesive cement, has been shown to be detrimental for effective dentin bonding (De Munck *et al.*, 2004). Most likely, the choice of milder acidic agents to remove the superficial loosely bound fraction of smear layer could somewhat enhance adhesion.

In the case of G-Cem, a self-adhering capacity to dentin may be supposed due to the incorporation of 4-META that bonds by a chelating reaction to calcium ions in apatite (Abo *et al.*, 2004). Water in

the cement composition is expected to help the conditioning reaction, reducing the time needed for interacting with the substrate. However, the relatively weak bonding potential and the high molecular weight of the functional monomer are expected to poorly contribute to the supposed chemical reaction, within a clinically reasonable time (Yoshida *et al.*, 2004).

The light discrepancy between demineralization and infiltration depths recorded for Multilink Sprint may be the result of a deeper diffusion of non-cured non-neutralized acidic monomers below the smear layer. Similarly to self-etching primers, these residuals may retain their etching potential forming an unprotected dentin zone and jeopardizing adhesion (Wang and Spencer 2005) (Carvalho *et al.*, 2005).

A bond strength study performed under same laboratory conditions (Mazzitelli *et al.*, 2008), attained results that correlate with present findings. Calibra obtained the highest bond strength and Bis-Cem the lowest (68% of Bis-Cem specimens produced pre-testing failures); Rely-X and G-Cem recorded bond strengths somewhat higher than Multilink Sprint and Bis-Cem, but due to the high standard deviations, differences were not encountered. Long-term bond strength results remain to be ascertained.

Intimate adaptation of self-adhesive cements to dentin was observed by SEM, but no hybrid layer or resin tags formation were evidenced. Other mechanisms (as chemical interactions) had been advocated to occur at these complex interfaces (De Munck *et al.*, 2004; Hikita et al., 2007). It should also be noticed, that decalcification (red line) of underlying dentin was not produced by any of these cements, so ionic bonding may also be impaired. Following the adhesion/decalcification concept, demineralization is a surface-controlled phenomena involving interaction with hydroxyapatite and depends upon adsorption of the acid anions onto hydroxyapatite. Acidity of the cements/adhesives may not be as determining as previously been thought (Yoshida et al., 2001).

It is worth mentioning that a standardized cementation pressure was applied in this experiment in consideration of previous investigations (Goracci *et al.*, 2006). The cement viscosity most likely

decreased while undergoing shear, producing better adaptation and reducing cement film thickness. However, such a thixotropic behavior does not necessarily allow a deeper interaction of auto-adhesive cements with the substrate (De Munck *et al.*, 2004).

In conclusion, self-adhesive cements were not able to completely demineralise/dissolve the smear layer and no decalcification/infiltration of dentin was observed. The presence of partially demineralized/infiltrated smear layer and/or micromechanical retention with dentin may be responsible for the previously reported adhesion values, always weaker than those of conventional resin-based cements (De Munck *et al.*, 2004; Mazzitelli *et al.*, 2008).

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Anexo VIII.2 (Chapter VIII.2)

Efecto de la presión pulpar en la adhesión entre cementos auto-adhesivos y la dentina.
(Effect of simulated pulpal pressure on self-adhesive cements bonding to dentin)

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Effect of simulated pulpal pressure on self-adhesive cements bonding to dentin

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ABSTRACT

Objectives. To evaluate the bonding effectiveness of self-adhesive luting cements to dentin in the presence of simulated hydrostatic intrapulpal pressure (PP).

Methods. Thirty composite overlays (Aelite All Purpose Body) were luted to deep-coronal dentin surfaces using four self-adhesive resin cements (Rely X Unicem, G-Cem, Multilink Sprint, Bis-Cem) and one total-etch system (Calibra). Half of the specimens resin cements were applied under a PP of 15 cm H_2O. After storage in a moist condition for 1 month (37 °C, 100% relative humidity), specimens were sectioned into microtensile beams (1 mm^2) and stressed to failure with the microtensile bond strength test (μTBS). Data were statistically analyzed with Kruskal–Wallis ranking ($p < 0.05$) and Mann–Whitney tests ($p < 0.001$). The fracture pattern was evaluated under SEM.

Results. Bond strength of Calibra fell significantly when PP was applied during bonding ($p < 0.05$). Rely X Unicem and Bis-Cem performed better under PP. No significant differences for Multilink Sprint and G-Cem bonded specimens were recorded with or without PP.

Significance. Simulated PP influences the adhesive performance of resinous cements. The predominance of acid–base reactions or radical polymerization may explain the different behavior of self-adhesive cements when changing substrate wetness. The application of constant intrapulpal perfusion should be considered when simulating luting procedures *in vitro*.

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1. Introduction

Successful bonding of luting agents to tooth structure is imperative for retention and marginal adaptation of indirect tooth-colored restorations [1]. Prosthetic preparations often require the removal of a large amount of enamel resulting in exposed dentin surfaces. Vital dentin is hydrated and characterized by an outward fluid flow from dentinal tubules [2–4].

Adverse chemical interactions and adhesive permeability were identified as the two main factors responsible for the reduction in bond strength when auto/dual-cured slow setting resin cements were coupled to bonding on hydrated dentin [5]. The trans-dentinal fluid movement under a slight positive pulpal pressure may permeate polymerized adhesive interfaces and hinder the subsequent coupling of the cement [3].

Conventional resin cements that rely on the application of etch-and-rinse adhesives are mostly affected by simulated pulpal pressure, due to the increase in dentin permeability after etching [6]. Large fluid shifts during bonding may permit water from dentin to mix with the hydrophilic monomers

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during solvent evaporation, plasticizing polymer chains and promoting hydrolysis of resin and collagen fibrillar components [3,6–10].

Self-etch luting systems do not require separate conditioning of dentin, since their adhesion mechanism is based on the partial retention of smear layer. Although this feature should render them less influenced by moisture contamination, degradation of resin–dentin bonds may also be expected to occur in self-etch systems, due to the presence of hydrophilic monomers and high solvent concentrations in the adhesive blends [10,11].

Simplified self-adhesive cements have been marketed to simplify clinical procedures and overcome the technique sensitivity of multi-step systems. These luting agents do not require any pretreatment of the tooth surface and their application is accomplished through a single clinical step.

The adhesive mechanism is claimed to rely on the chemical reaction between phosphoric acid monomers and hydroxyapatite of dental hard tissues [12,13]. Their application on smear layer-covered substrates should limit post-operative sensitivity and ideally, make these materials less susceptible to moisture.

Alternative strategies have been recently proposed in an attempt to limit water-induced interfacial changes, such as the application of static seating pressure during luting or an additional layer of hydrophobic resin [14,15]. However, the real benefit of these procedures under simulated pulpal pressure is uncertain.

Therefore, the aim of this study was to determine the bond strength of different self-adhesive cements to deep-coronal dentin with and without simulated pulpal pressure. The null hypothesis tested is that there is no difference in the bond strength of different adhesive cements to dentin regardless of the presence or absence of simulated pulpal pressure.

2. Materials and methods

2.1. Experimental design

Thirty human caries-free third molars stored in 0.5% Chloramine T solution at 4 °C were cut above the CEJ to expose flat deep-coronal dentin surfaces. The root of each tooth was cut below the CEJ with a slow-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water-cooling in order to expose the pulp chamber. The pulp tissue was completely removed with forceps, trying not to touch the pulp chamber walls.

Composite cylinders were made by layering two 2-mm thick increments of a nano-filled hybrid light cured composite (Aelite All-Purpose Body, Bisco, Schaumburg, IL, USA, shade A3, Batch no. 0500002459) in a split aluminum mold (ø8 mm; height: 4 mm). Each increment was light-cured for 40 s with a halogen-curing light Astralis 7 (Ivoclar Vivadent, Schaan, Liechtenstein). Light output was monitored at 600 mW/cm^2. Specimens were removed from the mold and additionally light-cured from five aspects for 40 s each on the portion previously in contact with the metal surface of the mold.

Resin blocks were abraded with #600 SiC-paper under water-cooling in order to simulate the clinical condition of sandblasting. Before bonding, each cylinder was cleaned with 37% phosphoric acid (Scotchbond Etchant, 3M ESPE, St. Paul, MN, USA) for 30 s, rinsed with deionized water for 20 s and air-dried.

2.2. Luting procedures

Half of the specimens ($n = 15$) were glued with cyanoacrylate (Super Attak Gel, Henkel Loctite Adesivi, s.r.l. Milan, Italy) to a Plexiglass slab (1.5 cm × 1.5 cm × 0.5 cm), taking care that the pulp chamber was completely glue-free. On one side of each Plexiglass plate a fissure was created with a diamond bur and a short length of 18-gauge stainless steel tube was glued parallel to the platform extending 2 cm out from the platform [16]. Each slab-tooth assembly was connected to a 20 mL syringe barrel through polyethylene tubing. All syringe barrels were filled with deionized water to produce a simulated hydrostatic pulpal pressure of 15 cm of H_2O at the dentin surface. Dentin was ground with #600 SiC-paper in order to create a thin smear layer. Then, the surface was etched with 37% orthophosphoric acid for 15 s and thoroughly rinsed with water. After assessing the presence of fluid transudation under a stereomicroscope at 40X to confirm the permeability of the dentin, before luting, the smear layer was re-created by means of a new grinding procedure (600 grit).

Five different luting materials were used: (1) Calibra (DeTrey Dentsply, Konstanz, Germany); (2) Multilink Sprint (Ivoclar Vivadent, Schaan, Liechtenstein); (3) Bis-Cem (Bisco, Schaumburg, IL, USA); (4) G-CEM (GC corp., Tokyo, Japan); 5 RelyX Unicem (3M ESPE, Seefeld, Germany).

All the materials were handled strictly following manufacturers' recommendations, at room temperature (23.0 ± 1.0 °C) and relative humidity (50 ± 5%). Application mode, chemical composition and pH values of the investigated materials are reported in Table 1.

When Calibra was used for luting, a silane solution (Calibra Silane Coupling Agent, DeTrey Dentsply) was applied to the composite surface to be bonded and spread by air blowing.

The luting procedure was performed under a constant pressure of 1 kg (0.098 MPa) by means of a metal tool until the seating of the material was complete. The seating force was applied for the first 5 min leaving the material to set in the self-curing mode. Finally, after 5 min of self-curing, two additional 20 s of light irradiations (Astralis 7) were performed from each side of the specimens to ensure optimal polymerization.

Bonded specimens were stored in a laboratory incubator for one month at 37 °C and 100% relative humidity until the microtensile bond strength test was performed. In the case of group 1, the simulated hydrostatic pulpal pressure was maintained until testing.

2.3. Microtensile bond strength test

Teeth were sectioned vertically into 1 mm-thick slabs with a slow-speed diamond saw (Isomet). Each slab was fixed on a glass platform with sticky wax and serially sectioned into 1 mm^2 sticks, according to the "non-trimming" method of the microtensile test. Each stick was measured with a digital caliper (Orteam s.r.l, Milan, Italy), glued with cyanoacrylate (Super Attak Gel) to the free-sliding halves of a Gerardeli's

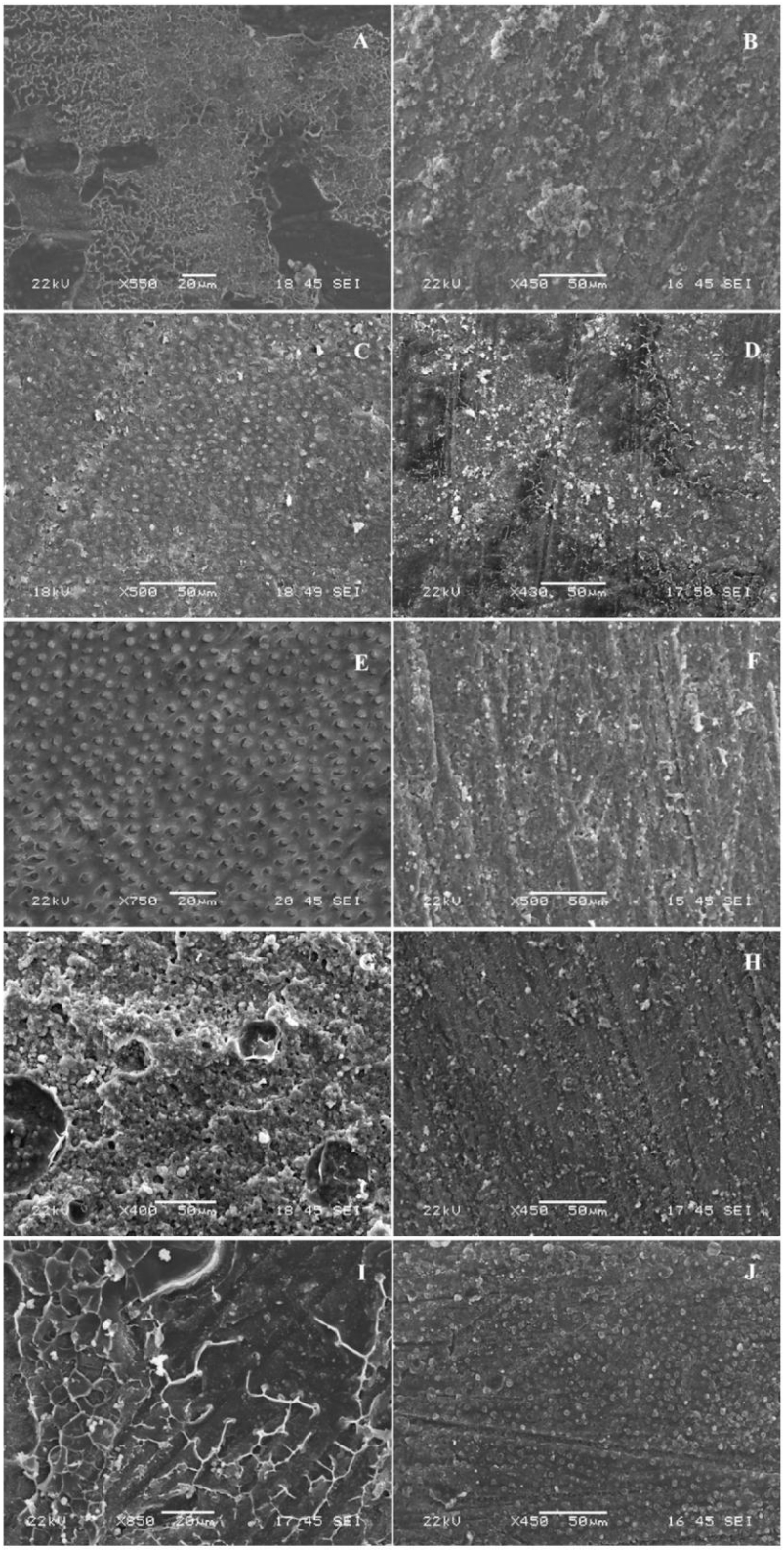

Fig. 1 – SEM microphotographs of representative fractured beams bonded respectively with or without PP: (A and B) Rely X Unicem; (C and D) Bis-Cem; (E and F) Multilink Sprint; (G and H) G-Cem; (I and J) Calibra. Trans-dentinal perfusion somewhat affected the extent of polymerization of Rely X Unicem and Calibra (A and I): areas of compartmentalized honeycomb structures and resin globules are detectable at the interface level. Light demineralization with the formation of resin tags in

Table 1 – Manufacturers, chemical compositions, pH values and application modes of the resin luting cements investigated in the study

Material	Composition	Application
Calibra (Detrey Dentsply) *Batch no.* 05110061, pH 0.4	*Prime&Bond NT:* Acetone; di- and tri-methacrylate resins; urethane dimethacrylate; PENTA; nanofiller-amorphous silicone dioxide; photoinitiators; stabilizers; cetylamine hydrofluoride. *Calibra: Base:* Barium boron fluoroalumino silicate glass; bis-phenol A diglydidylmethacrylate; polymerizable dimethacrylate resin; hydrophobic amorphous fumed silica; titanium dioxide; dl-camphoroquinone. *Catalyst:* Barium boron fluoroalumino silicate glass; bis-phenol A diglydidylmethacrylate; polymerizable dimethacrylate resin; hydrophobic amorphous fumed silica; titanium dioxide; benzoyl peroxide.	Silanize composite. Etch with 37% phosphoric acid for 15 s. Water rinse and air-dry. Apply adhesive in a single coat. Gently air-drying after 5 s. Light cure for 20 s. Mix base and catalyst (1:1). Apply and self-cure (5 min) Light-cure (40 s).
Rely X Unicem (3M ESPE) *Batch no.* 233110, pH 2.1	*Powder:* glass powder, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators, substituted pyrimidine, peroxy compound. *Liquid:* methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing initiators, light-curing initiators.	Mix cement. Apply, self-cure (5 min) and light-cure (40 s).
Multilink Sprint (Ivoclar-Vivadent) *Batch no. J22739*, pH 4.2	Dimethacrylates; adhesive monomer; fillers; initiators/stabilizers.	Auto-mix cement. Apply, self-cure (5 min) and light-cure (40 s).
G-Cem (GC) *Batch no.* 0611091, pH 2.7	UDMA; phosphoric acid ester monomer; 4-META; water; dimethacrylates; silica powder; initiators/stabilizers; fluoro-amino-silicate glass.	Mix cement. Apply, self-cure (5 min) and light-cure (40 s)
Bis-Cem (Bisco) *Batch no.* 0600011758, pH 2.1	Bis (hydroxyethyl methacrylate) phosphate (base); tetraethylene glycol dimethacrylate; dental glass.	Auto-mix cement. Apply, self-cure (5 min) and light-cure (40 s).

jig and tested in a universal testing machine (Triax Digital 50, Controls, Milan, Italy; cross-head speed: 0.5 mm/min) until failure.

Failure modes were evaluated by a single operator under a stereomicroscope (Olympus SZ-CTV, Olympus, Tokyo, Japan) at 40× magnification and classified as cohesive (within the cement, dentin or composite), adhesive (between composite/cement or at the cement/dentin level) or mixed.

3. Statistical analysis

Bond strength data were first analyzed for normality with the Kolmogorov–Smirnov test and the Levene's test for equal variance. All the sticks that failed prematurely were included and considered in the statistical calculations as "zero bond" values. As bond strength data were not normally distributed, Kruskall–Wallis Analysis of variance was applied to assess differences in bond strength among the experimental groups ($p < 0.05$). Mann–Whitney tests were used for post-hoc comparisons ($p < 0.001$).

4. Scanning electron microscopy evaluation (SEM)

Four fractured sticks from each experimental subgroup (previously classified as adhesive or mixed failures) were dehydrated with ascending ethanol solutions, mounted on metal stubs, gold-sputtered (Polaron Range SC 7620, Quorum Technology, Newhaven, UK) and evaluated under a scanning electron microscope (JSM-6060LV, JEOL, Tokyo, Japan) at different magnifications.

5. Results

5.1. *Microtensile bond strength test*

Mean microtensile bond strength values recorded in the groups tested are summarized in Table 2. Bond strengths were statistically influenced by the presence of simulated pulpal pressure ($p < 0.001$) and by the type of luting agent ($p < 0.05$).

the tubule orifices is evident in the case of Bis-Cem and Multilink Sprint (C and E). The authors do not know how short or long the tags are from this projection. The application of simulated pulpal pressure impaired G-Cem cohesive strength: frank detachments between the resinous matrix and the filler are evident in the cement bulk (G). In the absence of PP, no signs of interaction with dentin are evident for Rely X Unicem and G-Cem. Multilik Sprint cements showed a lower demineralizing ability and infiltration of dentinal tubules (B and H). Limited areas of poor polymerization are detectable in the Bis-Cem group (D). Tubules filled with adhesive/cement residues are visible when Calibra was applied (J).

Table 2 – Mean bond strength (S.D.) values (MPa) and failure mode distribution (%) recorded in each experimental group

Experimental groups	Pulpal pressure					No pulpal pressure				
	Failure mode				Mean (S.D.)	Failure mode				Mean (S.D.)
	PF	C	A	M		PF	C	A	M	
Multilink Sprint	74%	40%	40%	20%	2.3 (4.4) A	59%	20%	60%	20%	4.5 (6.4) a
Rely X Unicem	23%	37%	36%	27%	16.5 (12.5) B	34%	28%	54%	18%	11.4 (10.1) b*
Calibra	41%	48%	20%	32%	12.0 (11.7) BC	21%	28%	55%	17%	20.8 (13.5) c*
G-Cem	48%	43%	40%	17%	8.8 (9.0) C	37%	42%	54%	4%	10.5 (11.1) ab
Bis-Cem	34%	33%	50%	17%	12.4 (11.2) BC	68%	29%	57%	14%	2.4 (3.9) a*

PF: premature failures; C: cohesive (within the cement, dentin or composite); A: adhesive (between the composite and the cement or at the cement/dentin level) or M: mixed. Different letters in each column and asterisks (*) in each row indicates significant differences ($p < 0.001$).

When no pulpal pressure was applied, the total-etch cement system Calibra exhibited the highest luting strength. Rely X Unicem and G-Cem produced significantly lower bond strengths, while Bis-Cem recorded the lowest μTBS under the same laboratory condition. In the presence of simulated pulpal pressure, bond strength values of Calibra significantly decreased. The self-adhesive cements Rely X Unicem and Bis-Cem gave significant increases in bond strength. The bonding effectiveness of the self-adhesive cements Multilink Sprint and G-Cem were not influenced by the experimental conditions, since no significant differences were found in the presence or absence of simulated pulpal pressure ($p > 0.05$).

The percentage of failure mode distribution is summarized in Table 2. Specimens bonded with self-adhesive cements (Multilink Sprint, Rely X Unicem, G-Cem and Bis-Cem) recorded a higher percentage of cohesive failures within the cement layer under simulated pulpal pressure than when no pulpal pressure was applied. Higher percentages of adhesive failures were related to lower bond strengths. Adhesive failures occurred mainly at the cement/dentin interface. A remarkable percentage of pre-test failures (34–74%, Table 2) were recorded in all the experimental groups.

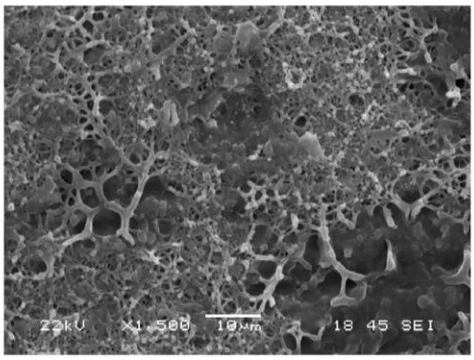

Fig. 2 – High magnification SEM image of a debonded beam luted with Rely X Unicem under PP (1500×). The fractured surface consisted of porous agglomerates and honeycomb structures, probably filled with water coming from the perfused dentin that made the cement/dentin interface irregular.

6. Scanning electron microscopy analysis (SEM)

SEM images of debonded beams are shown in Fig. 1 (with and without PP, respectively).

When Rely X Unicem was used, structural defects were observed in fractured specimens tested under pulpal pressure (Fig. 1A). These defects consisted of compartmentalized honeycombs and resin globules (Fig. 2) and were absent when no pulpal pressure was applied (Fig. 1B).

Under simulated PP, debonded specimens of Bis-Cem were characterized by the presence of dentinal tubules occluded with resin tags (Fig. 1C). The occurrence of globular interfacial agglomerates was assessed when using the cement without PP (Fig. 1D) (Fig. 3).

Multilink Sprint interacted with the underlying dentin forming short resin tags that were detected both in the presence or absence of pulpal pressure (Fig. 1E and F).

Under pulpal perfusion, a detachment of filler from the resinous matrix was noticed when luting with G-Cem (Fig. 1G).

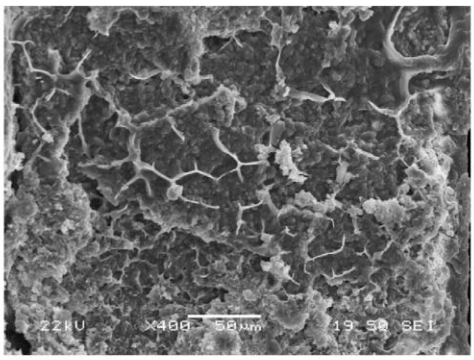

Fig. 3 – SEM image of a debonded beam luted with Bis-Cem when no pulpal pressure was applied (400×, bar 50 μm). The fracture pattern showed a rough, irregular interface. These sites may expedite restoration debonding.

This feature was not evident in the absence of pulpal pressure (Fig. 1H).

Irregular adhesive interfaces were evident for the total-etch system Calibra under trans-dentinal perfusion (Fig. 1I). When luting procedures were performed in the absence of pulpal pressure, demineralised/infiltrated areas with resin tags formation were detectable (Fig. 1J).

7. Discussion

The hydration state of dentin surfaces represents a critical variable during bonding procedures, especially when testing adhesive materials *in vitro* with the intent of simulating *in vivo* conditions [3]. The results of this investigation require the rejection of the null hypothesis, since microtensile bond strength was affected by both the presence of simulated pulpal pressure and the bonding cement.

Deep vital dentin is a highly permeable substrate in which hydrodynamic outward fluid flow may occur along dentinal tubules [17]. The presence of smear layer and smear plugs in dentinal tubules limits excessive transudation [18,19]. To achieve optimal dentinal sealing, resin monomers should flow into tubule orifices, which are water-filled, diffuse into the interfibrillar collagen spaces and properly polymerize forming hybridized resin tags [19].

Nevertheless, dentin wetness and fluid movement through bonded interfaces may hinder optimal resin seal [20,21]. In the absence of pulpal pressure, the bond strength of the tested etch-and-rinse luting system (Calibra) was significantly higher to that recorded on perfused dentin. The increased trans-dentinal permeability after smear layer removal may have counteracted adhesive penetration and exerted an inhibitory effect on polymerization.

The omission of HEMA in Prime&Bond NT has been considered advantageous in removing water, separating it from other components upon solvent evaporation [22]. The acetone contained in the adhesive blend is extremely volatile [23] and its rapid evaporation facilitates the formation of a monomer-rich phase, which may promote cross-linking [24]. However, excessive transudation of fluids from dentinal tubules and substrate moisture may exceed its water-chasing ability: with acetone evaporation exceeding that of water, the accumulation of the aqueous fraction accumulated in the adhesive film prior to polymerization tends to impair bonding [25].

As self-adhesive cements are applied on smear layer-covered dentin, simulated pulpal pressure should not significantly affect their behavior. Nevertheless, the simplified luting systems tested recorded differences in their tolerance to wetness and adhesive effectiveness. Manufacturers do not provide detailed information on the chemical composition of these cements. However, the adhesion mechanism of some self-adhesive cements seems closer to the behavior of conventional luting systems (i.e. silicate or zinc phosphate cements).

Rely X Unicem and Bis-Cem achieved higher bond strengths under simulated dentin perfusion than in the absence of PP revealing a setting acid–base reaction close to that of silicate cements. In the presence of water, silicate cement setting may occur due to the reaction between phosphoric acid and glass silicate fillers [26]. Theoretically, the phosphoric acid esters of self-adhesive cements behave similarly and need water to become ionized and acid-etch and interact with dentin [27]. Since water is not mentioned in their chemical composition and may only derive from the interaction of phosphoric acid groups and alkaline filler or tooth apatite, intrinsic dentinal wetness may have optimized these acid–base reactions allowing better setting. However, concerns remain regarding the ability of these high viscosity materials to etch through clinically relevant smear layers into the underlying dentin [28,29].

Despite the improvement in bond strength, Rely X Unicem produced areas of irregular adhesive interfaces under pulpal pressure. The observation of material discontinuity (presence of globules), "honeycomb structures" (Fig. 3) on the fractured dentinal side of the specimens may represent a separation phase of resin components and has been identified in previous studies that employed self-etch or etch-and-rinse luting systems [30,31]. In those studies, the authors suggested that the honeycomb structures were filled with water that permeated from dentinal tubules or represented incompletely polymerized regions due to water entrapment. Globules may be the result of the emulsion of resin cement hydrophobic components once in contact with water [32,33]. When stressed to failure, these abundant defects may act as stress raisers that expedite crack propagation through the resin cement bulk (Fig. 3). The higher number of cohesive failures that occurred among the experimental groups when luted under simulated intrapulpal pressure may be related to the excessive water sorption of the material [4,34], especially when compared to the control group, in which the adhesive failures at the cement/dentin interface were prevalent.

The absence of pulpal pressure (i.e. dentin perfusion) limited the auto-adhesive cement bonding potential, especially for Bis-Cem.

The presence of water in the chemical composition of G-Cem may explain the similar behavior exerted by the cement both on moist and perfused dentin. The bonding potential of the functional acidic monomer (4-META) despite its high molecular weight, may have contributed to the chemical reaction with dentin in both the experimental conditions tested [35,36].

The patent tubule orifices detected on dentinal substrates bonded with Multilink Sprint in the absence of pulpal pressure, may depend on the slight diffusion of low molecular weight acidic monomers from the high viscosity cement bulk through the smear layer (Fig. 1C). This appearance was more evident on perfused dentin where the cement exerted a superior etching potential, most likely due to acidic monomers dilution (Fig. 2C). However, deeper interaction with dentin does not always reflect a superior bonding potential. If not properly neutralized, these monomers may retain their etching potential affecting the polymerizing reaction and jeopardizing adhesion [33,37]. This may reflect a certain affinity of this simplified cement with multi-step resin-based luting systems.

It is worth mentioning that luting procedures have been previously performed under a sustained pressure [15]. Even if resin cements benefit from the application of seating pressure

during setting, it is doubtful that this counteracted fluid transudation from the underlying dentin [14,38]. It is more likely that the thixotropic behavior of the materials tested, that are maintained in a low viscosity condition under shear forces, lowered cement thickness allowing better substrate adaptation [13]. It may be speculated that the percentage of filler and the particle size may have influenced the results.

8. Conclusions

Although self-adhesive cements can make luting procedures faster and simpler, their adhesion mechanism should be further investigated. The predominance of acid–base reactions or radical polymerization may explain the different responses to substrate wetness and raise concerns regarding their universal application both on vital and pulpless teeth.

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Anexo VIII.3 (Chapter VIII.3)

Efecto de pre-tratamientos de superficie en la capacidad adhesiva de cementos auto-adhesivos y la dentina.
(Effect of surface conditionings on bond strength of self-adhesive cements to dentin)

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Effect of surface conditionings on bond strength of self-adhesive cements to dentin

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Short title: Dentin treatments and self-adhesive cements

Keyword*s*: self-adhesive cement, EDTA, polyacrylic acid, pulpal pressure, hydrophilic monomers, glass-ionomer cements, smear layer.

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Abstract

Objectives: To evaluate the bonding effectiveness of auto-adhesive resin cements luted to dentin pre-treated with EDTA or Polyacrylic acid under simulated hydrostatic intra-pulpal pressure. **Methods**: Three self-adhesive cements [Rely X Unicem (RXU), Bis-Cem (BC) and G-Cem (GC)] were used to lute twenty-seven composite overlays (Aelite All Purpose Body) to deep coronal dentin. Three groups were formed (n=9) according to the dentin pre-treatment performed: 1) No treatment; 2) 0.1 M EDTA was applied for 60 s and then water rinsed; 3) 10% Polyacrylic acid (PAA) was applied for 30 s and rinsed. Luting procedures were camed out under a simulated pulpal pressure of 15 cm H_2O that was maintained for 1 month until microtensile bond strength test (μTBS). Statistical analysis was performed with Kruskal-Wallis Analysis of Variance ($p<0.05$) and Mann-Withney post-hoc comparisons ($p<0.001$). Representative fractured sticks were evaluated under SEM. **Results**: Bond strength of BC decreased after EDTA or PAA treatment. GC performed better when luted on PAA conditioned dentin. No significant differences were observed for RXU in any of the experimental conditions. **Significance**: Self-adhesive cements responsiveness to dentin pre-treatment with mild acidic systems is material-dependent. Meanwhile Rely X Unicem and Bis-Cem showed to be more similar to conventional resin cements, G-Cem demonstrated a GIC-similar behaviour.

Introduction

Smear layer created during restorative procedures is a critical variable when luting bonded restorations [1,2]. The role of smear layer/plug for bonding is controversial. Since dentin is a permeable substrate [3], the presence of smear layer should limit post-operative sensitivity and excessive fluid transudation [4]. On the contrary, its complete removal may increase fluid movement through dentinal tubules and its entrapment at the dentin interface [5]. Excessive trans-dentinal fluid may inhibit cement polymerization, promoting resin hydrolysis and degradation of collagen fibrillar components, thus hindering optimal seal and bond durability [6,7]. On the other hand, smear layer may represent an inadequate area for bonding [8] and weak adhesive interfaces are likely to be formed [9,10].

Self-adhesive cements rely on a single clinical step, thus simplifying conventional luting procedures. Thanks to the presence of acidic monomers in their composition, they have been introduced with the idea of incorporating smear layer as intermediate bonding substrate.

Simultaneous demineralization/infiltration of smear layer and underneath dentin is expected to occur. However, the bonding effectiveness of these simplified resin cements on smear layer-covered dentin still remain a concern [11].

Recent data showed that self-adhesive cements might superficially interact with dentin, as smear layer partial demineralization and short resin tags formation have been observed [11,12]. The presence of partially demineralized/infiltrated smear layer at the adhesive interface may result in a relatively weak bonding mechanism [13]. However, it was noteworthy how dentin conditioning with 35% phosphoric acid before cementing

with Rely X Unicem was detrimental: the high cement viscosity may have limited resin infiltration in the enlarged dentinal tubules and exposed collagen mesh [14].

As the maintenance of dentin structural components (i.e. apatite crystallites in the collagen matrix) is important for relieving effective adhesion [13,15], the use of mild acidic conditioners (i.e. EDTA and Polyacrylic acid) which preserve mineral matrix and remove smear layer, should ideally improve the interfacial bond strength of self-adhesive cements to dentin [13]. Limited data are available in literature regarding the influence of these agents on the adhesion of self-adhesive resin cements to dentin.

Therefore, the aim of this study was to evaluate the bond strength of three self-adhesive resin cements to deep coronal dentin after conditioning the substrate with 0.1 M ethilediaminetretaacetic acid (EDTA) or 10% polyacrylic acid (PAA) and under simulated hydrostatic intra-pulpal pressure. The null hypothesis tested is that surface conditioning does not influence the microtensile bond strength of different self-adhesive cements to dentin in the presence of simulated pulpal pressure.

Materials and Methods

Samples preparation

Twenty-seven intact, non-carious human third molars stored in 0.5% Chloramine T solution at 4°C for preventing bacterial growth have been decoronated to expose flat enamel-free, deep-coronal dentin surfaces. The pulp chamber of each tooth was exposed after cutting the root below the CEJ with a slow speed diamond-impregnated saw (Isomet, Buehler Ltd, Lake Bluff, Il, USA) under water-cooling. The pulp tissue was carefully removed with a forceps, being worry to not touch the pulp chamber walls.

Two 2-mm thick increments of a nano-filled hybrid light cured composite (Aelite All-Purpose Body, Bisco, Schaumburg, IL, USA, shade A3, Batch n° 0500002461) were layered in a split aluminium mold (diameter: 8 mm; height 4 mm) to prepare composite cylinders. Each increment was light-cured for 40 s with a halogen-curing light (Astralis 7, Ivoclar Vivadent, Schaan, Liechtenstein, 600 mW/cm^2). The specimen was removed from the mold, additionally light-cured from five aspects for 40 s each on the portion previously in contact with the metallic surface of the mold.

Bonding procedure

Each tooth was glued with cyanoacrylate (Super Attak Gel, Henkel Loctite Adesivi, s.r.l. Milan, Italy) to a Plexiglass slab (1.5 x 1.5 x 0.5 cm). On one side of each Plexiglass plate a fissure was created with a diamond bur and a short length of 18-gauge stainless steel tube was glued parallel to the platform extending 2 cm out from the platform [16]. A polyethylene tubing joined each slab-tooth assemblage to a 20 ml syringe. All syringes were filled with deionised water to produce a simulated

hydrostatic pulpal pressure of 15 cm of H_2O at the dentin surface. A thin smear layer was produced with #600 SiC-paper.

Three experimental groups (n=9) were prepared according to the dentin pre-treatment performed: 1) No dentin pre-treatment was performed. 2) 0.1 M EDTA (pH 7.4), was scraped on dentin surface with a micro-brush for 60 s and then rinsed with deionised water for 10 s. 3) 10% polyacrylic acid, PAA (Voco, Cuxhaven, Germany, Lot: 691545), was applied with a micro-brush for 30 s, water rinsed for 30 s and then slightly air-dried.

Three subgroups (n=3) were formed according to the luting material: 1) Rely X Unicem, (RXU; 3M ESPE, Seefeld, Germany); 2) Bis-Cem, (BC; Bisco, Schaumburg, IL, USA); 3) G-Cem, (GC; GC corp., Tokyo, Japan). Materials were handled following manufacturer's instructions at room temperature (23.0°C ± 1.0°C) and relative humidity (50% ± 5%). Application mode, chemical composition and pH values of the tested materials are reported in Table 1.

Luting procedures were performed applying a constant standardized pressure of 40 g/mm^2 by means of a metallic tool [17]. The seating force was applied for the first 5 minutes leaving the material to set in the self-curing modality. Additional 20 s of light irradiations (Astralis 7, 600 mmW/cm^2; the tip was maintained at a distance of 5mm) from each side of the specimens were performed in order to ensure an optimal polymerization.

Bonded specimens were stored in a laboratory oven (37°C and 100% relative humidity) maintaining the simulated hydrostatic pulpal pressure for one month until the microtensile bond strength test.

Microtensile bond strength test

Teeth were detached from the Plexiglass slab with a scaffold and sectioned vertically into 1 mm-thick slabs with a slow-speed diamond saw (Isomet) under copious water cooling. Each slab was then serially sectioned into 0.9 x 0.9 mm sticks, according to the "non-trimming" technique of the microtensile test. Each stick was measured with a digital caliper (Orteam s.r.l, Milan, Italy), glued with cyanoacrylate (Super Attack Gel) to the free-sliding doors of a Gerardeli's jig and stressed to failure in tension by means of a universal testing machine (Triax Digital 50, Controls, Milan, Italy; cross-head speed: 0.5 mm/min).

Failure modes were assessed by a single operator under a stereomicroscope (Olympus SZ-CTV, Olympus, Tokyo, Japan) at 40x magnification and classified as cohesive (within the cement, dentin or composite), adhesive (between the composite and the cement or at the cement/dentin level) or mixed (adhesive and cohesive fractures occurred simultaneously).

Statistical analysis

Prematurely fractured sticks were included in the statistical analysis and considered as "zero bond" values. The normal and equal distribution of the bond strength data was first checked by Kolmogorov-Smirnoff and Levene's tests, respectively. As bond strength values were not normally distributed, Kruskall-Wallis Analysis of Variance was used to analyze the differences in bond strengths among the experimental groups ($p<0.05$) with the bond strength as the dependent variable, surface conditionings and luting cements as factors. A series of Mann-Whitney tests ($p<0.001$) were used for post-hoc comparisons. Calculations were handled using the SPSS 14.0 software (SPSS Inc.; Chicago, IL, USA).

Scanning Electron Microscopy (SEM) evaluation

Three fractured sticks were randomly selected from each experimental subgroup and dehydrated with ascending ethanol solutions, mounted on metallic stubs, gold-sputtered (Polaron Range SC 7620, Quorum Technology, Newhaven, UK) and evaluated under a Scanning Electron Microscope (SEM, JSM-6060LV, Jeol, Tokyo, Japan) at different magnification in the attempt of analyzing the fracture pattern.

Table 1. Chemical composition, pH values and application modes of the resin luting cements tested in the study.

Material	Composition	Application
Rely X Unicem (3M ESPE,) *Batch n°:270644* pH= 2.1	Powder: glass fillers, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators, substituted pyrimidine, peroxy compound. Liquid: methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing initiators, light-curing initiators	Mix cement. Apply, self-cure (5 min) and light-cure (40s)
Bis-Cem (Bisco) *Batch n°:0600010898* pH=2.1	Bis (Hydroxyethyl methacrylate) phosphate (Base); Tetraethylene glycol dimethacrylate; dental glass	Auto-Mix cement. Apply, self-cure (5 min) and light-cure (40s)
G-Cem (GC) *Batch n°:0611091* pH= 2.7	UDMA; phosphoric acid ester monomer; 4-META; water; dimethacrylates; silica powder; initiators/stabilizers; fluoro-amino-silicate glass	Mix cement. Apply, self-cure (5 min) and light-cure (40s)

Results

Mean microtensile bond strengths and standard deviations (SD) have been summarized in Table 2. Bond strengths were statistically influenced both by the dentin pre-treatment ($p<0.05$) and the luting cement ($p<0.001$).

RXU achieved the highest bond strengths when applied on no-treated dentin. No statistically significant differences were evidenced for RXU when dentin was conditioned with EDTA or PAA. Significantly higher bond strengths were recorded for BC when dentin was not conditioned. These values significantly fell after EDTA as well as PAA dentin pre-treatments and no differences were recorded between the two groups. 10% PAA etching significantly improved bond strength of GC to dentin when compared to the non-treated group. For the latter, data were similar to those recorded for the EDTA group.

The percentage of pre-testing failures and fracture modes recorded in the experimental groups are listed in Table 3. Most of the failures recorded in the experimental groups were cohesive within the cement (from 33% up 100%). A prevalence of adhesive failures (at the cement/dentin interface, 50%) were found for BC when luted on no-treated dentin. Mixed failures also occurred for all the cements on no treated dentin.

Table 2. Mean bond strength (SD) values (MPa) and post-hoc comparisons results obtained for the experimental groups (n=9). Different letters in each column and numbers in each row indicate significant differences ($p<0.001$).

Experimental Groups	**No Treated**	**EDTA**	**PAA**
Rely X Unicem	16.73(12.5) **BC1**	12.4(9.9) **B1**	14.87(15.5) **B1**
Bis-Cem	12.29(11.1) **AC2**	7.47(8.4) **AC1**	6.36(9.4) **A1**
G-Cem	8.03(8.2) **A2**	10.3(8.4) **BC12**	13.47(11.5) **B1**

Table 3. Percentage of failures recorded in each experimental group. **PF**: premature failures; **A**: adhesive (at the cement/composite or cement/dentin interfaces); **C**: cohesive (within the cement); **M**: mixed (a combination of A and C).

Experimental groups	**No Treatment**				**EDTA**				**PAA**			
Failure Mode	PF	A	C	M	PF	A	C	M	PF	A	C	M
Rely X Unicem	23%	36%	37%	27%	33%	47%	53%	0%	38%	28%	72%	0%
Bis-Cem	34%	50%	33%	17%	63%	39%	61%	0%	61%	0%	100%	0%
G-Cem	48%	40%	43%	17%	24%	32%	57%	11%	30%	21%	79%	0%

Scanning Electron Microscopy (SEM) results

SEM images of debonded sticks are shown in Fig. 1, 2 and 3.

When RXU was cemented on untreated dentin, structural defects consisting on compartimentized honeycombs and resin globules were observed (Fig. 1A). These defects were absent in the EDTA and PAA groups (Fig. 1B and C). SEM examination of debonded surfaces on the EDTA-treated dentin, were characterized by the presence of organic debris and voids within the cement layer (Fig. 1B). Extensive smear layer removal was noticed in the PAA etched group in which opened dentinal tubules with some protruding resin tags and exposed peritubular dentin were detectable. Collagen fibrils were also visible at the intertubular dentin level (Fig. 1C).

Partial removal of smear layer and the presence of a compact cement layer were seen when Bis-Cem was used on non-treated dentin. A less homogeneous adhesive interface was evidenced for BC when bonded to EDTA demineralized dentin: non-infiltrated thread-like formations were observed around the dentinal tubules. Dentinal tubules were visibly opened with scarce resin tags (Fig. 2B). In the PAA etched group, the cement layer had a porous structure with irregularities and multiple voids (Fig. 2C).

Voids were also detectable throughout the resin bulk when GC was used on non-treated dentin. Detachment of filler particles from resin matrix was evident (Fig. 3A). Open dentin tubules were assessed when dentin was treated with EDTA (Fig. 3B) with numerous resin tags infiltrating them. A more homogeneous infiltrated substrate was seen for GC when applied on PAA etched dentin with open and resin occluded dentin tubules (Fig. 3C).

Fig. 1: Representative fractured beams of Rely X Unicem applied on no pre-treated, EDTA and PAA-treated dentin, respectively. **A)** Cement residuals with an irregular structure consisting in sort of compartimentized honeycombs formations and resin globules are evident; **B)** Voids within the cement layer mixed with organic debris have been detected; **C)** Opened dentinal tubules and various resin tags formations extruding from tubules are evident. Intertubular dentin was also modified by PAA application, collagen appears partially exposed but not resin infiltrated.

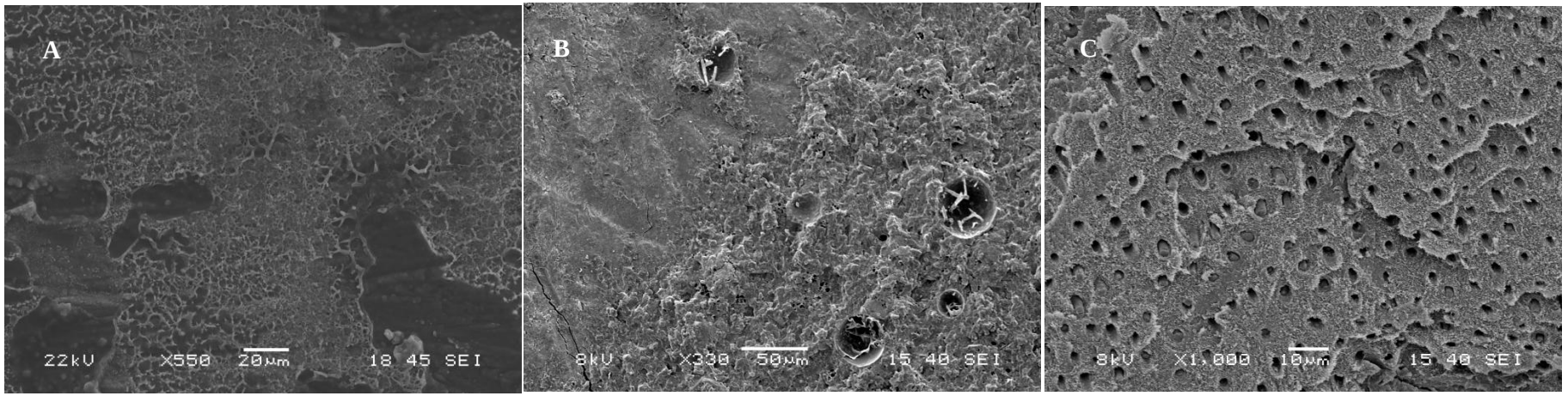


Fig. 2: Dentin sides of debonded beams of Bis-Cem applied on no pre-treated, EDTA and PAA-treated dentin, respectively. **A)** Partially opened dentinal tubules and areas completely covered by smear layer are detectable. The cement bulk is characterized by no-homogeneous composition and presence of voids; **B)** Partially opened dentinal tubules are alternated to smear layer debris that are still covering dentin. Thread-like formations were found around dentinal tubules with no frank signs of resin infiltration; **C)** Irregular and porous cement layer characterized by large dispersed voids.

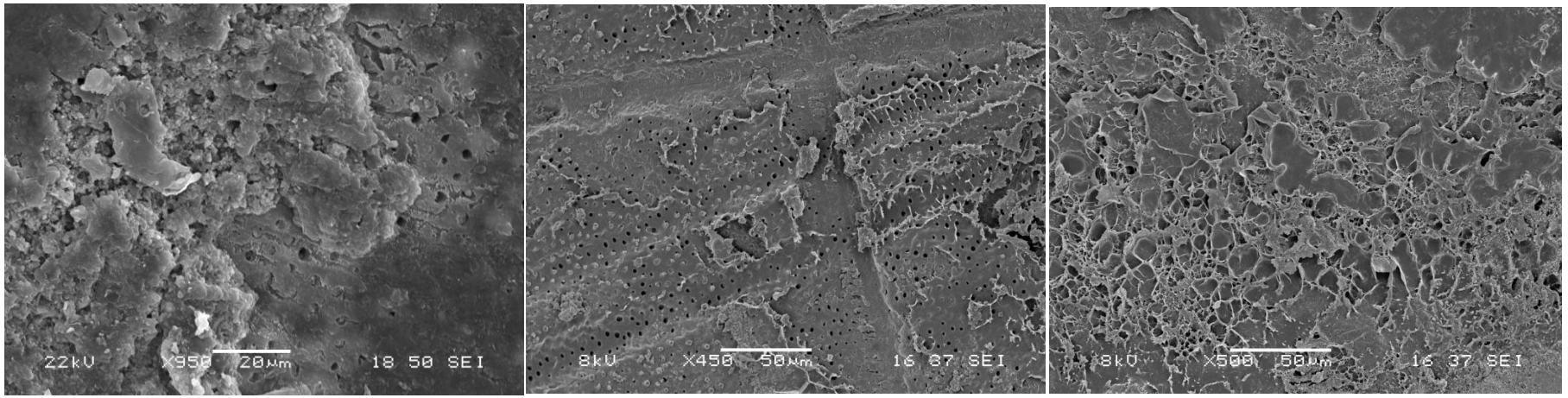
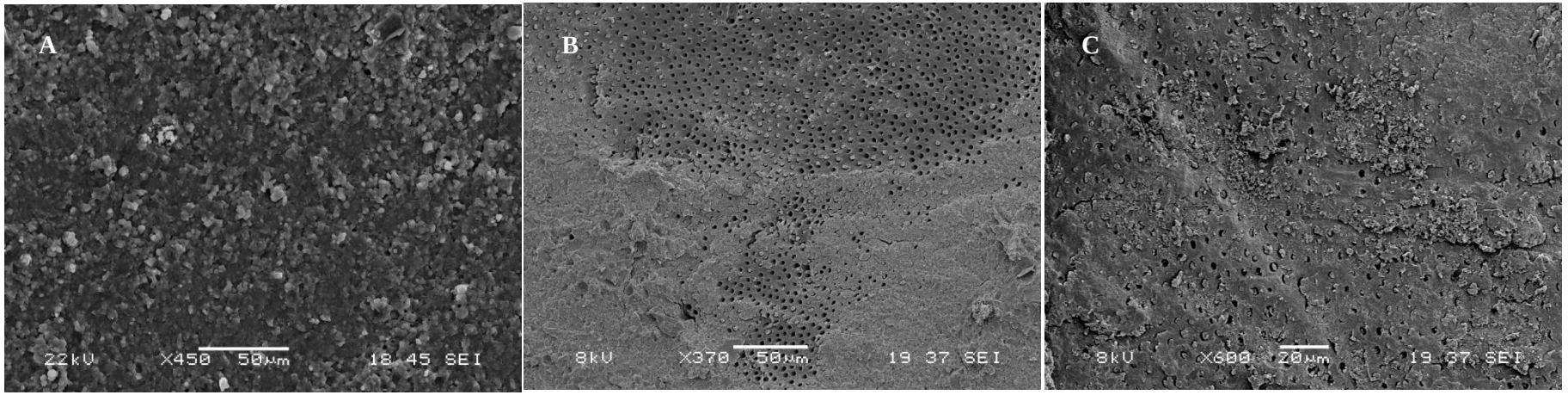


Fig. 3: Dentin side of fractured specimens luted with G-Cem applied on no pre-treated, EDTA and PAA-treated dentin, respectively. **A)** The cement bulk presented partial filler detachment from the resinous matrix. No underlying dentin is visible; **B)** Resin infiltration into the opened dentinal tubules is evident. **C)** Cement partially covers the tooth surface with opened dentinal tubules completely infiltrated by resin.



Discussion

The results of the study require the rejection of the null hypothesis, since both dentin pre-treatment and cement type influenced the microtensile bond strengths of self-adhesive cements to dentin.

Dentin conditioning is a basic requirement for ensuring effective bonding, as the presence of smear layer may hamper resin diffusion into dentinal tubules and underlying dentin substrate [9,10]. Smear layer removal through chemical solutions may also increase dentin surface energy, resulting on improved wettability [18].

Self-adhesive cements represent the last innovative approach when dealing with adhesive luting procedures. These cements are suitable for bonding to coronal [17] and root canal dentin [19] as well as restorative materials [20]. No dentin pre-treatments are required since the highly acidic hydrophilic monomer incorporated into the cements may interact with dentin. However, this technique may raise some concerns regarding the quality of resin/dentin bonds since smear layer is incorporated as intermediate substrate [11,12,14].

Previous studies reported that dentin conditioning with phosphoric acid before luting with self-adhesive cements is detrimental for achieving effective bonding [14,21]. Phosphoric acid dissolves the dentin mineral phase and induces collagen collapse jeopardizing hybrid layer formation [13]. On the contrary, EDTA demineralization and PAA etching may produce a suitable smear layer removal allowing interaction with the mineral phase without compromising the collagen matrix [13,22]. For this reason EDTA and PAA were chosen in this study as dentin conditioners before self-adhesive cements application.

The tested self-adhesive cements reacted differently to the dentin treatments evaluated in this study (Table 2). The reason could be found in the different nature and chemical composition of these cements [23] that make difficult classify them under the same nomenclature.

As smear layer is a permeable heterogeneous substrate where the components are weakly adherent each other [9], it represents a scarcely resistant layer to be bonded. However, the resin cement may infiltrate it throughout lateral diffusions [9]. The relatively high initial acidity (pH 2.1) of methacrylate esters of RXU allowed the material to partially dissolve smear layer and interact with the underneath dentin [24,25]. Although the achieved bond strength results, the bonded surface appeared quite irregular (Fig. 1A) and asymmetrical "honeycomb" structures, probably filled with water permeating through dentinal tubules [11], were observed. As these defects may represent the starting-point for stress propagation, some concerns may be raised on the bonding durability of these interfaces over time [13]. None of the two dentin pre-treatments (EDTA and PAA) increased the bond strengths of Rely X Unicem to dentin. The initial acidity of the cement should be sufficiently high and EDTA or PAA application did not allow further resin diffusion [26]. The numerous voids within the cement bulk and presence of organic debris that were detected during SEM analysis (Fig. 1B) may have counted for the high number of cohesive failures registered in the EDTA group. These defects were not observed in the PAA group, were SEM examination of fractured beams showed dentinal tubules homogeneously infiltrated by resin and areas of cement matrix still bonded to the tooth substrate (Fig. 1C). Polyacrylic acid is a polyelectrolyte having carboxylic acid as ionizable groups that dissolve smear layer in a reaction buffered by the P and Ca+ ions of hydroxyapatite,

leaving partial opened tubules and some smear plugs [27,28]. The phosphoric ester groups contained in RXU can react with the exposed collagen mesh and Ca+ ions and may establish an effective bond [29].

The Bis (Hydroxyethyl methacrylate) phosphate contained into Bis-Cem formulation is a water soluble methacrylate monomer with polar properties as it is suppose to improve wettability and reduce cement viscosity [30]. In a recent study Bis-Cem was found to be tolerant to moisture conditions [11], thanks to the high hydrophilicity of this monomer [31,32]: as the setting acid-base reaction seems similar to that of conventional silicate cements, Bis-Cem needs water to be ionized and react with dentin [11]. However, it may be speculated that these wetting monomers with a very low pH, may further inhibit the EDTA chelating efficiency thus having a detrimental effect on the ultimate adhesion process [33]. This statement was supported by the attained SEM results showing only few tubules completely smear plug-free (even after EDTA demineralization) with limited thread-like formations around them, revealing that the material is not able to penetrate into dentinal tubules (Fig. 2B). As the cement/substrate interaction is influenced by the surface energy [18,34], the limited effect exerted by PAA on dentin, did not facilitate the cement coupling mechanism. The porous cement structure characterized by the presence of big voids (Fig. 2C) was probably due to dioxide gas relief from the reaction between the cement highly acidic monomers and the dentin apatite carbonate exposed after PAA etching [35].

Higher bond strengths were achieved when G-Cem was luted on PAA etched dentin (Table 2). The fluoroaminosilicate glass and water contained in G-Cem (Table 1) may be somewhat similar to conventional glass-ionomers (GICs) [34]. GIC technology relies on chemical reaction with the substrate and in less extent on micromechanical

interlocking [28]. As for GIC, G-Cem may took benefits from the previous application of 10% PAA on dentin. The reaction with HA may be characterized by two consecutive phases. First, PAA forms H+ bonds with Ca+ ions determining smear layer dissolution and partial dentin demineralization. Then P and Ca+ ions are activated and incorporated into the cement mass establishing ionic reaction with the cement [34,36] and enhancing an intimate chemical contact between cement and tooth structure (Fig. 3C) (31). Micromechanical retention could not be promoted when pre-treating dentin with EDTA solution as its weak demineralizing effect may leave a smooth substrate [37]. However, the use of chelating agents may facilitate metal ions extractions from the glass filler of the cement which can be then combined with dentine for relieving an intermolecular bonding [38]. The addition of monomers as 4-META may contribute to the chemical interaction with dentin. Even though the sustained seating pressure could help resin to infiltrate dentinal tubules [39], the high molecular weight of G-Cem may have hampered cement diffusion when no pre-treatment was performed (Fig- 3A).

The rationale of simplifying luting techniques advocated by using self-adhesive resin cements may be contradicted if dentin pre-treatments are performed. Not all the cements evaluated in this study have been influenced by dentin conditioning treatments. The bonding mechanism of self-adhesive cements to smear-layer covered dentin may not be the same for every self-adhesive cement. A more specific assessment of these reactions and materials classification are necessary.

Conclusions

Self-adhesive cements responsiveness to EDTA and PAA dentin pre-treatment is material-dependant. Although based on a similar simplified technology, these cements have different chemical compositions that may differentiate their bonding mechanisms. Clinicians and researchers should be aware of the chemical composition and bonding characteristics of the cements in the attempt of choosing the optimal material for different clinical situations. Rely X Unicem and Bis-Cem closer to conventional resin cements, meanwhile G-Cem had a GIC-similar behavior.

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Anexo VIII.4 (Chapter VIII.4)

Valoración de la rugosidad de postes de fibra pre-tratados con diferentes acondicionamientos

(Surface roughness analysis of fiber post conditioning processes)

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Surface Roughness Analysis of Fiber Post Conditioning Processes

ABSTRACT

The chemo-mechanical surface treatment of fiber posts increases their bonding properties. The combined use of atomic force and confocal microscopy allows for the assessment and quantification of the changes on surface roughness that justify this behavior. Quartz fiber posts were conditioned with different chemicals, as well as by sandblasting, and by an industrial silicate/silane coating. We analyzed post surfaces by atomic force microscopy, recording average roughness (R_a) measurements of fibers and resin matrix. A confocal image profiler allowed for the quantitative assessment of the average superficial roughness (R_a). Hydrofluoric acid, potassium permanganate, sodium ethoxide, and sandblasting increased post surface roughness. Modifications of the epoxy resin matrix occurred after the surface pre-treatments. Hydrofluoric acid affected the superficial texture of quartz fibers. Surface-conditioning procedures that selectively react with the epoxy-resin matrix of the fiber post enhance roughness and improve the surface area available for adhesion by creating micro-retentive spaces without affecting the post's inner structure.

KEY WORDS: fiber post, surface treatment, AFM, confocal image profiler, micromechanical retention.

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INTRODUCTION

Considerable attention has been paid to the clinical applications of fiber posts. Reliable bonding can be achieved when post, luting materials, and dentin achieve good adhesion, thus forming a "mono-block" unit (Schwartz and Robbins, 2004). Most of the studies on fiber posts bonded to radicular dentin have stated that the majority of the failures occurred between the post and the cement (Baldissara *et al.*, 2006; Perdigão *et al.*, 2006). Recent investigations have been focused on improving this adhesive interface in attempts to enhance the durability of final restorations (Valandro *et al.*, 2006).

The benefit of applying silane-coupling agents as adhesion promoters has been reported (Aksornmuang *et al.*, 2004, 2006; Goracci *et al.*, 2005). However, the post/composite joint still remains relatively weak. Coupling of conventional epoxy-resin-based fiber posts to dental composites is hampered by the absence of chemical union between the epoxy resinous matrix and methacrylate-based resins (Monticelli *et al.*, 2006a).

Different post surface pre-treatments may improve adhesion of posts to composite resin (Balbosh and Kern, 2006; Monticelli *et al.*, 2006a). These are chemical and mechanical treatments intended to roughen the post surface, generating mechanical interlocks between the post and resin cements. They may include the use of etching solutions as well as physical roughening procedures, such as sandblasting (Balbosh and Kern, 2006; Monticelli *et al.*, 2006a,b).

Previously, conditioned surfaces have been analyzed by scanning electron microscopy (SEM) (Monticelli *et al.*, 2006b; Vano *et al.*, 2006). However, atomic force microscopy (AFM) may represent an alternative methodology with some additional advantages: It can work in air, requires little or no sample preparation, and provides high-resolution imaging of 3-D surface topography (Marshall *et al.*, 1995). A confocal imaging profiler is routinely applied to analyze surface texture, measuring the actual profile and standard numerical roughness parameters that can be calculated from the profile itself. It has been widely used for assessing the surface topography of dental implants (Hallgren *et al.*, 2001).

Therefore, the aim of this study was to evaluate the surface topography and changes in average roughness (R_a) provided by different fiber-post surface treatments through the combined use of atomic force (AFM) and confocal microscopy. The null hypothesis tested was that different surface treatments would neither modify the post's surface morphology nor affect its individual components (fiber/matrix).

MATERIALS & METHODS

Forty translucent quartz fiber posts #3 with a maximum diameter of 2.14 mm (DT Light Post, batch #120US0401A; RTD, St Egrève, France) were used for the study. The posts are made of unidirectional pre-tensed quartz fiber (60% vol) bound in an epoxy resin matrix (40% vol). Posts were divided into 8 groups (n =

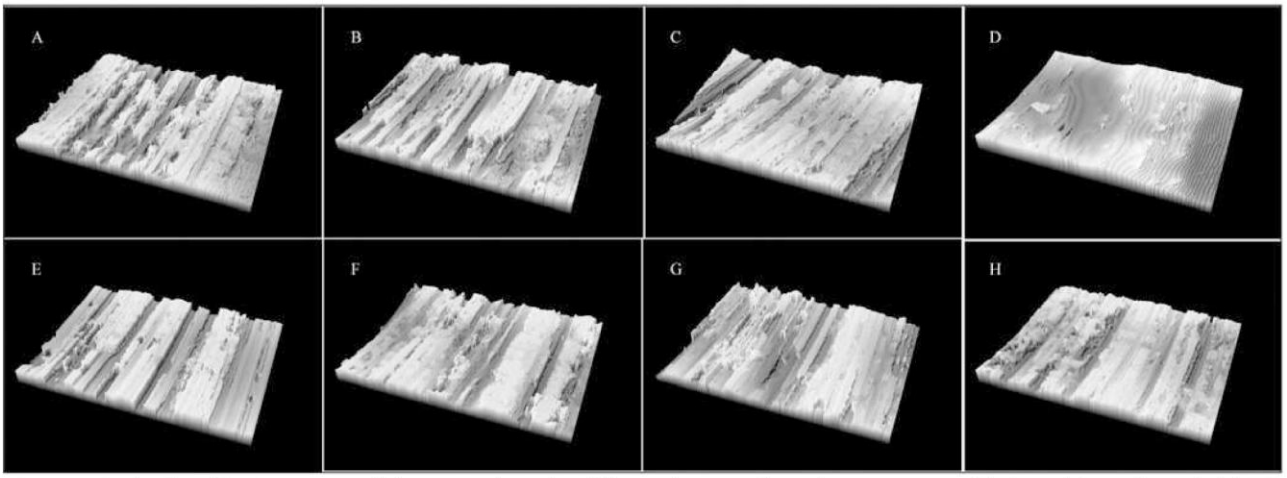


Figure 1. Confocal profiler 3-D images of the post surface after different chemo-mechanical pre-treatments. **(A)** Control (DT Light Post). **(B)** 30% hydrogen peroxide. **(C)** 10% hydrogen peroxide. **(D)** Silicate/silane coating (DT Light SL Post). **(E)** Hydrofluoric acid. **(F)** Potassium permanganate. **(G)** Sandblasting (Rocatec Pre). **(H)** Sodium ethoxide. The differences in colors between red and yellow represent the "peak" and the "valley" of the surface. A partial removal of the external layer of epoxy resin after conditioning treatments determined the partial exposition of the fibers. The oxidative etching procedures exerted their function mainly *via* a dissolution process of the resin matrix, leaving the quartz fibers undamaged. A more aggressive approach was determined by the application of HF. DT Light SL Posts were completely smooth, due to the superficial coating responsible for their chemical adherence to resin composites.

5) according to the surface pre-treatment performed: Group 1, no treatment; Group 2, 10% hydrogen peroxide (H_2O_2) for 20 min; Group 3, 30% hydrogen peroxide (H_2O_2) for 10 min; Group 4, 21% sodium ethoxide ($NaOCH_2CH_2$) for 20 min; Group 5, etching with potassium permanganate (KM_2O_4); Group 6, etching with 4% hydrofluoric acid for 1 min; Group 7, sandblasting; and Group 8, silicate/silane coating (DT Light SL post, batch #05/65; VDW GmbH, Munich, Germany).

Posts from Groups 2 and 3 were immersed in hydrogen peroxide solutions (for 20 and 10 min, respectively) (Panreac Quimíca SR, Barcelona, Spain) at room temperature (RT) and rinsed with de-ionized water (3 min). Fiber posts in Group 4 were etched with 21 wt% sodium ethoxide solution (Sigma-Aldrich Chem., GmbH, Steinheim, Germany) in ethanol (20 min) at RT, rinsed with pure ethanol and 50% ethanol in de-ionized water, and finally in de-ionized water to reach a stable pH of 7 (5 min for each cleaning bath).

The etching for group 5 was performed in three consecutive steps: (1) immersion in a conditioning solution (60 vol% of methyl-pyrrolidone in de-ionized water) for 3 min at 50-60° C (E-K Hole Cleaner, Elkem, Torino, Italy); (2) etching in an alkaline potassium permanganate solution (20 vol% in de-ionized water, pH 12-13) (E-K Hole Oxidizer, Elkem) for 10 min at 70-80° C; and (3) immersion in a neutralizing bath containing dilute sulphuric acid (10 vol% in de-ionized water) (E-K Hole Reducer, Elkem) for 5 min at 40-50° C to reduce and neutralize the excess permanganate and clean the post surface (Monticelli *et al.*, 2006b).

Posts in Group 6 were immersed in 4% hydrofluoric acid solution (Panreac Quimíca SR, Barcelona, Spain) for 1 min at RT and then extensively rinsed with de-ionized water. Samples of group 7 were sandblasted (Rocatec Pre, 3M ESPE, St. Paul, MN, USA) for 5 sec at 2.8 bar. The tip of the sandblasting device was held perpendicularly to the post at a distance of 1 cm. During the procedure, the post was rotated so that the aluminum oxide particles (110 μm) would be blasted on its entire surface. Posts in group 8 had already been coated with silicate and silane by the manufacturer; a patented protective layer ensured that the superficial coating was not contaminated or deactivated.

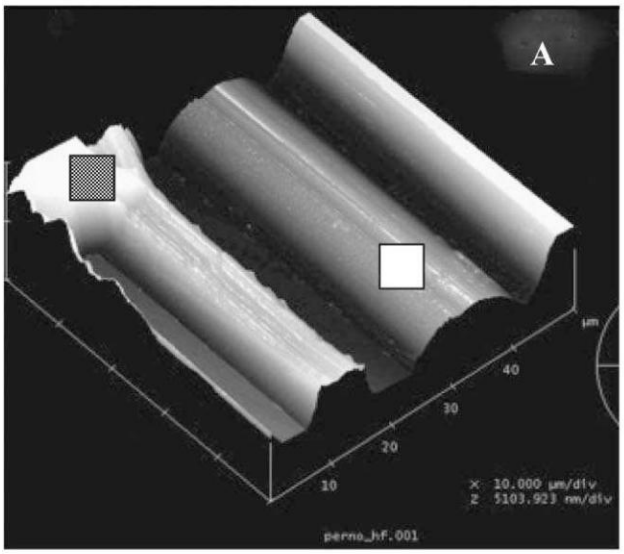
Each fiber post was then cut longitudinally with a slow-speed diamond saw under water cooling (Isomet 4000, Buehler, Lake Bluff, IL, USA), so that the post was divided into two equal halves. Posts of groups 1 to 7 were ultrasonically cleaned in de-ionized water (10 min), rinsed in 96% ethanol, and dried with an oil-free air stream. Posts from group 8 were gently air-dried, to avoid any possible alteration of the coating.

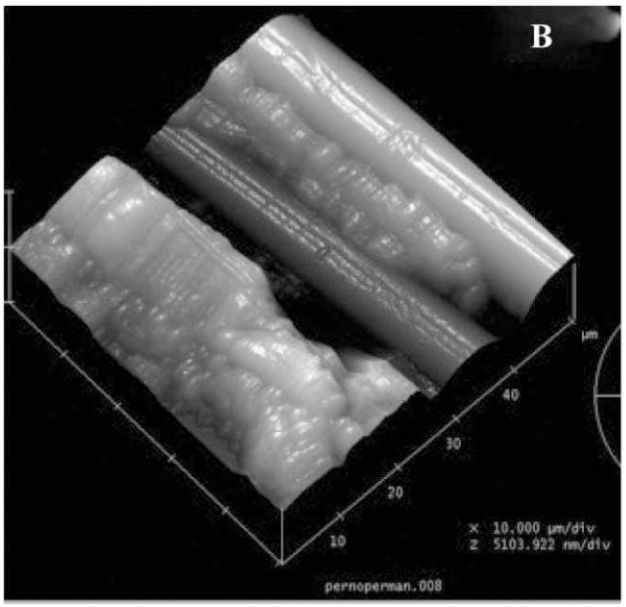
Confocal Microscopy

One half of each treated fiber post was evaluated under a confocal imaging profiler (Eclipse L150 Sensofar, Nikon, Tokyo, Japan), with a X50/0.80 numerical aperture and an extra-long working distance dry objective (Nikon), for the collection of reference images of the post surface. Images were captured by a CCD camera (Nikon) and reconstructed with a computer software program (plμ Confocal Imaging Profiler). Average surface roughness (R_a) recorded for each treated post (10 measurements each experimental group) was quantitatively expressed as a numerical value (in microns) and a graph of the profile.

Atomic Force Microscopy (AFM) Examination

The second half of each sample was evaluated by atomic force microscopy (AFM, Multimode Nanoscope IIIa, Digital Instruments, Veeco Metrology group, Santa Barbara, CA, USA). Images were taken in air. The tapping mode was performed with a 1-10 Ohm-Cm phosphorus-doped (n) Si tip (at 50 μ). Changes in vertical position provided the height of the images, registered as bright and dark regions. The tip-sample "tap" was maintained stable through constant oscillation amplitude (set-point amplitude). Fields of view at 50 x 50 μm scan size were considered for each post at a data scale of 1504 μ and recorded with a slow scan rate (0.1 Hz). A single operator analyzed the average surface roughness (R_a) of the matrix/quartz fiber of the post after different surface treatments, expressing it as a numeric value (in nanometers) with specific software (Nanoscope V530R35R). Five measurements





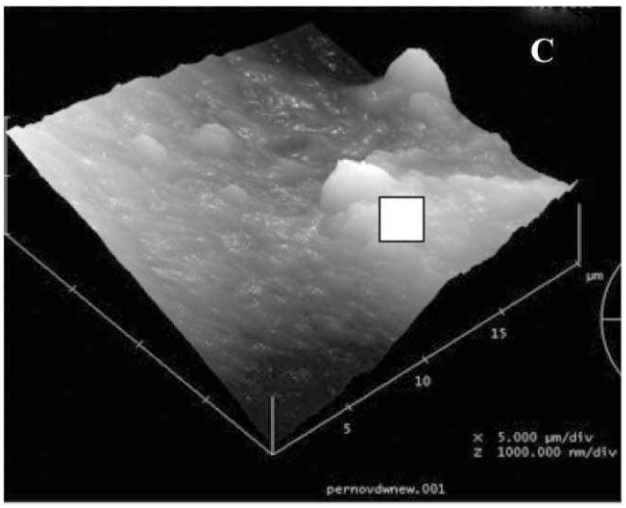


Table 1. Mean and Standard Deviation (SD) of Surface Roughness Values Recorded with a Confocal Image Profiler after Different Post Surface Pre-treatments.

Superficial Pre-treatment	Mean Roughness (SD, µm)
Hydrofluoric acid (4%)	3.929 (1.14) A
Sandblasting (Rocatec Pre)	4.042 (1.04) A
Potassium permanganate	3.210 (0.73) AC
Sodium ethoxide	3.149 (0.81) AC
Hydrogen peroxide (30%)	2.538 (0.36) BC
Hydrogen peroxide (10%)	2.824 (0.58) BC
Silicate/silane coating (DT Light SL Post)	2.539 (0.43) BC
Control (no treatment)	2.207 (0.56) BC

Same alphabetical letters indicate groups that are statistically similar ($p > 0.05$).

were performed for each pre-treated post, on both the epoxy matrix and quartz fibers, with a standardized rectangular spot (1.56 x 1.37 µm). Regarding the DT Light SL Posts, it was not possible to measure fiber roughness, since they were completely covered by the superficial coating.

Statistical Analysis

Surface roughness data and matrix/fiber average roughness values were statistically analyzed with one-way Analysis of Variance. The Student-Newman-Keuls test was used for *post hoc* comparisons. The level of significance was set at $p < 0.05$.

RESULTS

Post surface average roughness (R_a) resulting from digital images recorded by confocal microscopy (Figs. 1A-1H) revealed that chemo-mechanical conditioning treatments significantly modified surface roughness ($p < 0.001$) (Table 1). Etching with HF, sandblasting, and potassium permanganate and sodium ethoxide treatments resulted in a significant improvement in (R_a). 3-D confocal profiler images revealed a variation in post surface topography with micro-retentive space formation and fiber exposure.

Changes in average roughness (R_a) of the epoxy resin matrix were recorded by AFM analysis after all post surface pre-treatments (Table 2). HF attained the highest R_a value (Fig. 2A). After treatment with potassium permanganate, the resulting matrix was smoother (Fig. 2B). In the DT Light SL Post, quartz fibers were enshrouded by the silicate/silane coating (Fig. 2C). A significant increase in roughness of the superficial quartz fibers after treatment with hydrofluoric acid was detected (Fig. 2A). Fibers appeared to be fracture-free,

Figure 2. AFM images of treated quartz fiber post (50 x 50 µm). The squares (1.56 x 1.37 µm) show the area used for roughness measurements at the resin matrix (grey) and the fiber (white). **(A)** Hydrofluoric acid. The etching procedure was able to dissolve the resin matrix, but the effects were too corrosive, with exposed quartz fibers resulting in superficial blister formation. **(B)** Potassium permanganate. An intact fiber with no signs of damage is evident, and the matrix appeared smoother than with other treatments, most likely as a consequence of the resin-swelling step that preceded the etching procedure. **(C)** Silicate/silane industrial coating (DT Light SL Post). No quartz fibers are exposed on the post surface.

with no evident signs of degradation in the other experimental groups.

DISCUSSION

The results of this study revealed an increase in fiber post surface roughness after chemo-mechanical conditioning. The etching procedures reacted mainly with the epoxy-resin matrix, most likely by dissolution. Thus, the null hypothesis was rejected.

Most of the studies on fiber post morphology have been performed with scanning electron microscopy (SEM), providing only qualitative information (Monticelli *et al.*, 2006b; Vano *et al.*, 2006).

AFM has been widely used to investigate the structural changes determined by etching procedures on enamel and dentin (Marshall *et al.*, 1997; Hegedüs *et al.*, 1999; Saeki *et al.*, 2001; Lippert *et al.*, 2004), or for evaluating different biomaterials (Cross *et al.*, 2005). Together with the use of a confocal imaging profiler, this represents an effective methodology for analyzing not only a curved surface, like that of fiber posts, but also its modification after conditioning with chemical or physical agents. The average surface roughness can be qualitatively determined and converted into a numerical reading of the surface topography (Marshall *et al.*, 1997; Hallgren *et al.*, 2001). Moreover, AFM allowed for the quantification of treatment effectiveness on the post's individual components (matrix and fibers), expressing it as a nanometric increase in roughness.

The concept of conditioning artificial substrates to enhance bonding has precedents in dentistry, e.g., the etching of Maryland bridges (Thompson *et al.*, 1983; Thompson, 1984) or feldspathic porcelain restorations (Horn, 1983).

The rationale for conditioning the fiber post relies on the purpose of removing a surface layer of epoxy resin, rendering more quartz fibers available for silanization, and improving the fiber post surface bonding area. The etching potential of the alkaline chemicals used depends on its capacity to partially dissolve the epoxy resin matrix through a mechanism of substrate oxidation (Baskin *et al.*, 1979; Kirman *et al.*, 1998; Brorson, 2001). The spaces between the fibers provide sites for micromechanical retention of resin composites. Results of the present investigation confirmed the benefit of some chemo-mechanical treatments, also considering the previously reported bond strength results obtained at the fiber post/composite interface (Monticelli *et al.*, 2006b).

Sandblasting is commonly used for treating ceramic and composites, or as a part of the tribochemical silica-coating process (Saunders, 1990; Borges *et al.*, 2003). The efficacy of blasting zirconia and fiber posts with silica oxide (CoJet System, Praxair, Inc., Danbury, CT, USA) has been tested (Sahafi *et al.*, 2003, 2004a,b). Despite the satisfactory bond strengths achieved, the treatment was considered too aggressive for fiber posts, because of the risk of significantly modifying their shape and fit within the root canals (Sahafi *et al.*, 2004a). In this study, a significant increase in post surface roughness has been recorded after sandblasting (Rocatec Pre, 3M ESPE). The treatment was effective on the resinous matrix. However, no apparent signs of deterioration of the post were detectable. Dimensions of the aluminum oxide particles, as well as the time of application and distance, may have influenced these results.

Table 2. Mean (standard deviation) Average Roughness Values (R_a) of the Resinous Matrix and the Fibers Recorded under AFM after Different Post Surface Pre-treatments

Superficial Pre-treatment	Matrix Average Roughness (SD, nm)	Fiber Average Roughness (SD, nm)
Hydrofluoric acid (4%)	75.15 (14.3) A	58.15 (11.5) A
Sandblasting (Rocatec Pre)	36.03 (14.81) B	16.68 (12.9) B
Hydrogen peroxide (30%)	30.66 (7.96) B	9.09 (1.7) B
Sodium ethoxide	37.32 (15.3) B	12.09 (2.8) B
Hydrogen peroxide (10%)	28.23 (1.6) B	8.34 (5.2) B
Control (no treatment)	23.3 (14.3) BC	4.86 (1.9) B
Potassium permanganate	13.64 (7.9) CD	6.3 (3.7) B
Silicate/silane coating (DT Light SL Post)	6.61 (2.3) D	—

Same alphabetical letters indicate groups that are statistically similar ($p > 0.05$).

Hydrofluoric acid has recently been proposed for etching glass fiber posts (Vano *et al.*, 2006). The acid is able to "activate" the post surface, allowing for the formation of micro-retentive spaces. However, the texture of exposed quartz fibers was more irregular than with other treatments, with blister formation. As a consequence of the extremely corrosive effect of hydrofluoric acid on the glass phase (Addison and Fleming, 2004; Vano *et al.*, 2006), the technique may produce substantial damage to fiber post substructure, especially when used with extended application times. Thus, its application is discouraged.

Currently, the dental market offers posts that have already been pre-coated with combined silicate/silane layers. No fibers are exposed on the surface of the SL post, which appears relatively smooth. The adhesion mechanism is essentially based on the chemical interaction of the coating with the resin composite/luting cement. The industrial coating appears promising for simplifying the clinical procedures during post placement. Further investigations are needed to assess if post surface pre-treatments with chemical and/or mechanical agents can withstand longevity testing and influence their long-term clinical effectiveness.

In conclusion, atomic and confocal microscopy represents an effective method for evaluating fiber post surface topography. Etching with potassium permanganate or sodium ethoxide increases surface roughness through partial removal of the epoxy-resin matrix and improves the surface area available for adhesion by creating micro-retentive spaces. The choice of aggressive conditioning chemicals, such as hydrofluoric acid, should be avoided to prevent any damage to the quartz fibers.

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