Universidad Europea

TRABAJO DE FIN DE GRADO

Grado en Odontología

BIOMATERIALES INTELIGENTES.

ÙLTIMAS TENDENCIAS.

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1 RESUMEN

Introducción: Los nuevos composites a base de resina están cambiando rápidamente sus características y objetivos, avanzando hacia "materiales inteligentes". La aparición de los nanomateriales abrió nuevas fronteras en la odontología restauradora. Actualmente, la búsqueda está dirigida al desarrollo de productos que puedan simplificar los procedimientos y extender la vida útil de las restauraciones directas.

Objetivos: El objetivo de este estudio fue revisar y discutir los datos científicos en el campo emergente de los "materiales inteligentes" en la odontología restauradora. El enfoque de este trabajo fue la categorización de los compuestos inteligentes, la evaluación de su posible impacto en la práctica diaria y el análisis de sus ventajas y desventajas.

Materiales y métodos: Se realizó una búsqueda *on-line* en Pub-Med poniendo como filtro: "años 2016-2021". Se incluyeron estudios in vitro y estudios de casos clínicos.

Resultados: Para los composites universales, se consideraron relevantes 10 estudios, mientras que se seleccionaron 14 estudios para composites remineralizantes-antibacterianos. La mayoría de los estudios confirman un excelente resultado estético para todos los composites universales, que también mantienen óptimas propiedades mecánicas y un mayor efecto mimético después del blanqueamiento. En cuanto a los composites remineralizantes-antibacterianos, la combinación de NACP con DMAHDM muestra los resultados más efectivos, preservando la dureza marginal del esmalte y disminuyendo la contaminación bacteriana, teniendo la posibilidad de recarga de iones en estudios a largo plazo. Los materiales Ag-BCOMP y Zn-PBG muestran propiedades remineralizantes-antibacterianas, pero empeoran las propiedades mecánicas y estéticas.

Conclusiones: Los composites universales se pueden clasificar en One-Shade y Group-Shade. Exhiben buenos resultados en la práctica diaria, simplifican los procedimientos y tienen buenas

propiedades estéticas y mecánicas. Sin embargo, la calidad de los resultados depende de la profundidad de la restauración, el tipo de cavidad y el sustrato dental. Los composites remineralizantes-antibacterianos se pueden dividir en partículas remineralizadas y partículas metálicas. Las partículas remineralizadas pueden ayudar a preservar la longevidad de la restauración, la aparición de caries recurrentes, y tienen buenas propiedades mecánicas y estéticas. Las partículas metálicas necesitan un mayor desarrollo, con buenos efectos remineralizantes-antibacterianos, pero malas propiedades mecánicas y estéticas.

2 *ABSTRACT*

Statement of the problem New resin-based composites are rapidly changing their characteristics and purposes, moving towards "smart materials". The uprising of nanomaterials opened new frontiers in restorative dentistry. The search is presently aimed at the development of products which can simplify procedures and extend the lifespan of direct restorations.

Purpose of the study The aim of this study was to review and discuss scientific data in the emerging field of "smart materials" in restorative dentistry. The focus of this work was the categorization of smart composites, assessment of their possible impact on day-by-day practice and analysis of their advantages and disadvantages.

Materials and methods An on-line PubMed search was performed by filtering for years 2016-2021; *in vitro* studies and clinical case studies were included.

Results For universal composites, 10 studies were considered relevant, while 14 studies were selected for remineralizing-antibacterial composites. The majority of the studies confirms an excellent esthetic result for all universal composites, which also maintain optimal mechanical properties and increased mimetic effect after bleaching. Regarding remineralizing-antibacterial composites, the combination of NACP with DMAHDM shows the most effective results, preserving marginal enamel hardness and diminishing bacterial contamination and the

possibility to be Ion-recharged in long-term studies. Ag-BCOMP and Zn-PBG materials show antibacterial-remineralizing properties but worsening of mechanical and esthetic properties.

Conclusions Universal shade composites can be classified as One-Shade and Group-Shade. They show good results in day-by-day-practice, simplifying procedures and having good esthetic and mechanical properties. However, the quality of the results relys on depth of the restoration, type of cavity and dental substrate. Remineralizing-antibacterial composites can be divided in remineralized particles and metallic particles. Remineralized particles can help in preserving restoration longevity, recurrent caries appearance and have good mechanical and esthetic properties. Metallic particles need further development, having good remineralizing-antibacterial effects, but poor mechanical and esthetic properties.

3 INTRODUCCIÓN

La regeneración de los tejidos duros se ha vuelto cada vez más importante a medida que pasa el tiempo, junto con el aumento de la expectativa de vida y la subsiguiente necesidad de materiales por la regeneración de tejidos duros más y más eficaces. Los materiales inteligentes se pueden definir como materiales diseñados, que tienen una o más propiedades que pueden cambiar significativamente de manera controlada por estímulos externos, como estrés, temperatura, humedad, pH y campos eléctricos o magnéticos. Los materiales inteligentes han existido durante muchos años y han encontrado un gran número de aplicaciones. El uso de los términos "*smart*" e "*intelligent*" para describir materiales y sistemas vino de los Estados Unidos y comenzó en la década de 1980, a pesar del hecho de que algunos de estos llamados materiales inteligentes habían existido durante décadas. Las primeras aplicaciones de materiales inteligentes comenzaron con tecnologías magnetostrictivas. Esto implicó el uso de níquel como fuente de sonar durante la Primera Guerra Mundial, para encontrar U-boats alemanes por las fuerzas aliadas [(1)].

Hace tiempo, los materiales restauradores en odontología eran desarrollados para ser materiales inertes y para que pudiesen sobrevivir lo mas posible en el medio oral.

Hoy en día, la filosofía de desarrollo de estos materiales está cambiando. Los biomateriales mas avanzados son receptivos a los estímulos, que sean físicos o químicos, y dan respuestas siempre mas efectivas a medida que la tecnología va desarrollándose.

En odontología, según el comportamiento que tengan con el medio ambiente y las estructuras con que se encuentran a contacto, los biomateriales se pueden clasificar como bioinertes (pasivos), bioactivos, y biosensibles o materiales inteligentes. Algunos investigadores, demarcan una línea de separación entre materiales "*intelligent*" y materiales "*smart*" , donde los primeros son materiales que tienen de por si una efectiva inteligencia, en el sentido de que pueda tomar decisiones o repararse sola. Otros dicen que un material que simplemente responde a estímulos no es verdaderamente "*smart*". En nuestro estudio, intentaremos tratar de algunos materiales que tengan características dinámicas o únicas, diseñados especialmente para dar un tipo especifico de respuesta a estímulos, bacterias, fuerzas etc…

Los biomateriales incluidos en este estudio involucrarán resinas dentales inteligentes que responden al entorno en el cual se han incorporado, creando un efecto mimético y permitiendo responder al pH para proteger las estructuras dentales; polímeros inteligentes para modular especies de biofilm lejos de una composición patógena y cambiar hacia una composición saludable y materiales inductores de la remineralización de estructuras dentarias. Estos nuevos materiales proporcionan unas oportunidades completamente nuevas y óptimas para mejorar la ingeniería de tejidos duros y la regeneración.

3.1 EVOLUCIÓN DE LOS COMPOSITES

3.1.1 MATERIALES PLÁSTICOS

Antes del desarrollo de los polímeros, muchos materiales llamados "plásticos" provenían de resinas naturales o exudados y tejidos de plantas, insectos y animales.

Se vio que una vez calentados, cambiaban de estado, volviéndose mas blandos y moldeables, permitiendo de darle formas antes de que se enfriasen [(2)].

Uno de los primeros materiales plásticos, fue la goma laca, una resina producida por las hembras de un pequeño insecto que infecta las plantas de higos, inicialmente usado como material para recubrir madera y metales, más tarde se le incorporaron materiales de relleno, inicialmente madera, para objetos decorativos, y luego minerales, de manera que pudiese ser utilizado para objetos sometidos a fuerzas. Los primeros discos fonográficos y los discos de gramófono de 78 RPM (Revoluciones Por Minuto), estaban hechos por goma laca.

En el periodo entre 1910 y 1950, se desarrolló la termoplástica. Los polímeros termoplásticos tienen un cambio físico con el calor pasando por cadena larga, movimiento segmentario y distorsión [(2)]. Cuando se calientan entonces pueden ser presados en una forma diferente de la originaria y al enfriarse, retienen la misma forma. Fue durante el siglo 20 que se empiezo a tener un conocimiento mas profundo de la polimerización, con el primer concepto de macromoléculas. Fue el premio nobel Dr. Herman Staudlinger el primero en escribir el termino "macromoléculas " en su trabajo sobre la hidrogenación de la goma, datado 1922 [(3)].

A empiezos de 1900 la definición de plástico se refería simplemente a un material que si sometido a calor, se volvía en fluido y, una vez enfriado, volvía a estar duro, pero manteniendo la forma que se le había dado. Desde el 1900 hacia delante, la definición fue expandida para aceptar materiales que polimerizan por reacción química, a través de una reacción química, o de la evaporación de un solvente [(4)]. El empiezo de siglo 20 coincide con la explosión de los plásticos polimerizables, en las primeras 3 decadas del siglo 20 se desarrollaron una serie de nuevos productos como el polistireno, la bakelite, el nylon, el teflón, el poliamido y la resina epoxidica, muchos de los cuales, justo después de haber salido al comercio fueron propuestos por su uso en odontología.

La motivacion de esta explosión es la creciente búsqueda de materiales que pudiesen sustituir la goma natural, sobre todo después de la primera guerra mundial.

La primera verdadera alternativa fue descubierta en 1931 cuando Wallace Carothers y otros en el instituto Dupont inventaron el neoprene, también ahí se inventó el primer polímero completamente sintético, el Nylon [(5)].

3.1.2 EL ACRÍLICO

El acido acrílico estaba muy bien conocido desde finales de 1900, pero sin duda fue después del 1901, cuando por su thesis de doctorado el Dr. Röhm fabricó polímeros de acido acrílico transparentes, que se desarrolló este material. Era posible producir polímeros solidos y transparentes, pero faltaban las materias primas para poderlos producir de manera efectiva.

En 1927 Röhm produce Acryloid y Plexigum, y en 1931, empieza la producción de Plexiglass (2).

Hasta 1940, se desarrolla una producción siempre mas amplia de productos acrílicos, casi todos fueron usados clínicamente en odontología. Los primeros productos tenían una serie de problemas ligados a las técnicas de producción y los precios de las máquinas, resultando en un producto de coste elevado, y de supervivencia breve en el utilizo clínico, pero en 1936, se encontró la Vernonite, un polimethil metacrilato procesado con calor, al principio usado solo por las bases de prótesis removibles, y sucesivamente usado en incrustaciones, coronas y prótesis fijas parciales. "Se estima que en el 1946, PMMA representaba aproximadamente el 95% del mercado de las bases de prótesis" (6).

Fue después de la secunda guerra mundial que se empezó a usar la polimerización "fría", "química" o de "auto-curado" en odontología.

Este cambio permitió por primera vez poner un material de restauración estético de manera directa. La reacción consistía en una oxido-reducción (REDOX) donde, después de que un electrón se había transferido dentro de agentes de iniciación, se formaba un radical libre a temperatura ambiente. Al formarse este radical libre, empezaba un proceso de polimerización.

Otra vez los materiales tenían unos problemas como la estabilidad del color y de dimensión, después de la polimerización, las resinas tenían un proceso de contracción y de alteración del color, este proceso terminaba con una alta incidencia de manchas en los composites y infiltración marginal de las restauraciones [(2)].

3.1.3 TEGDMA y Bis-GMA

Los primeros intentos en mejorar las restauraciones en PMMA no resolvieron los problemas clínicos, las mejoras más significativas se vieron en los años 50-60 del siglo 20.

El primero en pensar incorporar relleno inorgánico en metacrilato y resinas acrílicas con alto peso molecular, fue el doctor Rafael Bowen (National Institute of Standards and Technology), que en el 1962, patentó el bis-GMA (Bisfenol-A glucidil metacrilato): nacieron los composites. El nacimiento de bis-GMA estimuló grandemente la producción comercial de los composites. Los primeros usos de composites en forma de pasta – liquido fueron desarrollados por parte de Robert Chang (1969) y Henry Lee (1970) [(7)].

Es importante demarcar que estos materiales no estaban solo compuestos por el monómero bis-GMA. Este monómero presenta una alta viscosidad por la presencia de dos grupos hidroxilos que resultan en un enlace intermolecular de hidrogeno muy fuerte; para resolver este problema de elevada viscosidad, los productores solían diluir el monómero con un co-monomero mas fluido: trietilenglicolo dimetacrilato (TEGDMA) [(8)].

Las resinas contenientes TEGDMA y BISGMA siguen teniendo un porcentaje de reducción entre el 1,5 y el 3 % y en los últimos años se han propuesto siempre mas aleaciones de materiales para limitar la reducción o “shrinkage” de los composites para la restauración dentaria como el UDMA y el Bis-EMA. Materiales como los siloranos fueron propuestos a inicio de los años 2000, como nuevos materiales monomericos. Los composites que los contienen vienen llamados composites “metacrilate-free” y salieron al mercado ofreciendo un nivel de reducción inferior al 1%, por eso fueron muy estudiados y la mayoría acabo por ser excluida del mercado por ausencia de evidencia científica de una reducción clínicamente apreciable.

Por lo que atañe las partículas de relleno, generalmente se usan óxidos y cristales inorgánicos, siendo primariamente clasificados según el tamaño del relleno inorgánico, pero pudiendo ser clasificadas también según su tipo (composición de vidrio), morfología (tamaño, distribución y forma), densidad, radiopacidad, índice de refracción y porosidad superficial [9].

3.1.4 GRABADO Y ADHESIVO

El uso del composite fue tremendamente mejorado por el uso del grabado acido. Probablemente ningún otro único acontecimiento en odontología ha cambiado tan radicalmente la filosofía y la metódica de trabajo como la "odontología adhesiva".

En el 1955 Michael Buonocore escribía: "Una de las mayores deficiencias de los materiales acrílicos y otros sistemas de obturación es la falta de adhesión a la estructura dentaria. Un material de relleno que pueda formar fuertes uniones a las estructuras dentales ofrecería muchas ventajas en respecto a los actuales. Con este material, se podría utilizar una forma de resistencia en la preparación de la cavidad, y un sellado eficaz de fisuras, cavidades y lesiones cariosas tempranas." [10]

En el articulo aconsejaba utilizar acido ortofosforico 85% para acondicionar el esmalte de los márgenes de una preparación para mejorar la retención mecánica de los polímeros; aunque la metódica no fue utilizada hasta finales de los años 60.

Desde aquí se publicaron varios estudios sobre efectos de grabado acido en dentina y en esmalte con varios productos y concentraciones, haciendo progresar el desarrollo de los adhesivos de resina a la estructura dentaria a través de varias etapas que se empezó a llamar "generaciones".

"Cada generación de productos mejoró los valores de fuerza de los enlaces y se diseñó para funcionar con respecto a los últimos conocimientos de química, microestructura y entorno de la interfaz de enlace. " [11]

Con cada generación se iban modificando las estrategias para la retención de las resinas de manera que se pudiese aprovechar de los mejoramientos en el conocimiento de los materiales y la química, hasta llegar a los "wet bonding" para disfrutar de la "capa hibrida", conocidos también como "tree step", que dan el máximo de adhesión conocida, y los "one step" o adhesivos universales que no necesitan de grabado acido separado y disminuyen los errores datos por un procediemiento incorrecto, con buenos valores de adhesión, aunque menores que la técnica "tree step". [(12)]

Esto, se refleja en una selección diferente del tipo de adhesivo según el tipo de preparación cavitaria sobre la cual vamos a trabajar.

3.1.5 COMPOSITES HOY EN DÍA Y NANOTECNOLOGÍA

Los composites contemporáneos están formados por tres fases principales:

1. Fase orgánica, que consiste en matriz de resina, es el componente que, sometido a luz, cuando es sometido a luz, sufre polimerización.
2. Fase dispersada constituida por el material de "filling" o relleno, esta embebido en la matriz. Esta fase es lo que da las propiedades mecánicas de resistencia y estética al composite.
3. Fase interfacial, consiste en los agentes copulantes, que forman un enlace entre la matriz y el relleno.

Los composites convencionales, (donde la fase dispersada estaba compuesta de un microrelleno), gracias a su estética, se han utilizado mucho para hacer reconstrucciones en dientes anteriores, aunque en las primeras generaciones aún se planteaba la duda que no tuviesen las propiedades mecánicas adecuadas.

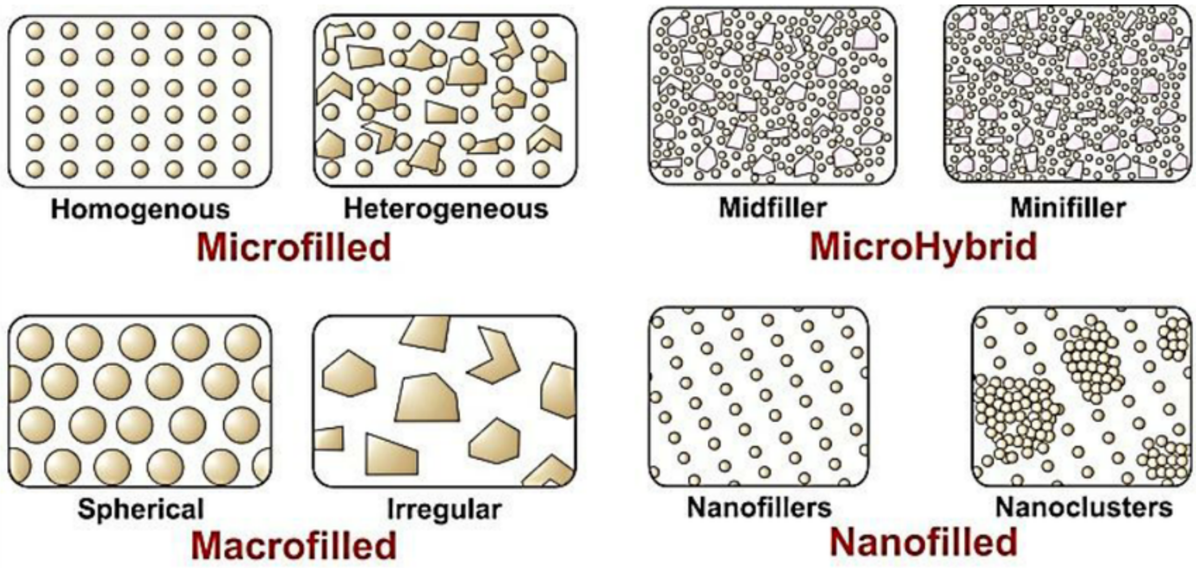

Ilustración 1. Clasificacion de los composites según el tamaño de las particulas y la estructura. Khurshid Z, Zafar M, Qasim S, Shahab S, Naseem M, AbuReqaiba A. Advances in nanotechnology for restorative dentistry. Materials (Basel). 2015;8(2):717–31

A empiezo de años 2000 se incorporó en la odontología una nueva manera de desarrollar los composites: la Nanotecnología.

"Nanotechnology is artistic engineering on a scale of less than 100 nm to accomplish desired design, functions and performance of end products. It engages the characterization and control of materials at the atomic or molecular level" [1]

(La nanotecnología es ingeniería artística en una escala de menos de 100 nm para lograr el diseño, las funciones y el rendimiento deseados de los productos finales. Se ocupa de la caracterización y el control de materiales a nivel atómico o molecular.)*(13)*

Esto ha permitido crear partículas siempre mas pequeñas y diseñadas de maneras que algunas se uniesen entre ellas para crear "nanoclusters" que simulan una partícula de microrelleno, mientras otras se quedan en estado de nanopartícula separada creando composites híbridos de nanorelleno. Esto ha mejorado mucho los composites en cuanto a pulido, precisión del

[1] Khurshid Z, Zafar M, Qasim S, Shahab S, Naseem M, AbuReqaiba A. Advances in nanotechnology for restorative dentistry. Materials (Basel). 2015;8(2):718–6

emparejamiento de color, translucencia, modulo de elasticidad, resistencia al desgaste, microdureza etc... (14)

Estas mejoras han determinado que los composites fuesen los materiales de elección en ambos sectores posteriores y anteriores.

Las nanoestructuras que se encuentran hoy en día en los composites son (15):

- Nanorods: similares a los prismas de hidroxiapatita, podrían ayudar a hacer materiales mas semejantes a la estructura cristalina básica del esmalte dentario.
- Nanoesferas: unidades te tamaño nanometrico que se pueden producir de maneras diferentes según el objetivo de la partícula. En los composites pueden tener el objetivo de dar un alto efecto mimetico (particulas prepolimerizadas de vidrio de bario, oxidos esféricos mixtos, composites prepolimerizados, rellenos esféricos de silicio y zirconia etc…), o un efecto remineralizador y antibacteriano (nanoparticulas core-shell de CHX-ACP, nanoesferas de ACP, nanoesferas de Ag).
- Nanotubulos: unidades de forma tubular de vario tipo investigadas sobre todo por el recubrimiento de implantes en titanio en relacion con la formación de hidroxiapatita.
- Nanofibras: estudiadas por su posibilidad de liberar medicamentos, estructuras para el diseño de tejidos. También se han realizado nanofibras para producir cerámicas con contenido de flúor y hidroxiapatita.

Tras la llegada de la nanotecnología, los composites no solo serán materiales inertes, sino que tendrán repercusiones activas sobre el comportamiento clínico de las reconstrucciones, volviendo los composites en verdaderos materiales inteligentes.

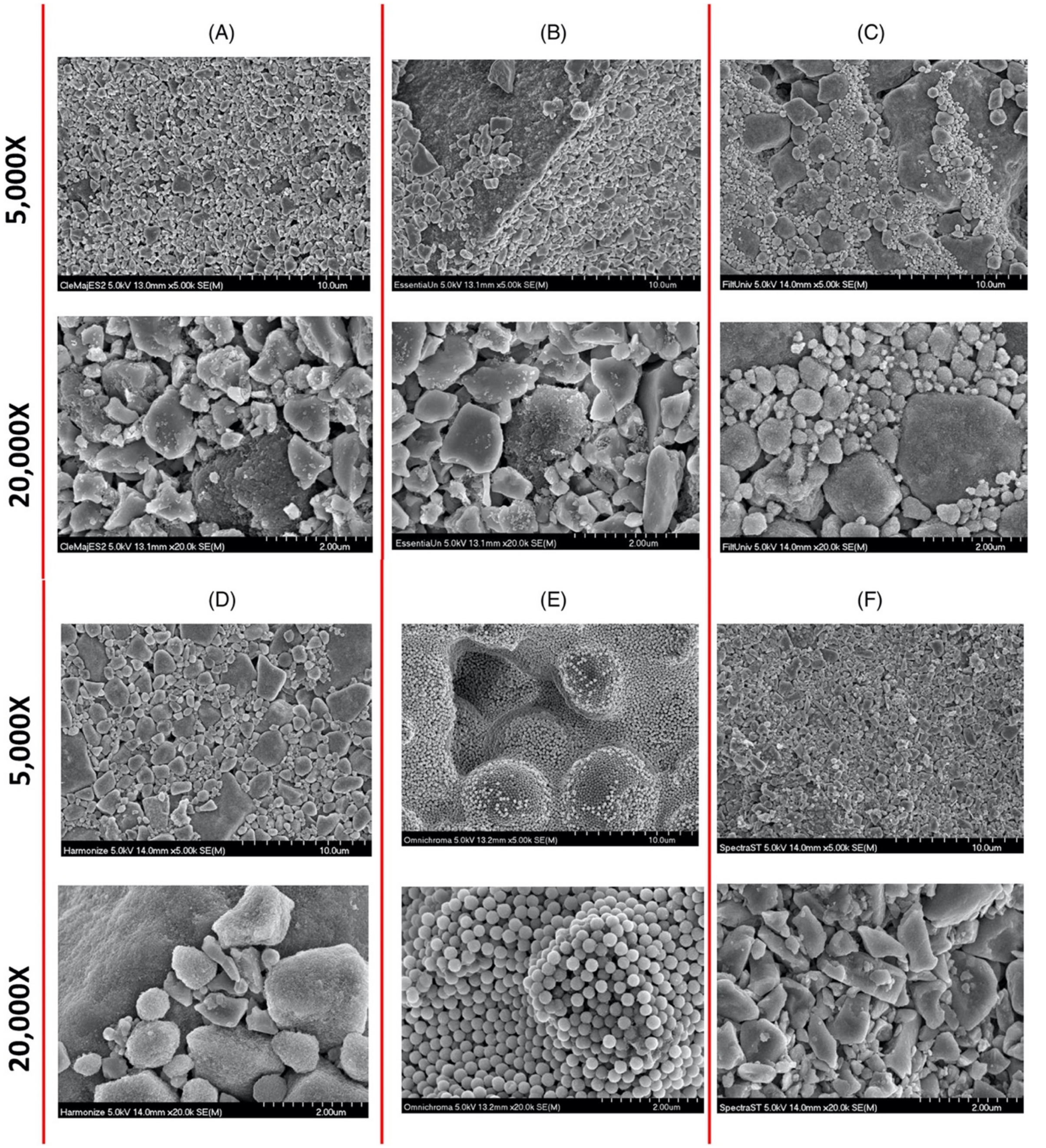

Imagen 1 Perdigao et al. Fotografías a 20'000X del relleno de los nanocomposites one shade mas utilizados: (A) Clearfil Majesty ES-2 Premium (Kuraray Noritake Dental, Inc.); (B) Essential Universal (GC Europe); (C) Filtek Universal (3M Oral Care); (D) Harmonize (Kerr Corp.); (E) Omnichroma (Tokuyama Dental America, Inc.); (F) TPH Spectra ST (Dentsply Sirona). Perdigão J, Araujo E, Ramos RQ, Gomes G, Pizzolotto L. Adhesive dentistry: Current concepts and clinical considerations. J Esthet Restor Dent. 2020;(November):10

4 *3. OBJETIVOS DEL TRABAJO*

4.1 **3.1 OBJETIVO PRIMARIO**

1) Clasificar los diferentes tipos de materiales de acuerdo con la revisión bibliográfica realizada.

4.2 **3.2 OBJETIVOS SECUNDARIOS**

1) Determinar de qué manera los materiales "inteligentes" pueden mejorar tratamientos dentales más habituales.
2) Analizar de acuerdo con la revisión realizada las principales ventajas e inconvenientes de cada uno de los tipos de materiales revisados.

5 *4. METODOLOGIA DEL TRABAJO.*

5.1 **CRITERIOS DE INCLUSIÓN:**

Artículos de los últimos 5 años con relevancia internacional.

Artículos que traten de biomateriales inteligentes que respondan a estímulos.

Artículos que traten de odontología restauradora.

5.2 **CRITERIOS DE EXCLUSIÓN:**

Artículos que hablen de biomateriales inteligentes en regeneración ósea.

Artículos que traten regeneración de tejidos periodontales.

Artículos con mas de 5 años.

Artículos sin relevancia internacional.

5.3 **RECOGIDA DE DATOS**

Por lo que corresponde a la introducción, hemos pensado útil hacer un resumen de la historia de los composites, manteniendo cierta libertad para la búsqueda de artículos, no hemos puesto limites de año de publicación y no hemos puesto criterios de inclusión y exclusión.

Por lo que se refiere a la discusión de los resultados y las conclusiones, la búsqueda se empezó planteando una análisis de los resultados de artículos de los últimos 10 años con las keywords: “Smart” “Biomaterials” y “dentistry” para encontrar unas revisiones genéricas de los materiales inteligentes en odontología, en que se encontraron en el motor de búsqueda pub med 66 artículos, de estos se utilizaron 2 artículos de revisión dentro de los cuales se eligieron los materiales sobre que se hará el estudio. Después de haber analizado las posibilidades y aplicado los criterios de inclusión y exclusión, se decidió tomar en cuenta dos categorías de materiales. Los materiales que hemos decidido estudiar son:

- Composites y adhesivos con función antimicrobiana.
- Composites “universales” o “one shade”.

La búsqueda se dividió entonces en dos apartados, poniendo como palabras clave: “universal + shade+ composites” y “remineralizing + antibacterial + composites” en el motor de búsqueda Pub Med, poniendo como filtros: “Publicados en los últimos 5 años” y “Texto entero”. La búsqueda dio respectivamente 26 resultados por “Universal + shade + composites” y 32 resultados por “remineralizing + antibacterial + composites ”. De estos se eligieron 10 estudios sobre composites one shade, y 14 sobre los composites antibacterianos y/o remineralizadores.

Aunque haya pocos estudios clínicos y no existan controles de larga duración; los autores piensan que, siendo la intrínseca naturaleza del estudio, la búsqueda de nuevos materiales y el efecto que puedan tener en el futuro de la odontología; hemos decidido quedarnos con estos criterios de inclusión.

Titulo de búsqueda:	Tot. artículos encontrados:	Tot. Artículos después criterios de inclusión y esclusion:	Tot artículos seleccionados por el estudio:
Universal + shade + composites	63	24	10
Remineralizing + antibacterial + composites	51	30	14

Tabla 1: Ilustracion de la metodología de trabajo.

6 *DISCUSIÓN DE RESULTADOS.*

Este estudio se pone como objetivo la revisión de la bibliografía existente sobre los nuevos materiales inteligentes en la odontología restauradora, y una clasificación de esos materiales, intentando dar una visión general sobre los composites con efecto mimético (también llamados "universales" o "one shade") y los composites con actividad antimicrobiana y remineralizadora, dando una visión total de los estudios existentes, evaluando las capacidades cromáticas, mecánicas y antibacterianas de los composites, para poder tener una visión completa del estado de la tecnología, evaluar el impacto que pueden tener en los tratamientos mas habituales y evaluando las ventajas y desventajas de cada material. La importancia de tener una visión completa sobre estos materiales se encuentra en el hecho que la odontología restauradora utiliza como material de rutina el composite de resina, siendo un material relativamente barato, clínicamente aceptable y con una buena duración en el tiempo.

Desde la mitad de los años '90 los materiales poliméricos basados en metacrilato han ido sustituyendo las viejas amalgamas para las restauraciones de cavidades siempre mas complejas y extensas, esto es, gracias al aumento progresivo de las propiedades mecánicas después de la polimerización (dureza, capacidad de pulido, rango de tonos o matices); de las propiedades de utilizo antes de la polimerización (manipulación, tamaño de incrementos en la técnica de estratificación), del aumento del rendimiento de los adhesivos a través de diferentes técnicas de grabado y de adhesivo (tres pasos, grabado selectivo) y de adhesivos siempre mas fáciles de utilizar (adhesivos universales) gracias al desarrollo de las técnicas de aislamiento absoluto, que permiten un utilizo mas seguro de los composites y adhesivos. Desde los primeros composites auto-polimerizantes y sin adhesivos del profesor Bowen, pasando a través de la practica adhesiva del profesor Buonocore, hasta los composites de nueva generación, el enfoque del desarrollo de los materiales ha cambiado de manera impresionante.

6.1 **COMPOSITES UNIVERSALES.**

Los composites universales son unos materiales “Smart” según nuestra definición, porque tienen unas nanopartículas diseñadas de manera que respondan al color del entorno en el cual se aplican para reflejarlo y tener un efecto mimético acentuado. En el estudio de Y. Lee et al. se sugieren unos criterios prácticos para la evaluación de los materiales para restauraciones directas, planteando el concepto básico según que la translucidez del composite es el factor que mas influye en el resultado estético y mimético del composite [16]. Otros autores plantean también el problema que dependiendo del composite que se utiliza, se tendrán resultados de opalescencia y translucencia diferentes, sea entre diferentes marcas o diferentes tipos de composites. En el estudio de 2021, C. Lucena et al se planteaban el objetivo de evaluar los parámetros de opalescencia y translucencia de 3 composites one-shade (Omnichroma; Venus Pearl; Venus Diamond) y un composite group shade (Filtek Universal A2), se hicieron unos discos de composite con espesores de 0,5, 1,0 y 2,0 mm. Se evaluò la reflectancia con un espectroradiometro. La translucencia fue calculada con unos ΔE obtenidos con los parámetros CIEDE2000 aplicados a una ecuación de coeficientes. Los resultados fueron que cada espécimen tenía unas diferencias estadísticas significativas de translucencia y opalescencia.

Estos resultados se observaron ambo entre especímenes de composites diferentes del mismo espesor, y entre diferentes espesores del mismo composite [(17)].

AUTORES	AÑO DE PUBLICACIÓN	COMPOSITES MIMETICOS ESTUDIADOS	TIPO DE ESTUDIO
de Abreu et al.	2020	Tokuyama Omnichroma	In vitro
R.Lyer et al.	2020	Tokuyama Omnichroma	In vitro
Chen et al.	2020	Tokuyama Omnichroma	In vitro
Durand et al.	2020	Filtek Universal Harmonize Tokuyama Omnichroma	In vitro
M. Evans	2020	Tokuyama Omnichroma	In Vitro
Perdigão et al.	2020	Tokuyama Omnichroma, Essentia Universal Filtek Universal SimpliShade Universal Composite TPH Spectra ST	Review Study - Clinical cases
Fanfoni et al.	2020	Ceram.X®Universal Ceram	In vitro
Habib et al.	2016	X-Tra Fil	In vitro

R. Lyer	2020	Tokuyama Omnichroma Tetric Evoceram TPH Spectra ST	In Vitro
C. Lucena	2021	Tokuyama Omnichroma Venus Diamond Venus Pearl Filtek Universal A2	In Vitro

Tabla 2. Articulos utilizados en el apartado "composites universales"

Hay pocos composites universales en comercio, con propiedades y indicaciones diferentes, aunque vayan aumentando con el paso del tiempo, gracias a las potenciales ventajas de utilizo y de estética.

Los composites universales suelen tener menos tonalidades de color. Generalmente tienen un único tono (*one shade*), o tonos de grupo (*group shades*) para cubrir todos los colores de la guía VITA®. Esto, en todos casos, simplifica ampliamente el trabajo clínico del odontólogo a la hora de elegir el composite, permitiendo cubrir un espectro mas amplio con cada tono de composite, en caso de los composites miméticos "*group shade*", o incluso adaptarse a todos los matices existentes en caso de los nuevos composites *one-shade*.

En el estudio De Abreu et al., los composites miméticos Tokuyama Omnichroma fueron comparados con unos composites *multishade* (Tetric Evoceram, Filtek Universal, and TPH Spectra Universal). La metódica consistió en evaluar 60 obturaciones de tipo III en zonas estéticas a través de fotografías bajo luz polarizada usando las "*CIELab color coordinates*", un sistema de evaluación de los colores de la *International Commission on Illumination* que consiste en tres coordinadas, l* por la luminosidad del objeto, a* por el croma en el eje verde-rojo b* en el eje amarillo azul. Las coordinadas se sacaron por parte de 6 estudiantes de doctorado, que demostraron una discriminación de colores superior, usando el índice ISO/TR

28642:2016. Los composites *one-shade* dieron valores mas bajos de emparejamiento que los *multishade* [18].

L. Durand, comparaba composites universales con un control de un composite *multishade*: (Omnichroma, Harmonize, Filtek Universal y Filtek Z350XT como composite control), a través de un sistema de evaluación donde se fabricaron discos de composite obturados con los composites estudiados. Se evaluó el nivel de mimetismo a través de un espectroradiometro y las diferencias de color a través de las coordinadas CIEDE2000 (sistema de calculo de la diferencia de color de la *International Commission on Illumination)*. Las coordinadas de color y el potencial de ajuste de la translucidez dependían del material dental. Entre los composites estudiados, se registraron los mayores potenciales de ajuste de color, ligereza, tonalidad y translucidez para Omnichroma, con unos buenos resultados por todos los demás composites universales en comparación con el control [19].

Abdelraouf et al. hicieron un estudio *in vitro* sobre composites X-Tra Fil (*one shade*) y Grandio

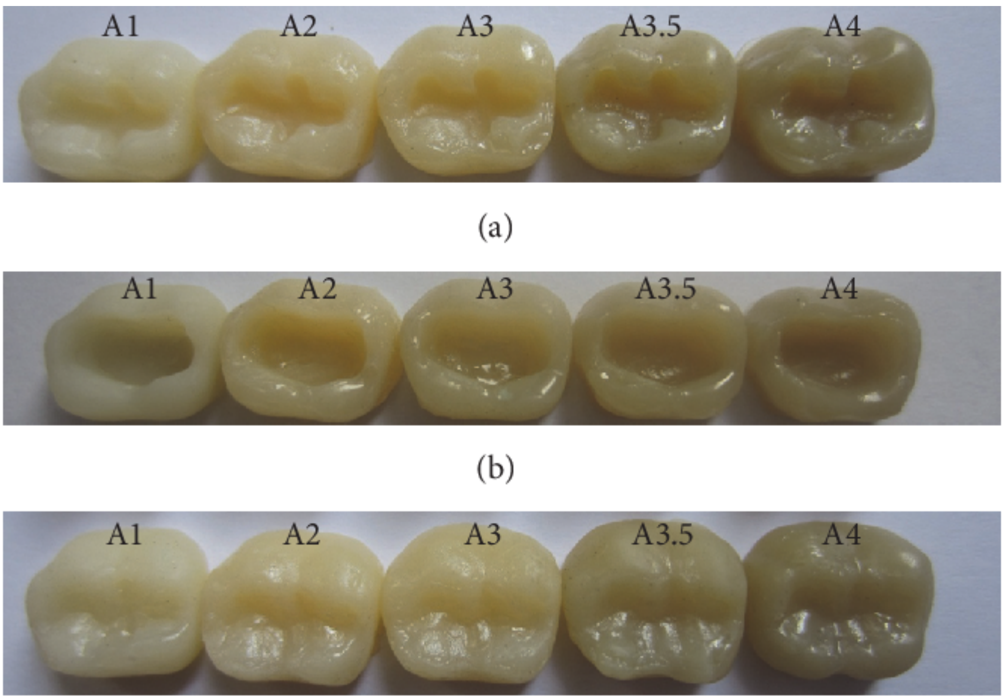

Imagen 2. Modelos de composite de resina semejantes a dientes en tonos A1, A2, A3, A3.5 y A4. (a) Preparación de cavidades pequeñas. (b) Preparación de cavidades más grandes. (c) Después de rellenar con composite de resina bulk fill de tono universal.

(*multishade*) en cavidades de clase 1 en molares de resina. Los especímenes tenían matices desde el A1 hasta el A4. Se evaluaron las restauraciones usando las coordinadas CIELAB, y los resultados se evaluaron a través del sistema ANOVA, seguido por la prueba de Bonferroni (ecuación para comparar diferentes hipótesis entre si) para detectar las diferencias significantes. La evaluación visual fue ejecutada por parte de 7 observadores de sexo femenino (4 odontólogos y 3 científicos) con una visión de colores normal, evaluada a través de la prueba de Ishiara. Todos los observadores fueron entrenados sobre la manera de evaluar los colores y puestos en un ambiente estandarizado, en una habitación con colores neutros, a una distancia y angulación igual por todos los sujetos.

El composite universal *bulk-fill* demostró un emparejamiento al color *in vivo* aceptable; sin embargo, puede no ser la selección ideal cuando la estética es la principal preocupación del paciente. Puede ser mejor evaluar la concordancia de colores y el efecto de mezcla *in vivo* en lugar de *in vitro*, ya que es una mejor simulación de la condición clínica [(20)].

En el *review study* de Perdigao et al. Se estudiaron varios casos clínicos en sectores estéticos y blanqueamientos, además de analizar varios de los estudios que nosotros también hemos considerado. Se concluyó que las resinas compuestas universales eran más fáciles de manejar y utilizar que las resinas compuestas convencionales, y al mismo tiempo proporcionaban una excelente estética (imágenes 3 y 6) [(21)].

Imagen 3 Perdigao et al. Cierre de múltiples diastemas en una paciente de 29 años. (A) Línea de sonrisa preoperatoria; (B) Labio en posición de reposo; (C) Vista retraída de los dientes anteriores superiores; (D) Vista derecha retraída; (E) Vista izquierda retraída; (F) Mockup con Omnichroma (Tokuyama Dental America, Inc.) aplicado en el incisivo central derecho y Essentia Universal (GC Europe) aplicado en el incisivo central izquierdo. Decidimos restaurar los dientes con Omnichroma (G) Remoción de maqueta; (H) Vista postoperatoria de las restauraciones de Omnichroma. Perdigão J, Araujo E, Ramos RQ, Gomes G, Pizzolotto L. Adhesive dentistry: Current concepts and clinical considerations. J Esthet Restor Dent. 2020;(November):12

El estudio de Chen et al. Se simularon unas cavidades de clase 1 en unos bloques de composite *multishade* previamente polimerizados, usando los matices A1, A2, A3, A4. Estas cavidades fueron restauradas con composites *Clustered Nano Filled*, *Microhibrid Filled* y *Supra Nano Filled*. Los parámetros de color fueron comparados con CIELAB y CIEDE2000, y los datos fueron comparados con un análisis de varianza de una vía (ANOVA), seguida por la prueba de Duncan. Con estos datos, se hizo una comparación entre el tamaño y la forma de las partículas de relleno en la influencia del color estructural del diente. Los resultados del estudio fueron que los composites *supra nano filled* se revelaron significantemente mas miméticos en los colores con valor mas alto, o sea en los colores mas claros [22].

En el estudio de R. Lyer et al. se hizo un estudio con el objetivo de evaluar el emparejamiento de tonos de tres composites universales *one shade*. Se hicieron tres grupos: Omnichroma, Tetric EvoCeram, y TPH Spectra ST. Los composites fueron puestos en preparaciones oclusales (5mm de diámetro por 2 mm de profundidad) de dientes acrílicos con tonos A2, B1, B2, C1 y D3. Se polimerizaron con un único incremento. Se midieron los parámetros CIEDE2000 obtenidos con VITA Easyshade V y los valores de ΔE se calcularon con el sistema ANOVA de dos vías, poniendo como resultado estadísticamente significativo $P < .05$. Tres dientes fueron además restaurados con formas anatómicas y evaluados por parte de 30 sujetos con los criterios: 1-Mejor emparejamiento, 2-Intermedio, 3-Peor emparejamiento. En la evaluación instrumental, se vio que Omnichroma y TPH Spectra TS tenían valores de ΔE mas bajos en tonos mas claros, mientras Tetric Evoceram tenía valores bajos en todos los colores. En la evaluación visual, Tetric Evoceram tenía un mejor emparejamiento de color en tonos oscuros (C2, D3), mientras Omnichroma y TPH Spectra ST en colores mas claros [23].

Como se nota en el estudio de R. Lyer et al., diferentes composites tienen comportamientos diferentes, no solo dependiendo del entorno, sino que, como demostrado en el estudio de C. Lucena, dependiendo del tipo de material y del espesor de la restauración, se obtienen parámetros diferentes.

Acerca de las calidades mecánicas de los composites miméticos se han encontrado pocas informaciones. La mayoría de los estudios se centra en el resultado estético, y la composición de los composites universales varía tan poco de los composites tradicionales, que se puede pensar con suficiente seguridad que tengan las mismas calidades mecánicas; no obstante, se han encontrado tres estudios donde se evalúan factores mecánicos y físicos como el grado de conversión, la proporción y profundidad de polimerización, la microdureza, el estrés de contracción y el comportamiento clínico.

Fanfoni et al. se centraron en la evaluación del porcentaje de conversión, polimerización, microdureza y profundidad de polimerización de un composite group shade (Ceram X Universal), y otros multishade (Ceram X Duo Enamel, Ceram X Duo Dentin Tetric EvoCeram Dentin, Tetric EvoCeram Enamel). Se prepararon unas muestras de 2 mm de espesor con aleaciones de composites, para obtener el tono A3 (en caso de composites multishape), polimerizándolas durante 40 segundos. Se utilizó un FTIR-ATR (*Fourier Transform InfraRed Attenuated Total Reflectance equipment*) para medir la profundidad de curado. Subsecuentemente estos especímenes fueron sometidos a un indentador de Vickers, complementado con una maquina de ensayo de microdureza, para medir el VHN (*Vickers Hardness Number*) de la superficie y de la parte mas profunda, calculando con la ecuación: (VHR= (Bottom – VHN_{mean} / Top - VHN_{mean}) × 100. La VHR fue considerada como una medida de la profundidad de curación de los composites bajo las condiciones probadas, VHR >80% fue considerada como la unidad arbitraria para un material adecuadamente curado.

El estrés de contracción se ha medido a través de dos cilindros de metal, recubiertos con un composite sin relleno en una parte, puestos a una distancia de 2 mm dentro de un extensómetro, llenando la distancia entre los dos con una cantidad fija de composite (15mg) y midiendo la distancia después de haber polimerizado los composites durante 40 segundos, cada experimento fue repetido 10 veces en una habitación con una temperatura de entre 19 – 22 °C. Todas las propiedades de los compuestos del estudio dependían del material. En particular, DC (profundidad de polimerización*)*, RC (tasa de polimerización), VHN y VHR, se vieron afectados por la naturaleza del material (composición y relleno), el tono y la translucidez. El

CS (estrés de contracción), fue independiente de las características ópticas de los materiales. Los composites Ceram.X® dieron el mejor rendimiento en términos de CS y RC. Sin embargo, considerando que, para todos los composites probados la DC promedio se mantuvo por debajo del 55% después de 40 s de fotopolimerización, los autores sugerían un aumento del tiempo de curado o una reducción del espesor de la capa en el entorno clínico. Todos los composites que se habían probado, con 2mm de espesor demostraron un DC poco satisfactorio con VHR <80%, justificando las recomendaciones de usar los materiales con espesores de menos de 2mm [(24)].

Otro aspecto importante de los composites miméticos es la teoría según la cual, siendo unos composites que mimetizan con el entorno una vez polimerizados, podrían ser útiles en paciente que serán posteriormente sometidos a blanqueamientos dentales, siendo que, cambiando el color del entorno, los composites universales podrían adaptarse al nuevo color. Sobre este tema M. Evans hizo un estudio sobre el comportamiento clínico de Tokuyama Omnichroma. La evaluación se hizo en 25 dientes extraídos en que se fabricaron cavidades posteriormente restauradas con el composite Omnichroma. Los dientes fueron medidos de manera visual en la guia de color VITA y sucesivamente sometidos a colorímetro. Las evaluaciones se hicieron antes del blanqueamiento, después de 5 tratamientos y después de 10 tratamientos de blanqueamiento. Se realizó un análisis estadístico y se compararon los valores de ΔE obtenidos con el colorímetro a través del sistema de calculo CIELAB. También se hizo un análisis visivo para determinar si era posible percibir un cambio entre los 3 grupos a simple vista. En la comparación se vio que había cambios significativos de ΔE, sobre todo comparando los grupos de 0 y 10 tratamientos. El ΔE diente/composite era mucho mas bajo después de 10 tratamientos que después de 5 y 0. En conclusión, había un descenso significante de ΔE desde el grupo 0 al grupo de 10 tratamientos. Como ya demostrado en estudios precedentes, la diferencia de tono entre el composite y el diente disminuye a medida que el color se hace mas claro. Además el composite demostró de poder cambiar de tono a medida de que la estructura alrededor se ponía mas clara, esto en ambos colorímetro y análisis visual [25].

Unos resultados similares se habían obtenido también en casos clínicos del estudio de Perdigao et al. Donde el composite aumentaba su efecto mimético a medida que el color del entorno se ponía mas claro a través de los blanqueamientos (Imagen 6).

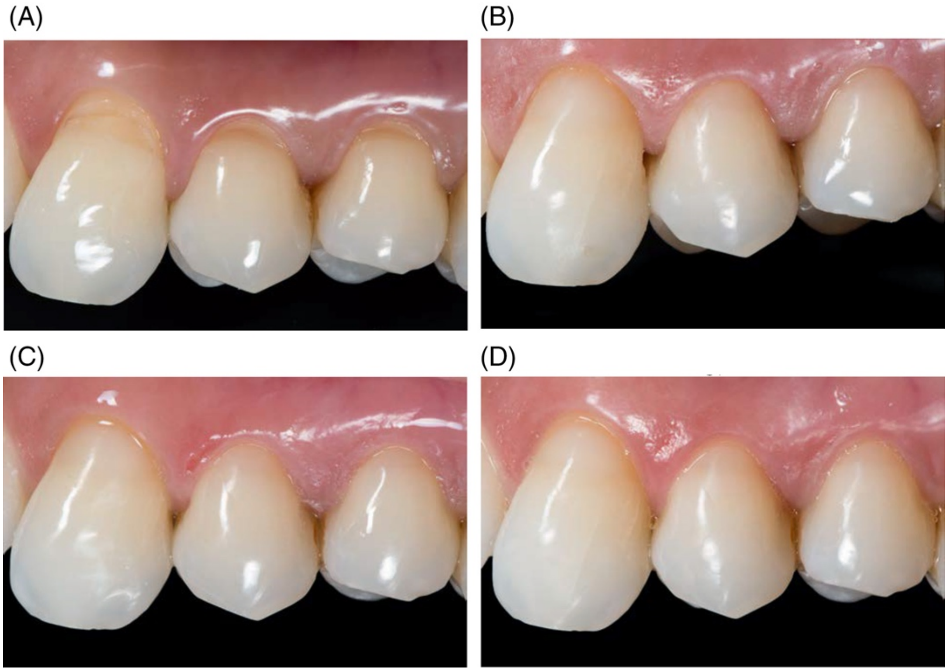

Imagen 4. Perdigao et al. (A) Vista preoperatoria de NCCL en el canino y premolares superiores izquierdos. Se utilizaron las siguientes resinas compuestas universales: Omnichroma (Tokuyama Dental America, Inc.) para el canino maxilar izquierdo; Filtek Universal (3M Oral Care) para el primer premolar superior izquierdo; y Essentia Universal(GC Europa) para el segundo premolar superior izquierdo (B) Vista posoperatoria de una semana. La paciente preguntó si podía blanquearse los dientes (C). Después de 3 semanas de blanqueamiento en casa con mascarillas a medida (D). Dos semanas después de terminar el régimen de blanqueamiento. Todas las restauraciones se mezclaron muy bien con la estructura dental blanqueada. Perdigão J, Araujo E, Ramos RQ, Gomes G, Pizzolotto L. Adhesive dentistry: Current concepts and clinical considerations. J Esthet Restor Dent. 2020;(November):13

6.2 COMPOSITES CON CALIDADES REMINERALIZANTES Y ANTIBACTERIANAS.

En los últimos 5 años se han ido desarrollando composites con efectos antibacterianos y remineralizantes. Esto da una nueva perspectiva al desarrollo de los materiales de restauración, dando unas características "Smart" a unos materiales que hasta hace 30 años casi no se usaban y que hoy en día no solo se usan ampliamente, sino que son los materiales de elección por la mayoría de los tratamientos de reconstrucción.

AUTORES	AÑO DE PUBLICACIÓN	MATERIAL CON EFECTO (1)REMINEALIZANTE/ (2)ANTIBACTERICO ESTUDIADO	TIPO DE ESTUDIO	TIPO DE PARTÍCULAS:
K. Zhang et al.	2016	(1) NACP (2) QAM	In vitro	NANOPARTICULAS REMINERALIZADAS
W. Zhou et al.	2020	(1) NACP (2) DMAHDM	In vitro	
W. Zhou et al.	2020	(1) NACP (2) DMAHDM	In vitro	
W. Zhou et al.	2020	(1) NACP (2) DMAHDM	In vitro	
Y. Al Dulaijan et al.	2018	(1) NACP (2) DMAHDM	In vitro	
G. Bhadila et al.	2020	(1) NACP (2) DMAHDM	In vitro	
G. Bhadila et al.	2020	(1) NACP (2) DMAHDM	In vitro	
G. Bhadila et al.	2020	(1) NACP (2) DMAHDM	In vitro	
G. Bhadila et al.	2020	(1) NACP (2) DMAHDM	In vitro	
Y. Yang et al.	2021	(1) NACP (2) CHX	In vitro	
H. Mitwalli et al.	2020	(1) nCaF2 (2) DMAHDM (2)MPC	In vitro	
M. Lee et al.	2020	(2)Zn-PBG	In vitro	NANOPARTICULAS METÁLICAS
L. C. Natale et al.	2017	(1) CaP (2) Ag	In vitro	
X. Chatzistavrou et al.	2018	(2) Ag-BGCOMP	In vitro	

Tabla 3. Artículos utilizados en el apartado "composites con actividad remineralizante y antibacteriana"

6.2.1 NACP – DMAHDM (NANOPARTICULAS REMINERALIZADAS)

Las sustancias con efecto antimicrobiano y remineralizador más estudiadas y fabricadas son sin duda las QAM (metacrilados de amonio cuaternario) acopladas con nanoparticulas de calcio fosfato (NACP). Zhang et al. Focalizaron un estudio sobre la incorporación de QAM con diferente longitud de cadena alquilica (CL) en composites, con el objetivo de evaluar las propiedades mecánicas y los efectos sobre el biofilm. Sintetizaron 5 QAM con longitud de cadena desde 3 hasta 18, (DMAPM (CL3), DMAHM (CL6), DMADDM (CL12), DMAHDM (CL16) y DMAODM (CL18)), incorporándolos dentro de un nanocomposite que contenía 20% de NACP y 50% de relleno de vidrio. Notaron que el nanocomposite adicionado con NACP y DMAHDM disminuía la actividad metabólica del biofilm y la producción de ácido de 10 veces en comparación con el composite control, y disminuia de 2 veces las unidades formadoras de colonias (CFU) de los microorganismos, estreptococcos y S mutans. El DMAHDM se demonstró entonces el metacrilado de amonio cuaternario que dío mejores resultados (Imagen 7) y que por esto, entre los QAM, es el que más se ha usado en los estudios que hemos tomado en consideración en esta revisión de la literatura [26].

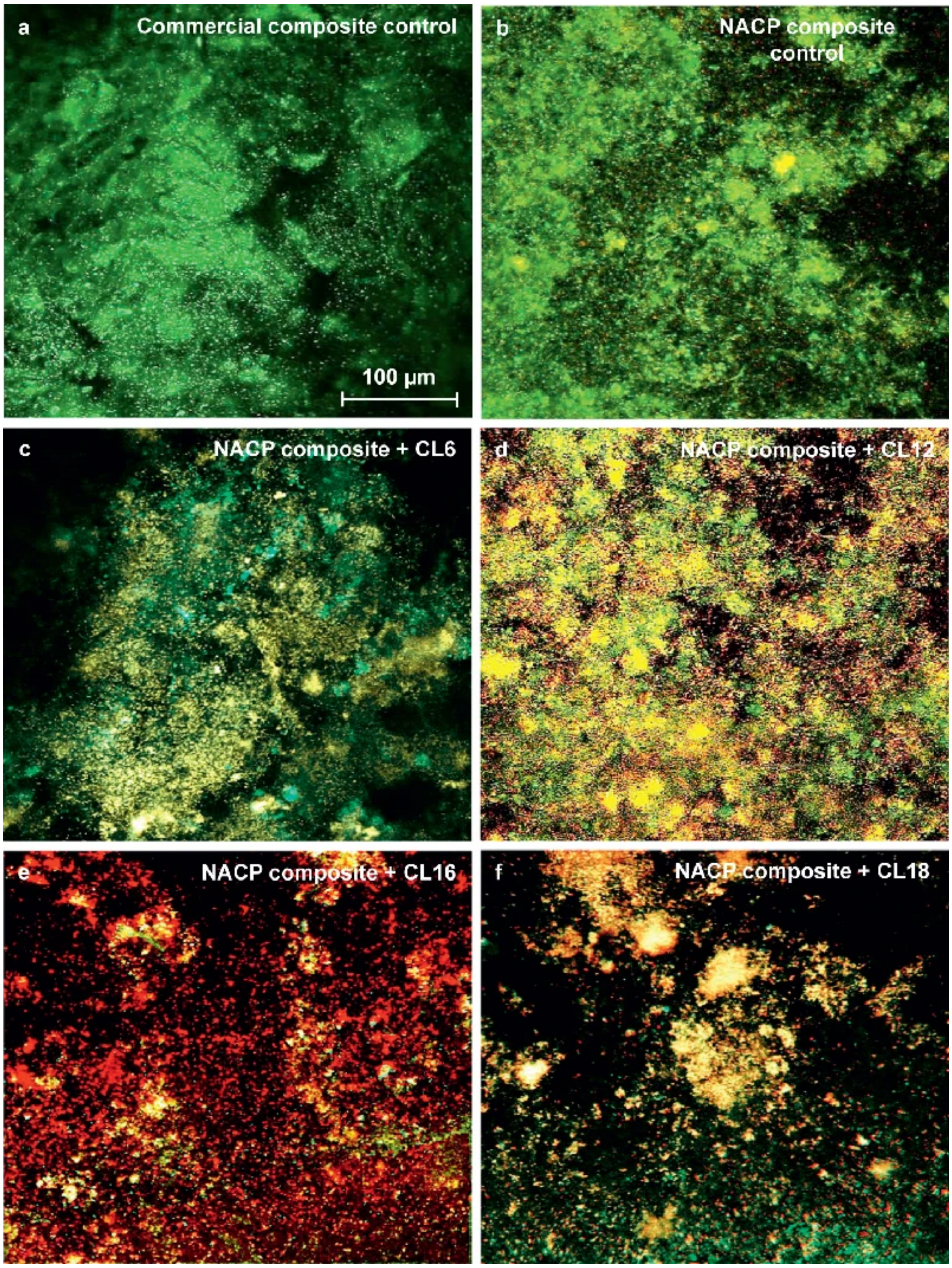

Imagen 5. ***Imágenes representativas vistas al CLSM (confocal laser scanning microscopy) extraído del estudio de Zhang et al.*** *El nombre del material se indica en cada imagen y la ampliación de todas las imágenes es la misma que en* ***a.*** *Las bacterias vivas se tiñeron de verde y las bacterias muertas se tiñeron de rojo. Las bacterias vivas y muertas que se co-localizaron aparecieron de color amarillo o naranja. El composite comercial y el nanocomposite NACP sin QAM tenían principalmente bacterias vivas. El aumento de CL mejoró la actividad antibacteriana, con CL16 produciendo principalmente tinciones rojas y anaranjadas. CL, longitud de la cadena; NACP, nanopartículas de fosfato cálcico amorfo; QAM, metacrilatos de amonio cuaternario. Zhang K, Cheng L, Weir MD, Bai YX, Xu HHK. Effects of quaternary ammonium chain length on the antibacterial and remineralizing effects of a calcium phosphate nanocomposite. Int J Oral Sci [Internet]. 2016;8(1):48-49*

W. Zhou et al. en 2020 publicaron 3 estudios sobre composites con adición de NACP+DMAHDM, en

el primero se evaluó la eficacia de dimethil-amino-hexadecil metacrilato (DMAHDM) y de fosfato de calcio amorfo (NACP) sobre caries recurrentes. NACP Y DMAHDM se incorporaron en composite. Los sujetos se dividieron en 4 grupos: grupo control comercial (Heliomolar), el grupo control experimental (0% DMAHDM + 0% NACP), el grupo antibacteriano (3% DMAHDM + 0% NACP) y el grupo antibacteriano y remineralizador (3% DMAHDM + 30% NACP).

Se estudiaron las propiedades mecánicas de los especímenes a través de una "*universal testing machine*". Posteriormente los especímenes; estériles y pulidos; fueron puestos en 24 pocillos y fue inoculado en cada uno de ellos 1,5ml de medio de cultivo con 10^7 CFU/ml de S. mutans, fueron cultivados durante 24 h y entonces trasferidos en otros pocillos con nuevo agar corazón cerebro (BHI) y incubados durante otras 24 h. Los discos fueron luego analizados por el recuento de bacterias vivas y muertas con unos kits de viabilidad bacteriana BacLight (fluorescencia) y evaluados con un microscopio de epifluorescencia invertido (Imagen 8), evaluados por el recuento de CFU y suplementados con una solución del 0,2% de sacarosa por 3h, comparando el grado de absorbancia de los especímenes con la curva estándar del acido láctico.

También en el mismo estudio se evaluó el grado de desmineralización del esmalte dental en dientes bovinos expuestos a S.mutans durante 7 días, fabricando unas losetas de esmalte con cavidades restauradas con los 4 grupos del estudio y poniéndolas en cultivos similares a los de las primeras pruebas. Se evaluaron luego con un indentador de Vickers y se hizo un análisis estadístico de los resultados a través de un análisis de variancia de una vía y de dos vías usando un software de estadística, poniendo $P < 0,05$ como dato significante.

Se obtuvieron las conclusiones que el DMAHDM disminuyó efectivamente la producción de ácido láctico y polisacáridos del biofilm de S. mutans en el compuesto, reduciendo el biofilm con UFC de 4 veces. Comparando los grupos de control el composite con DMAHDM tenia dureza de esmalte 1,5 veces mayor y en comparación con los grupos de control, el compuesto con contenido de DMAHDM produjo una dureza de esmalte 1,5 veces mayor. Con una mayor incorporación de NACP para neutralizar los ácidos biofílicos y aumentar el pH, el compuesto de 3% DMAHDM + 30% NACP proporcionó efectos sinérgicos con capacidades antibacterianas y de remineralización significantes ($P < 0,05$) y produjo una dureza de esmalte 2 veces mayor que los dos grupos de control [27].

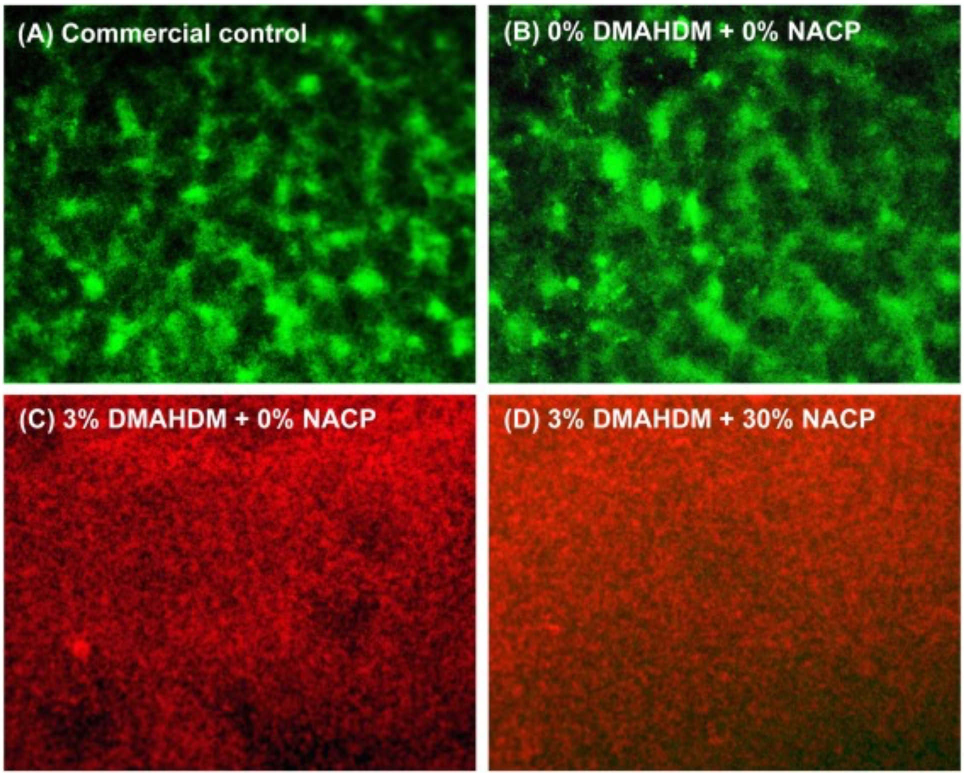

Imagen 6. Zhou et al. Imágenes representativas de tinción en vivo / muerto de biopelículas de S. mutans de 2 días en materiales compuestos. (A) Control comercial; (B) 0% DMAHDM + 0% NACP; (C) 3% DMAHDM + 0% NACP; (D) 3% DMAHDM + 30% NACP. Las bacterias vivas se tiñeron de verde y las bacterias muertas se tiñeron de rojo.

Zhou W, Peng X, Zhou X, Weir MD, Melo MAS, Tay FR, et al. In vitro evaluation of composite containing DMAHDM and calcium phosphate nanoparticles on recurrent caries inhibition at bovine enamel-restoration margins. Dent Mater [Internet]. 2020;36(10):1349.

En su segundo estudio W. Zhou et al. usaron los mismos composites, con las mismas concentraciones de DMAHDM y NACP y sometiéndolos a pruebas similares, pero con concentraciones y tiempos de exposición mas largos. Tuvieron, como esperado, resultados similares al primer estudio, con una disminución estadísticamente relevante de caries marginal y una optima preservación de la dureza del esmalte, además de un gran efecto antibacterico (imagen 9).

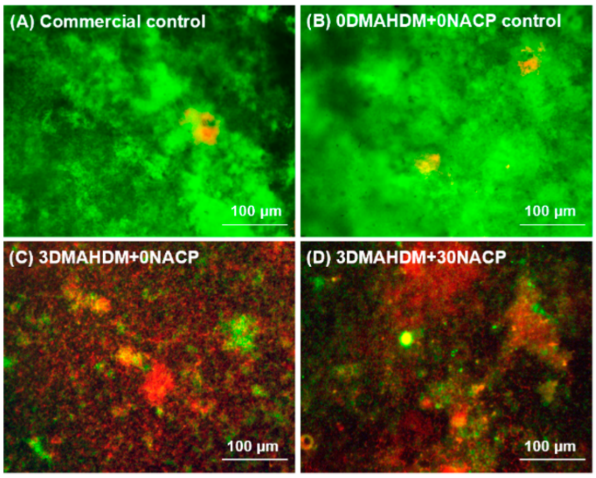

Imagen 7 Zhou et al. Imagenes representativas de bacterias vivas/muertas después de ser cultivados durante 48h en composites. (A) control comercial. (B) control 0DMAHDM+0NACP (C) 3DMAHDM+0NACP. (D)3DMAHDM+30NACP. Las bacterias vivas fueron coloreadas en verde y las muertas en rojo. Zhou W, Peng X, Zhou X, Bonavente A, Weir MD, Melo MAS, et al. Novel nanocomposite inhibiting caries at the enamel restoration margins in an in vitro saliva-derived biofilm secondary caries model. Int J Mol Sci. 2020;21(17):4

El composite adicionado solo con DMAHDM había protegido de forma efectiva la formación, la viabilidad y el potencial cariogénico del esmalte, resultando en una dureza de esmalte marginal del 25% mayor que en el composite control. El composite adicionado con NACP+DMAHDM resultó en una dureza de esmalte del 50% mas alta, esto se reflejó en una dureza de esmalte expuesto a entorno acido, abajo del biofilm, que coincidía con la del esmalte sano [28].

En el tercer estudio, fabricaron unos composites adicionados con NACP y DMAHDM con el objetivo de evaluar la inhibición de "*Streptococcus mutans*", "*Lactobacillus acidophilus*" y "*Candida Albicans*" en un modelo de caries de raíz recurrente "*biofilm-based*" para proteger la dureza de la dentina radicular por primera vez. En este estudio también se usaron materiales y metodos similares al estudio precedentes. Se hicieron 5 grupos: control comercial (Heliomolar), control de composite experimental (0%NACP, 0% DMAHDM), composite mineralizador (30% NACP), composite antibacteriano (3%DMAHDM), composite antibacteriano-remineralizador (30%NACP+3%DMAHDM) que fueron probados con discos en vitro y en losas de incisivos bovinos. Se analizó el biofilm, la producción de acido láctico, el recuento de CFU, las bacterias vivas/muertas, la liberación de Ca y P. Se concluyó que los composites que conteniasn NACP + DMAHDM habían inhibido con mucho éxito los biofilm patógenos y habían preservado la dureza de la dentina en los márgenes de las restauraciones y habían proporcionado iones Ca y P [29].

Bhadila et al hicieron 4 estudios sobre composites adicionados con NACP y DMAHDM. El primer estudio en orden temporal vertía sobre la liberación a largo plazo de iones Ca y P y el potencial de remineralización de un NACP-DMAHDM bioactivo.

Se hicieron tres grupos: (1)Control Heliomolar; (2) Composite+20%NACP+50%vidrio; (3) Composite+3%DMAHDM+20%NACP+50%vidrio, primero los 3 grupos fueron puestos en pocillos con agar corazón cerebro suplementados con 1,5 ml de solución con concentración de 10^7 CFU/ml de S.mutans y 1% de sacarosa para medir la capacidad de inibicion bacteriana de cada grupo. El grupo 2 y el 3 fueron luego sometidos a una solución de NaCL tamponado a ph4 con acido láctico, se dejaron durante 70 días, luego se recargaron y se volvieron a dejar en la solución por 14 días, el proceso de recarga y de inmersión de 14 días se repitió por 12 veces, por un total de 6 meses de experimentación.

Los resultados fueron que los composites seguían con su efecto remineralizante durante largos tiempos y que podían ser recargados varias veces, previniendo la desmineralización, la producción de acido láctico y el crecimiento de biofilm al mismo tiempo [30].

En los otros 3 estudios se usaron materiales similares por lo que concierne los porcentajes de sustancias bioactivas, pero se cambiaron las resinas para que fuesen resinas con bajo porcentaje de contracción de polimerización.

Los objetivos eran de desarrollar unos composites antibacterianos y reminaralizadores con bajo porcentaje de contracción de polimerización, evaluar los efectos a largo tiempo de estos composites sobre la desmineralización marginal del esmalte y evaluar sus propiedades mecánicas y citotóxicas.

Se sometieron las muestras a pruebas similares a las del primer articulo, para determinar CFU de biofilm, producción de acido láctico, y medición de liberación de Ca y P; pero se adicionaron con unas pruebas para medir el porcentaje de contracción de polimerización.

Los resultados fueron que los composites tenían efectos antibacterianos y remineralizadores notables; disminuyendo un mínimo de 4 veces los recuentos de UFC y de producción de ácidos lácticos; seguían teniendo efectos remineralizadores hasta después de 3 meses sumergidos en una solución acida, teniendo efectos remineralizadores sobre la dureza del esmalte marginal a la restauración, que era 2 veces mas alta que la del composite control.

Los composites redujeron sustancialmente el estrés de de polimerización en comparación con los composites tradicionales, teniendo hasta un 36% de reducción de estrés. Al mismo tiempo no tuvieron ningún efecto negativo sobre las propiedades mecánicas y sobre el grado de conversión del composite después de la polimerización [31] [32] [33].

Y. Al Dulaijan et al. hicieron un estudio sobre composites adicionados con NACP con posibilidad de ser recargado y DMAHDM. Los objetivos eran de observar las capacidades antimicrobianas, mecánicas y de liberación de iones. Se fabricaron 2 composites, uno con NACP y el otro con adición de DMAHDM además que NACP. En este caso también se sometieron los composites a test similares a los estudios anteriores y el composite control fue el mismo que en los estudios de G. Bhadila et al. (Heliomolar).

Los resultados enseñaron que el modulo de conversión y la flexión fueron las mismas del composite control ($p < 0.1$). El composite con NACP-DMAHDM inhibió la actividad metabólica del biofilm y la producción de acido láctico y redujo las unidades formadoras de colonias del biofilm (CFU) de 3-4 veces. Los composites con NACP y NACP-DMAHDM tenían una liberación y una posibilidad de recarga de iones Ca y P similares ($p < 0.1$). La adición de QAM no interfería con la recarga de iones [(34)].

El estudio de H. Mitwalli tenía como objetivo desarrollar un nuevo nanocomposite que contuviese DMAHDM, MPC (2-metacriloxyloxyetilfosforilcolina) y nanoparticulas de calcio – flúor, para tener un composite que fuese antibacteriano (DMAHDM), repelente de proteínas (MPC) y capaz de liberar flúor ($NCaF_2$.). Se hicieron unos composites con adición de 3%MPC+3% DMAHDM+15% $NCaF_2$+55% vidrio, en una resina Bis-GMA y TEGDMA (BT), y unos composites control: control comercial (Heliomolar); control experimental(BT + 70% vidrio); composite remineralizador (BT + 15% nCaF2 + 55% vidrio) composite antibacteriano y remineralizador (BT + 15% $nCaF_2$ + 3% DMAHDM + 55% vidrio), composite repelente de proteínas, remineralizador y antibacteriano (BT + 15% nCaF2 + 3% MPC + 55% vidrio). Se sometieron a unas pruebas para evaluar la liberación de Ca y F, las propiedades mecánicas, la evaluación de la actividad metabólica del biofilm y el recuento de CFU. Los resultados fueron que el composite BT+3%MPC+3% DMAHDM+15% $NCaF_2$, tenía unas capacidades antibacterianas superiores a los otros composites, mientras iguales capacidades remineralizadoras que el composite BT + 15% $nCaF_2$ + 3% DMAHDM + 55% vidrio. A nivel de características mecánicas, se vio que la incorporación de MPC daba como resultado una bajada en las propiedades mecánicas, mientras el composite antibacteriano y remineralizador exhibía excelentes propiedades mecánicas, similares a las del composite comercial de control (Heliomolar). En conclusión, se vio que el composite con combinación de nCaF2+DMAHDM, además de tener óptimas calidades mecánicas, tenia una fuerte acción antibacteriana, evitando la producción de acido láctico y disminuyendo la CFU del biofilm de 4 veces [35].

Y. Yang et al. incorporaron clorhexidina (CHX) con nanoparticulas de calcio fosfato (NACP) en unos composites de resina, con el objetivo de mejorar sus propiedades remineralizadoras y antibacterianas.

Las nanopartículas de CHX / ACP "*core-shell*" (nanoparticulas compuestas que contienen un núcleo interior recubierto con una o más capas (*shells*) de diferentes materiales) (36), fueron sintetizadas y caracterizadas mediante tecnología de "*vesicule templating*" (producir nanocápsulas poliméricas huecas a partir de productos químicos de bajo coste)[37] y también fueron evaluadas sus propiedades antibacterianas y de liberación sostenida. Posteriormente, las nanopartículas sintetizadas fueron incorporadas al composite de resina dental al 1%, 5% o 10% en peso, para obtener diferentes grupos experimentales. Se evaluaron las propiedades físicas, incluida la profundidad de curado, la tasa de conversión de polimerización y las propiedades mecánicas del composite de resina modificada. También se evaluó la habilidad de remineralización con el sistema SEM (*standard error calculator*), mientras que la capacidad antibacteriana de la resina modificada fue calculada con el método del recuento en placa, después de haber dejado la resina en medio de cultivo (BHI) a 37° por 28 días.

En el análisis físico de las partículas se notó que las nanoparticulas *core-shell* se habían desarrollado de manera correcta, se podía observar una cascara de ACP y el interior relleno de CHX, teniendo un efecto de liberación de calcio, fosfato y CHX, sin interferir con las propiedades mecánicas de los composites. Las resinas con contenido del 5% por arriba de nanopartículas de CHX/ACP inhibían el crecimiento de S. Mutans aunque cultivadas y dejadas en agua con un efecto de envejecimiento inmediato de las bacterias del 92%. En adición, las partículas habían tenido un efecto remineralizante estadísticamente significativo, después de haber verificado a través de un microscopio SEM (scanning electron microscope) [38].

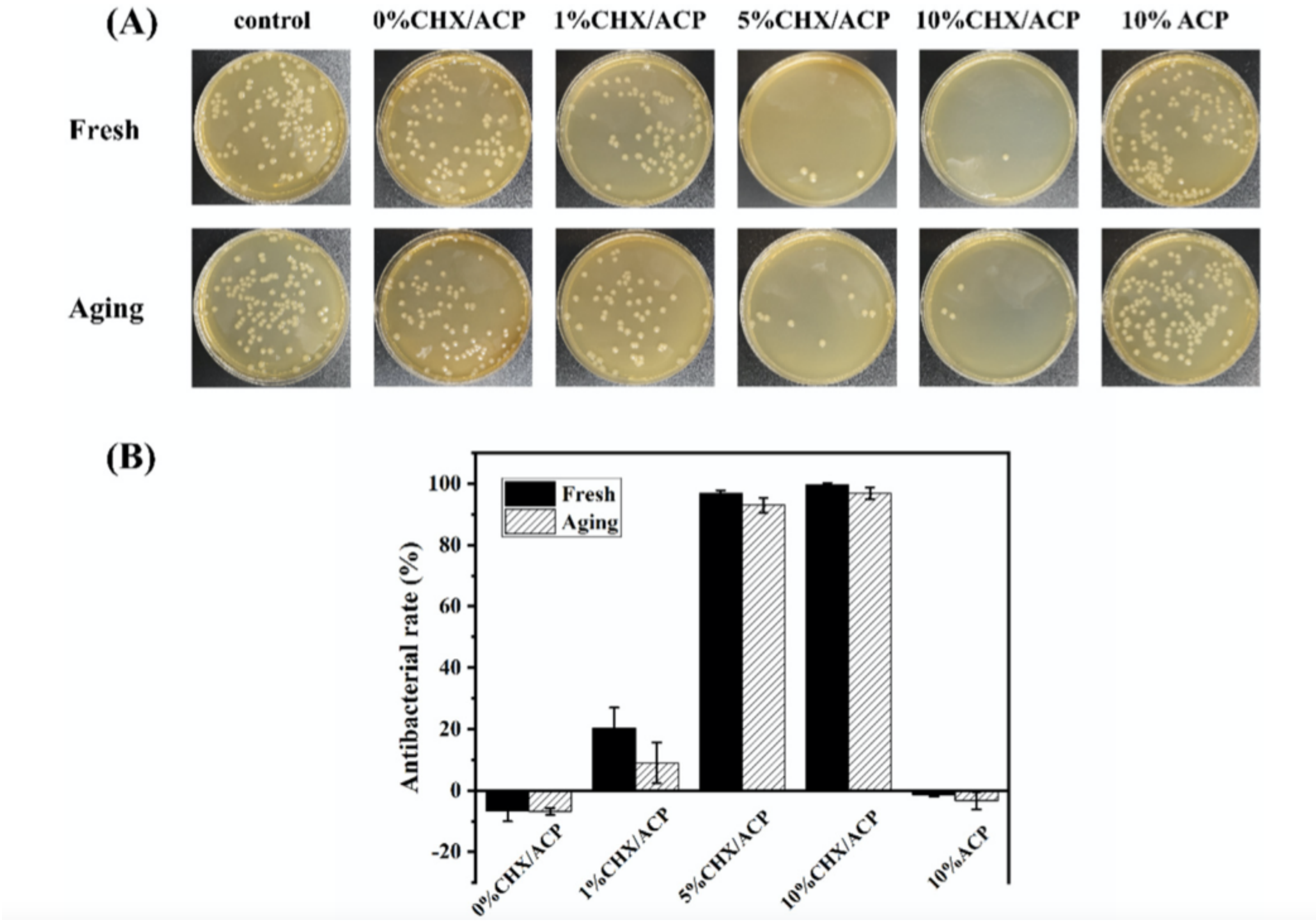

Imagen 8. Yang Y. Las fotos del recuento de placas de la prueba antibacteriana de la resina compuesta con diferentes contenidos de nanopartículas CHX/ACP (A), y tasas antibacterianas (B).

Yang Y, Xu Z, Guo Y, Zhang H, Qiu Y, Li J, et al. Novel core–shell CHX/ACP nanoparticles effectively improve the mechanical, antibacterial and remineralized properties of the dental resin composite. Dent Mater [Internet]. 2021;10. Available from: https://doi.org/10.1016/j.dental.2021.01.007

6.2.2 Ag - Zn-PBG (NANOPARTICULAS METALICAS)

L. Natale et al. en 2017 estudiaron la posibilidad de fabricar nanoparticulas metálicas de plata (Ag^0) a partir de fosfato de plata sometido a radiaciones UV-Vis (<530nm), con el objetivo de formar partículas híbridas de calcio fosfato/fosfato de plata que tuviesen la posibilidad de ser un relleno antibacteriano y remineralizador por los composites de resina. Se fabricaron entonces partículas híbridas de fosfatos y se incorporaron en porcentajes del 20—30% en unas resinas de dimetacrilato para investigar su efecto remineralizador y antibacteriano. Se hicieron tres grupos según el tipo de relleno: CaP 20-30%, CaP/Ag 20-30%, Filtek Z250 Unfilled resin. La formación de nanoparticulas metálicas de plata en las resinas adicionadas con CaP y Cap/Ag (después de haber expuesto las resinas a radiaciones visibles a través de una lámpara de polimerización con una emisión máxima de 470nm), se acreditó gracias al análisis de la superficie fracturada del composite con un microscopio SEM. La liberación de calcio y fosfato de los materiales que contenían las partículas mezcladas fue similar a las que contenían partículas de CaP puro, mientras que las colonias de Streptococcus mutans se redujeron en tres órdenes de magnitud en relación con el control, lo que puede atribuirse a la liberación de plata. A nivel estético, las propiedades ópticas de los materiales que contenían partículas mixtas de fosfato se vieron comprometidas por la presencia de plata (39).

X. Chatzistavrou et al. hicieron un estudio in vitro sobre los efectos de vidrio bio-activo derivado de sol-gel dopado con Ag, con el objetivo de conseguir un material antimicrobiano y bioactivo para evitar el desarrollo de bacterias, y que tuviese un enlace estricto con los tejidos alrededor de el. El vidrio bioactivo fue incorporado dentro de unas resinas de composites con concentraciones de 5,10 y 15% de peso, de manera que los nuevos composites dopados con Ag (Ag-BCOMP) pudiesen tener efectos antibacterianos y bíoactivos. Se observaron las propiedades microestructurales con microscopio SEM, y el análisis elemental del Ag-

BGCOMP desarrollado. La fuerza de unión total (TBS) se midió inmediatamente y después de 7 y 14 días de inmersión en el medio usando una prueba de microtensión. Se evaluó la capacidad de los Ag-BGCOMP para formar una capa de apatita en su superficie después de la inmersión en fluido corporal simulado (SBF), así como la inhibición del crecimiento de bacterias en un biofilm formado por Streptococcus mutans. Se observó una distribución microestructural homogénea de partículas de Ag-BG en el compuesto de resina para todos los Ag-BGCOMP. Las mediciones de TBS mostraron una diferencia no estadísticamente significativa entre las muestras de control (Ag-BG 0% en peso) y las muestras de Ag-BGCOMP. Además, la fuerza de unión total entre el tejido dental circundante y el material de restauración no presentó ningún cambio estadísticamente significativo para todos los casos, incluso después de 3 meses de inmersión en el medio. La bio-actividad de los Ag-BGCOMP también se demostró por la formación de una capa de fosfato de calcio en la superficie de las muestras después de la inmersión en SBF. Se vio actividad antibacteriana para todos los Ag-BGCOMP, con diferencias estadísticamente significativas entre las muestras de control y los Ag-BGCOMP. De acuerdo con esto, se encontró que el número de bacterias muertas en la biopelícula aumentaba significativamente con el aumento de la concentración de Ag-BG en los Ag-BGCOMP (Imagen 11) [40].

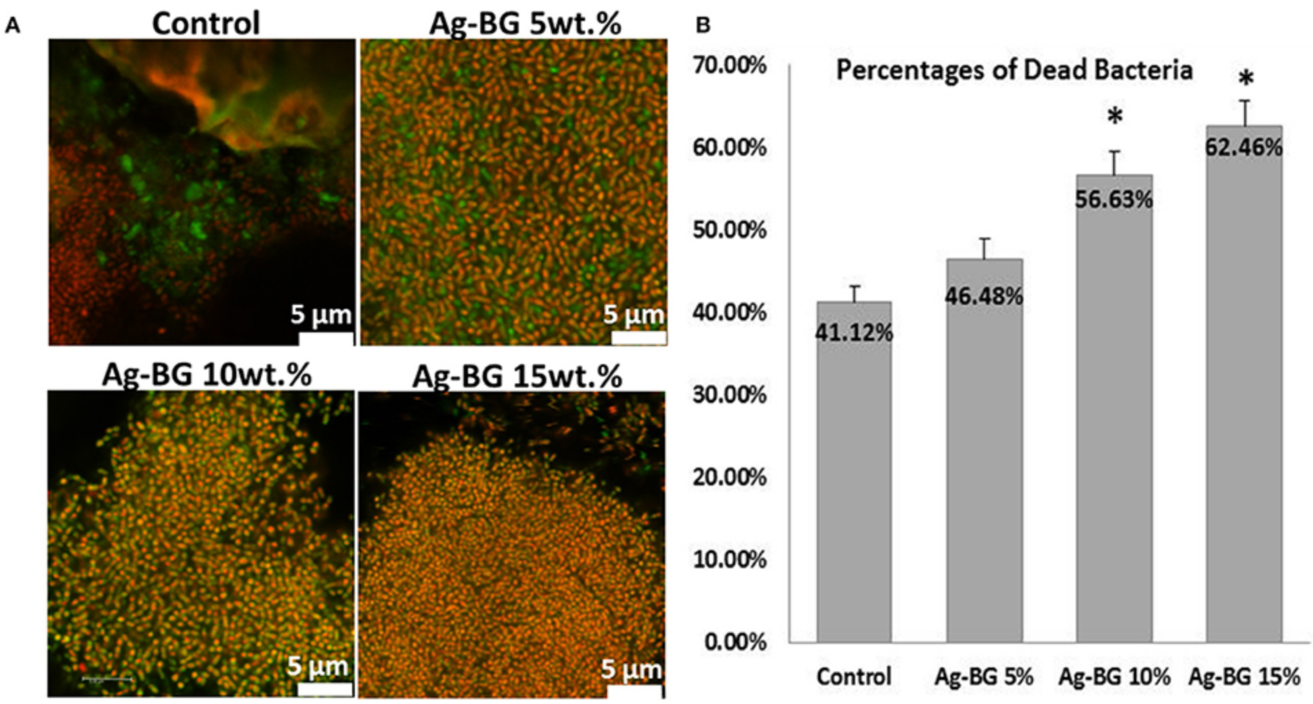

*Imagen 9. Chatzistavrou et al. Imágenes representativas al CLSM de las bacterias vivas y muertas en las biopelículas formadas en la superficie de las muestras de Ag-BGCOMP con diferentes concentraciones en Ag-BG (A). Resultados del análisis cuantitativo de las imágenes que muestran el porcentaje de bacterias muertas en el biofilm para cada grupo (B). * muestra la diferencia estadísticamente significativa entre los grupos. Chatzistavrou X, Lefkelidou A, Papadopoulou L, Pavlidou E, Paraskevopoulos KM, Christopher Fenno J, et al. Bactericidal and bioactive dental composites. Front Physiol. 2018;9(FEB):9*

M. Lee et al, hicieron un estudio sobre la actividad antibacteriana frente a Streptococcus mutans (S. mutans) de una resina fluida dopada con un vidrio a base de fosfato dopado con zinc (Zn-PBG) para averiguar el efecto preventivo hacia la caries secundaria. Los composites se prepararon con 0 (control), 1,9, 3,8 y 5,4% en peso de Zn-PBG. Fueron evaluados la resistencia a la flexión, el módulo elástico, la microdureza, la profundidad de curado, la liberación de iones, el tamaño de la zona de inhibición y el número de unidades formadoras de colonias y se analizaron utilizando ANOVA. La resistencia a la flexión del control fue significativamente mayor que la de las muestras de Zn-PBG ($p < 0{,}05$), aunque todas las muestras cumplían con la Norma Internacional ISO 4049. La microdureza no fue significativamente diferente para el grupo de control y los grupos de 1,9 y 3,8% en peso, pero el grupo de Zn-PBG con 5,4% en peso tuvo una microdureza significativamente menor ($p < 0{,}05$). Además, las resinas compuestas liberaron cada vez más iones P, Ca, Na y Zn con un aumento en el contenido de Zn-PBG ($p < 0,05$). Despues de haber sometido las resinas a un recuento de unidades formadoras de colonias, se vio una reducción significativa en la viabilidad de S. mutans ($p < 0,05$) con un aumento en el contenido de Zn-PBG [41].

7 CONCLUSIONES

1. Se propone una clasificación de los materiales inteligentes en odontología restauradora basada en los objetivos intrínsecos de los materiales, siendo estos divididos en composites remineralizadores y antibacterianos, y composites universales.

   Dentro del grupo de composites universales, los materiales se pueden dividir en dos grupos según las propiedades estéticas:

   - **composites One-Shade**

   - **composites Group-Shade**

   Dentro del grupo de composites con efecto remineralizador y antibacteriano, se pueden dividir por la naturaleza de las partículas de relleno, siendo estas divididas en dos grupos:

   Partículas remineralizadoras:

   NACP-DMAHDM

   NACP-CHX

   nCaF2-DMAHDM-MPC

   Partículas metálicas:

   -Ag-BCOMP

   -Zn-PBG

2. Dentro de las limitaciones del estudio, se vio que los composites universales hoy en día permiten un utilizo en sectores posteriores como en sectores anteriores, simplificando la practica diaria, lo que significa emparejar el color del composite con el color del diente de manera simplificada, obteniendo resultados estéticos con mas facilidad por parte del profesional. Proporcionan óptimas propiedades mecánicas, con un resultado estético satisfaciente, que sin perjuicio puede depender del espesor de la restauración, del tipo de

preparación y del substrato dentario. También se revelan eficaces a la hora de tener que hacer un blanqueamiento dental, pudiendo cambiar su color al mismo tiempo que el diente blanqueado y hasta aumentando su emparejamiento a medida que se aclara el tono del diente. Los composites con efecto remineralizador y antibacteriano pueden aumentar la duración en el tiempo de restauraciones directas, además de evitar caries secundarias en coronas y raíces, lo que seria muy útil en reconstrucciones directas realizadas sobre pacientes susceptibles a caries o pacientes ancianos.

Se considera imprescindible la realización de pruebas *in vivo* de larga duración y con muchos especímenes para poder confirmar los resultados in vitro por todos los materiales.

3. Los composites universales tienen un efecto mimético que puede armonizarse con tonos de la guia VITA desde A1 a D3, disminuyendo el numero de composites usados dentro de una misma reconstrucción y facilitando la elección del composite a la hora de reconstruir un diente. Sin embargo, tienen valores de emparejamiento con el color del entorno generalmente mas bajos que los composites *multishape*. Según algunos autores serían menos recomendables por sectores anteriores, aunque algunos estudios que hemos analizado en esta revisión de la literatura, presentaban casos clínicos de sectores anteriores con estéticas satisfacientes y análisis in vitro con resultados igualmente buenos. Sin duda se recomienda hacer mas estudios clínicos en vivo de sectores anteriores, para tener datos ciertos. Otro aspecto positivo de los composites universales es el cambio de color que se ha visto en los dos estudios que trataban de blanqueamientos, dentro de los cuales se nota que no solo cambian color al mismo tiempo que el diente blanqueado, sino que se emparejan mejor al aclararse del color. Los composites con efecto remineralizador mejoran de manera impresionante la potencial duración de las restauraciones, proporcionando mas dureza de esmalte, evitando la colonización de bacterias cariogénicas y disminuyendo significativamente la caries recurrentes y marginales. En el caso

de los composites adicionados con nanoparticulas remineralizadas (NACP-DMAHDM) las propiedades mecánicas de los composites no son alteradas, siendo además capaces de tener una recarga de iones a largo plazo, lo que proporciona efecto de larga duración. Los composites adicionados con Zn-PBG, tienen como desventaja el hecho de proporcionar unas calidades mecánicas menores que las de los composites tradicionales. Los composites adicionados con Ag-BGCOMP, tienen una dureza similar a la de los composites tradicionales, aunque ligeramente menor, pero dan como desventaja en algunos estudios la alteración de color del composite.

8 RESPONSABILIDAD

El trabajo cumple con las responsabilidades sociales de sostenibilidad económica y medioambiental, en cuanto se encuentran unas mejoras objetivas en la estética y en la prestación clínica de los materiales restauradores, además de una mejora de la calidad de vita de los pacientes a la hora de utilizarlos.

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Review Article

Biosmart Materials: Breaking New Ground in Dentistry

Vijetha Badami and Bharat Ahuja

Department of Conservative Dentistry and Endodontics, A.M.E'S Dental College, Hospital and Research centre, Bijengere Road, Raichur 584103, India

Correspondence should be addressed to Vijetha Badami; vijetha.mds@gmail.com

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By definition and general agreement, smart materials are materials that have properties which may be altered in a controlled fashion by stimuli, such as stress, temperature, moisture, pH, and electric or magnetic fields. There are numerous types of smart materials, some of which are already common. Examples include piezoelectric materials, which produce a voltage when stress is applied or vice versa, shape memory alloys or shape memory polymers which are thermoresponsive, and pH sensitive polymers which swell or shrink as a response to change in pH. Thus, smart materials respond to stimuli by altering one or more of their properties. Smart behaviour occurs when a material can sense some stimulus from its environment and react to it in a useful, reliable, reproducible, and usually reversible manner. These properties have a beneficial application in various fields including dentistry. Shape memory alloys, zirconia, and smartseal are examples of materials exhibiting a smart behavior in dentistry. There is a strong trend in material science to develop and apply these intelligent materials. These materials would potentially allow new and groundbreaking dental therapies with a significantly enhanced clinical outcome of treatments.

1. Introduction

Materials science is not what it used to be. Traditionally materials used in dentistry were designed to be passive and inert, that is, to exhibit little or no interaction with body tissues and fluids. Materials used in the oral cavity were often judged on their ability to survive without interacting with the oral environment.

The present scenario has changed. Many of the advanced materials at the forefront of materials science are functional: they are required to perform things and to undergo purposeful change. They play an active part in the way the structure or device works.

Perhaps the first inclination that an "active" rather than "passive" material could be attractive in dentistry was the realisation of the benefit of fluoride release from materials. This both reflects and permits a change in material philosophy. The same is true in many other areas of engineering, such as aerospace, automotive engineering, biomedicine, and robotics.

Materials used in dentistry can be classified as bioinert (passive), bioactive, and bioresponsive or smart materials based on their interactions with the environment.

Smart materials can be defined as designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, and electric or magnetic fields [1]. These materials are also referred to as responsive materials.

Smart materials have been around for many years and they have found a large number of applications. The use of the terms "smart" and "intelligent" to describe materials and systems came from the USA and started in the 1980s despite the fact that some of these so-called smart materials had been around for decades. Early smart material applications started with magnetostrictive technologies. This involved the use of nickel as a sonar source during World War I to find German U-boats by Allied forces.

Smart behaviour occurs when a material can sense some stimulus from its environment and react to it in a useful, reliable, reproducible, and usually reversible manner. A really

From vulcanite to vinyl, a history of resins in restorative dentistry

Frederick A. Rueggeberg, DDS, MS[a]
School of Dentistry, The Medical College of Georgia, Augusta, Ga.

This article provides historical background on the development of resin-based dental restorative materials. With an understanding of the evolution of these materials, clinicians can better appreciate both the complexity of and similarities among the wide variety of resins and polymerization techniques available today. Common problems associated with the use of resin-based materials are explained, and more advanced resin-based systems currently under development are briefly reviewed. (J Prosthet Dent 2002;87:364-79.)

The purpose of this article is to provide historical background on factors of interest and importance in the development of resin-based dental restorative materials. With an understanding of their evolution, the clinician can better appreciate both the complexity of and similarities among the wide variety of resins and polymerization techniques available today. An appreciation for more advanced resin-based systems currently under development, but yet to become commercially available, also may be gained.

Dental clinicians are always looking for the ideal restorative material. This material should be tooth-colored, long-lasting, and strong; it should adhere to tooth structure; and it should be able to be made directly within the preparation site: a direct, esthetic restorative material. The latter 2 factors may be the most desirable. Of all types of restorative materials, the polymeric classification best fulfills these requirements, as neither metals nor ceramics have successfully been able to be fabricated or placed in such a manner.

History indicates that use of new types of materials for restorative purposes has often shortly followed the development and introduction of new technology and methods to the scientific world. The dental community, in its search for better, less expensive, easier-to-handle materials, is often quick to adapt a rising technology for new and different purposes.

The use of resin-based restorative materials in dentistry has risen exponentially. Hardly a single clinical procedure is accomplished without use of one or more of these products, which include sealants, dentin bonding agents, restorative composites, fiber-reinforced resin materials, cementing and lining agents, denture base materials, denture teeth, denture liners, maxillofacial prosthetic products, core buildup materials, orthodontic appliances, splinting materials, temporary restorative materials, and veneers.

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[a]Professor and Director, Section of Dental Materials.

PRIOR TO 1900

Before synthetic polymer systems were developed, many items classified as "plastic" materials were developed from natural resins or exudates and tissues from plants, animals, and insects. It was found that heating these materials would put them in a softened state, permitting them to be molded and shaped prior to their cooling. The first examples of such materials were horns and hoofs of animals.[1] With respect to insect exudates, the most notable are shellac products, which are still in use today.[2] These materials are derived from resins produced by tiny insects (Coccus Lacca) that infest fig trees: literally Shell Lacca, from whence we derive the word "shellac."[3] Early use of the product was as a protective coating and decorative finish for woods and metals. Later, the product was mixed with wood fillers to provide a moldable substance, and bulk products (primarily decorative cases) were produced. As the photography industry grew, the need for inexpensive yet decorative picture frames increased, and shellac was used to fulfill the need. Later, more durable products such as early phonograph discs and 78-rpm records were made by incorporating mineral filler.[4] Even though this material offered ease of shaping with increased temperature, there is no recorded use of shellac for dental purposes.

Gutta-percha

An important and well-known plant exudate used in dentistry is gutta-percha, also known as Corallite. This product is quite similar in structure to natural rubber, differing only by a cis- or trans-relationship (Fig. 1).[5] The difference in configuration between these 2 molecules is slight and relates to how carbon atoms are attached to the unsaturated carbon-to-carbon double bond: either in-line with (cis, natural rubber), or trans (gutta-percha) to the polymer chain. This small difference results in large differences in physical properties. In the bulk state, natural rubber is soft and highly flexible, has a low melting point, and is tacky. Conversely, gutta-percha is tough and hard, has a high melting point, and exhibits little flexibility.[6]

Dr William Montomerie first introduced gutta-per-

History of Science

Hermann Staudinger and the Origin of Macromolecular Chemistry

*Rolf Mülhaupt**

Keywords:
history of science · ketenes · macromolecular chemistry · polymers · Staudinger, Hermann

1. Introduction

On December 10th, 1953 Hermann Staudinger's pioneering research on macromolecules was acknowledged by the award of the Nobel Prize for Chemistry.[1] The headline "High Polymers being High Honors" went all around the world.[2] Staudinger had discovered the molecular blueprints of high molecular weight natural and man-made polymeric materials. His revolutionary concept, involving linking of a large number of small monomer molecules by means of covalent bond formation to form macromolecules, marked the beginning of the new era of molecular design of high molecular weight structural and functional polymeric materials. At the beginning of the 20th century the trial-and-error-type polymer development was aimed primarily at imitating natural polymeric materials such as silk, natural rubber, and ivory. Most early imitations exhibited rather poor product qualities with respect to those of the corresponding natural products. It was Staudinger's molecular blueprint that was applied successfully to design modern high-value-in-use polymers with property profiles unparalleled in nature. Polymeric materials are exceptional with respect to their unique combination of attractive cost/performance ratio, low-energy demand during preparation and processing, flexible supply of feedstocks, attractive ecobalances and ecoefficiency, easy processing with short cycle times typical for the modern industrial mass production, and their extraordinary versatility with respect to their property profiles, application ranges, and recycling of wastes.

No other class of materials is capable of matching similarly diversified property profiles. As a function of their molecular and supermolecular architectures it is possible to render polymers rigid like steel, soft, or rubbery, permeable or impermeable, conducting or insulating, optically transparent or opaque, durable or biodegradable. Typical polymer applications include food packaging, light-weight construction and engineering materials, functional textiles, corrosion-resistant coatings, durable adhesives, agricultural films used to enhance food production, and biomedical applications ranging from artificial teeth and dental fillings to advanced drug-release systems and biocompatible materials for bone, cartilage, and tissue replacement. Since the mid 1970s industrial polymer production increased tenfold and is now rapidly approaching 200 million metric tons per year.[3] In nature the annual production of biopolymers such as carbohydrates is much larger, exceeding 200 billion metric tons per year, and exploits photosynthesis based upon carbon dioxide, water, and solar energy. Today high molecular weight polymer products are integral parts of our daily life and secure high quality of life. Staudinger's visions remain important key issues in modern macromolecular chemistry, materials science, and biotechnology. His concepts continue to provide the solid and still expanding base on which we build new structural and functional polymers in the fields of our modern key technologies.

2. Staudinger's Route to Macromolecular Chemistry

Hermann Staudinger's academic career is exceptional, especially with respect to the outstanding scientific achievements of young Staudinger and his very rapid academic career development. Important stages of his life and his research were highlighted by Hermann Staudinger himself in his "*Arbeitserinnerungen*" (work memoirs).[4] Several authors have published Hermann Staudinger's bibliography and acknowledged his scientific contributions.[5] Hermann Staudinger, born in Worms, Germany on March 23, 1881, started to study botany with Klebs at the University of Halle in 1899. Soon he was attracted by the field of chemistry in the laboratory of Volhard and decided to shift his academic focus to chemical research. After studying chemistry in Darmstadt and Munich, he got his PhD degree in 1903 in Halle, only four years after his enrolment at the university. His PhD thesis with Vorländer in Halle was concerned with the addition of malonates to unsaturated compounds.[6] In the same year he accepeted an assistant position with J. Thiele at the University of Strasbourg. During his research in Thiele's laboratory, which was aimed at exploring the conversion reactions of carboxylic acids into the corresponding aldehydes, Staudinger discovered the ketenes as a new class of chemical substances in 1905. When he treated diphenylchloroacetyl chloride with zinc,

[*] Prof. Dr. R. Mülhaupt
Institut für Makromolekulare Chemie
Albert-Ludwig-Universität Freiburg
Stefan-Meier-Strasse 31
79104 Freiburg (Germany)
Fax: (+49) 761-203-6319
E-mail: rolf.muelhaupt@makro.uni-freiburg.de

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AN INTERNATIONAL HISTORIC
CHEMICAL LANDMARK

The Establishment of Modern Polymer Science By Wallace H. Carothers

WILMINGTON, DELAWARE
NOVEMBER 17, 2000

AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Communications

History of resins in dentistry.

Peyton FA

Dental Clinics of North America, 01 Apr 1975, 19(2):211-222
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Abstract

The period of 175 years from 1800 to 1975 represents one of significant advancement in prosthetic and restorative dental service. The transition from the time of ill-fitting dentures, fashioned from naturally occurring materials, to the application of synthetic resins for a long list of dental and surgical purposes described in this symposium represents a typical example of technical and professional advancement that has taken place throughout the world society during this same period. As noted in the beginning of this report, the advancement in dentistry has been possible through the cooperative efforts of contemporary scientists in many related fields. If denistry retains this good working relationship, as it is expected to do, then the advancements within the next two generations can significantly change and improve the practice of dentistry from what is presently known, by the application of additional new and modified dental resins.

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Review

Resin composites in dentistry: the monomer systems

Anne Peutzfeldt

Department of Dental Materials, School of Dentistry, Faculty of Health Sciences, University of Copenhagen, Denmark

Peutzfeldt A: Resin composites in dentistry: the monomer systems. Eur J Oral Sci 1997; 105: 97–116. © Munksgaard 1997

The present review outlines the history of monomers used in resin composites, motivates further development, and highlights recent and ongoing research reported in the field of dental monomer systems. The monomer systems of most present-day resin composites are based on BisGMA, developed some 40 years ago, or derivatives of BisGMA. In the remaining resin composites, urethane monomers or oligomers are used as the basis of the monomer system. The main deficiencies of current resin composites are polymerization shrinkage and insufficient wear resistance under high masticatory forces. Both factors are highly influenced by the monomer system, and considerable efforts are being made around the world to reduce or eliminate these undesirable properties. The use of fluoride-releasing monomer systems, some of which are under investigation, has been suggested to mitigate the negative effects of marginal gaps formed in consequence of polymerization shrinkage. The very crux of the problem has also been approached with the synthesis of potentially low-shrinking/non-shrinking resin composites involving ring opening or cyclopolymerizable monomers. By the use of additives with a supposed chain transfer agent function, monomer systems have been formulated that improve the degree of conversion of methacrylate double bonds and mechanical properties. Many promising monomer systems have been devised, the implementation of which may be expected to improve the longevity of resin composite fillings and expand the indications for resin composites.

Anne Peutzfeldt, Department of Dental Materials, School of Dentistry, Nørre Allé 20, DK-2200 Copenhagen N, Denmark

Telefax: +45-35326505
E-mail: apz@odont.ku.dk

Key words: dental materials; polymers; restorative resins

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Dental resin composites were introduced commercially in the mid-1960s for the restoration of anterior teeth (1, 2). Since their advent, resin composites have undergone significant development, which continues to improve the longevity of resin composite restorations. However, despite vast improvements which have expanded indications for their use, present-day resin composites still have shortcomings limiting their application. Inadequate resistance to wear (loss of anatomic form) under masticatory attrition, and marginal leakage due to polymerization shrinkage are often cited as being the main problems of resin composites. These disadvantages warrant a conservative approach to class I and II cavities and constitute the major hindrance for acceptance of resin composite restorations as a viable alternative to amalgam (3, 4).

A composite material has been defined as a "three-dimensional combination of at least two chemically different materials with a distinct interface separating the components" (5). Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin matrix, and generally encompass three main components: (1) the resin matrix comprising: (i) a monomer system, (ii) an initiator system for free radical polymerization, and (iii) stabilizers for maximizing the storage stability of the uncured resin composite and the chemical stability of the cured resin composite; (2) the inorganic filler consisting of particulates such as glass, quartz, and/or fused silica; and (3) the coupling agent, usually an organo-silane, that chemically bonds the reinforcing filler to the resin matrix.

Obviously, the properties and hence the performance of resin composites are dependent upon the three basic components of the material. Some of the properties are mainly related to the filler and the coupling agent, whereas other properties mainly stem from the resin matrix. The first group of


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A SIMPLE METHOD OF INCREASING THE ADHESION OF ACRYLIC FILLING MATERIALS TO ENAMEL SURFACES

MICHAEL G. BUONOCORE, D.M.D., M.S.

Eastman Dental Dispensary, Rochester, N. Y.

ONE of the major shortcomings of the acrylics and other filling materials is their lack of adhesion to tooth structure.[1-4] A filling material capable of forming strong bonds to tooth structures would offer many advantages over present ones. With such a material, there would be no need for retention and resistance form in cavity preparation, and effective sealing of pits, fissures, and beginning carious lesions could be realized.

In our attempts to obtain bonding between filling materials and tooth structure, several possibilities are being explored. These include (1) the development of new resin materials which have adhesive properties; (2) modification of present materials to make them adhesive; (3) the use of coatings as adhesive interface materials between filling and tooth; and (4) the alteration of the tooth surface by chemical treatment to produce a new surface to which present materials might adhere.

This last approach is the subject of this paper, but since it concerns itself only with treatment of intact enamel surfaces, it has only limited application to the broader problems of restorative dentistry.

In industry, phosphoric acid and preparations containing it have been used to treat metal surfaces to obtain better adhesion of paint and resin coatings.[5] Although the increased adhesion is believed to be due primarily to the removal of surface and other contaminants, the conversion of the oxides or the surface of the metal itself to phosphates or the adsorption of phosphate groups on the metal surface may contribute to the effect. Since the enamel surface has probably reacted with various ions, saliva, and so on, to which it has been exposed for long periods of time, and its tiny imperfections filled in by a variety of adventitious materials, the composition of the superficial surface may be quite different than the underlying enamel.[6] As a result, any receptivity to adhesion which the original tooth structure may have had for acrylic materials may have been lost. It was felt that perhaps an acid treatment of the enamel surface might render it more receptive to adhesion in the same manner as it does for metals.

EXPERIMENTAL

Two methods were used for treating the enamel surfaces. The first involved the use of a 50 per cent dilution of a commercial phosphomolybdate

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ARTICLE 2

THE SCIENCE OF BONDING: FROM FIRST TO SIXTH GENERATION

GERARD KUGEL, D.M.D., M.S.; MARCO FERRARI, M.D., D.D.S., PH.D.

A B S T R A C T

Background. Adhesive dentistry has revolutionized restorative dental practice during the past 30 years. Improved adhesive materials have made resin-based composite restorations more reliable and long-standing.

Clinical Implications. This article reviews the evolution of bonding from the first generation to current bonding materials. It discusses the composition and effectiveness of the various iterations. Current products are highlighted to improve clinical use and performance of the materials.

As we enter the new millennium, it is important for us to examine the past. The principles of adhesive dentistry date back to 1955 when Buonocore, using techniques of industrial bonding, postulated that acids could be used as a surface treatment before application of the resins.[1] He subsequently found that etching enamel with phosphoric acid increased the duration of adhesion under water. In 1963, Buonocore demonstrated his insight into adhesion dentistry when he discussed the difference in bonding to enamel and to dentin,[2] particularly when he referred to Dr. Bowen's attempts to investigate substances that will displace water from tooth surfaces[3] with the idea that they could be used as pretreatment for enamel or dentin. Buonocore then stated that they could even be incorporated into the adhesives.[3]

In the late 1960s, Buonocore suggested that it was the formation of resin tags that caused the principal adhesion of the resins to acid-etched enamel.[4] The idea that resin penetrates the microporosities of etched enamel and results in a micromechanical bond is well-accepted today.

As time went on, variations in duration of the acid-etching procedure and concentration of the phosphoric acid, along with alternative acids, were tested for the etching of enamel.[5-7] The current thinking is that a 30 to 40 percent phosphoric acid etch of 15 seconds is acceptable.

The ability to bond reliably to enamel is now well-accepted, but as Buonocore suggested in 1963, adhesion of our restorative materials to dentin has proved to be more elusive.[3]

Early attempts to bond to dentin resulted in poor bond strengths.[6] This is not surprising given the fact that while enamel contains little protein, dentin is 17 percent collagen by volume. This collagen is inaccessible due to surrounding hydroxyapatite crystals.[9] The dentinal tubules are the only pores available for micromechanical retention. These tubules contain fluid, which would be an impediment to bonding. The number of tubules available for bond also varies depending on location, with deep dentin having more tubules than superficial dentin.[8] Other factors such as age of teeth, direction of tubules and of enamel prisms, presence of cementum and type of dentin can affect dentin bonding.[10,11]

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State of the art etch-and-rinse adhesives

David H Pashley, DMD, PhD[*,1], **Franklin R Tay, BDSc, PhD**[2], **Lorenzo Breschi, DDS, PhD**[3], **Leo Tjäderhane, DDS, PhD**[4], **Ricardo M Carvalho, DDS, PhD**[5], **Marcela Carrilho, DDS, PhD**[6], and **Arzu Tezvergil-Mutluay, DDS, PhD**[7]

[1]Department of Oral Biology, Medical College of Georgia, School of Dentistry, Augusta, GA, USA [2]Department of Endodontics, Medical College of Georgia, School of Dentistry, Augusta, GA, USA [3]Department of Biomedicine, University of Trieste, Trieste, Italy and IGM-CNR, Unit of Bologna c/o IOR, Bologna, Italy [4]Institute of Dentistry, University of Oulu and Oulu University Hospital, Oulu, Finland [5]Department of Prosthodontics, Bauru School of Dentistry, University of São Paulo, Bauru, Brazil [6]GEO/UNIBAN, Health Institute, Bandeirante University of São Paulo, São Paulo, Brazil and Piracicaba Dental School, State University of Campinas, Piracicaba, Brazil [7]Department of Prosthetic Dentistry, Institute of Dentistry, University of Turku, Turku, Finland

Abstract

Etch-and-rinse adhesive systems are the oldest of the multi-generation evolution of resin bonding systems. In the 3-step version, they involve acid-etching, priming and application of a separate adhesive. Each step can accomplish multiple goals. This review explores the therapeutic opportunities of each separate step. Acid-etching, using 32-37% phosphoric acid (pH 0.1-0.4) not only simultaneously etches enamel and dentin, but the low pH kills many residual bacteria. Some etchants include anti-microbial compounds such as benzalkonium chloride that also inhibits matrix metalloproteinases (MMPs) in dentin. Primers are usually water and HEMA-rich solutions that ensure complete expansion of the collagen fibril meshwork and wet the collagen with hydrophilic monomers. However, water alone can re-expand dried dentin and can also serve as a vehicle for protease inhibitors or protein cross-linking agents that may increase the durability of resin-dentin bonds. In the future, ethanol or other water-free solvents may serve as dehydrating primers that may also contain antibacterial quaternary ammonium methacrylates to inhibit dentin MMPs and increase the durability of resin-dentin bonds. The complete evaporation of solvents is nearly impossible. Manufacturers may need to optimize solvent concentrations. Solvent-free adhesives can seal resin-dentin interfaces with hydrophobic resins that may also contain fluoride and antimicrobial compounds. Etch-and-rinse adhesives produce higher resin-dentin bonds that are more durable than most 1 and 2-step adhesives. Incorporation of protease inhibitors in etchants and/or cross-linking agents in primers may increase the durability of resin-dentin bonds. The therapeutic potential of etch-and-rinse adhesives has yet to be fully exploited.

Keywords

Acid-etchants; Primers; Adhesives; Durability; MMPs

*Corresponding authordpashley@mail.mcg.edu.

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Review

Advances in Nanotechnology for Restorative Dentistry

Zohaib Khurshid [1,†], Muhammad Zafar [2,†,*], Saad Qasim [3,†], Sana Shahab [4,†], Mustafa Naseem [5,†] and Ammar AbuReqaiba [6,†]

1. School of Materials and Metallurgy, University of Birmingham, Birmingham B15 2TT, UK; E-Mail: ZXK338@bham.ac.uk
2. Department of Restorative Dentistry, College of Dentistry, Taibah University, Al-Madina Al-Munawara 41311, Saudi Arabia
3. Materials Science and Engineering Department, Kroto Research Institute, University of Sheffield, Sheffield S3 7HQ, UK; E-Mail: s.qasim@sheffield.ac.uk
4. Department of Dental Materials Science, Sir Syed College of Medical Sciences for Girls, Karachi 75500, Pakistan; E-Mail: drsanashahab@gmail.com
5. Department of Community and Preventive Dentistry, School of Dentistry, Ziauddin University, Karachi 75600, Pakistan; E-Mail: mustafanasim@hotmail.com
6. ISF Medical Unit, Qatar and Dental Materials Science, Faculty of Dentistry, the University of Hong Kong, Hong Kong, China; E-Mail: aabureqaiba@isf.gov.qa

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: MZAFAR@taibahu.edu.sa; Tel.: +966-507-544-691.

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Abstract: Rationalizing has become a new trend in the world of science and technology. Nanotechnology has ascended to become one of the most favorable technologies, and one which will change the application of materials in different fields. The quality of dental biomaterials has been improved by the emergence of nanotechnology. This technology manufactures materials with much better properties or by improving the properties of existing materials. The science of nanotechnology has become the most popular area of research, currently covering a broad range of applications in dentistry. This review describes the basic concept of nanomaterials, recent innovations in nanomaterials and their applications in restorative dentistry. Advances in nanotechnologies are paving the future of

Nanocomposites: Past, present, and future of dentistry

11

Aarati Panchbhai
Sharad Pawar Dental College & Hospital, DMIMSDU, Wardha, Maharashtra, India

The recent advent of nanotechnology has enabled manipulation of the conventional dental composites at a nanoscale level, resulting in newer and advanced materials called nanocomposites. Thanks to their light weight, efficient mechanical properties, and light-conducting properties, nanocomposites can be used in many ways.

Restoration is one of the vital specialties of dentistry. In spite of improvements in materials used for restorative dentistry, there is no material that is ideal for this dental application. The conventionally used silver amalgam comes with issues of toxicity and poor esthetics. The conventional composite restorative materials have better esthetics, but lack adequate strength; hence, they cannot be used in posterior areas of dentition, and are highly technique-sensitive. In addition, there are issues of wear resistance, polymerization shrinkage, and microhardness, which are essential in posterior occlusal restorations. Hence, there is a need for dental materials with properties that are better suited for restorative dentistry.

Conventional dental composite resins, due to their superior esthetics and shade-matching properties, have been widely used as the material of choice for restoring anterior teeth. However, their application in the posterior stress-bearing areas has remained questionable due to the lack of adequate physical and mechanical properties. In these composites, the resin matrix is reinforced with nanosized filler particles, resulting in significantly improved mechanical properties. The resultant improvement in physical properties, coupled with superior esthetics, has made nanocomposites the material of choice in anterior, as well as posterior, class I and II restorations.

The emergence of nanocomposites has enabled the use of a single restorative material, universally, in various areas of the oral cavity, as these composite materials possess not only favorable esthetic properties, such as high initial polish and polish retention, but also excellent mechanical properties and improved handling characteristics.

11.1 Development of composites

Conventional dental resin-based composites (RBC) were plagued by the issues of shrinkage, viscosity, moisture contamination, and changes with aging. The composition largely included the two polymers triethylene glycol di-methacrylate (TEGDMA) and 2, 2′-bis glycol methacrylate (Bis-GMA). Later, the Bis-GMA was replaced with other dimethacrylates to overcome the issues associated with conventional compositions.

In the development of the composites, the three main components, which can be modified, are the inorganic fillers, the organic resin matrix, and the silane coupling agents. For increasing the mineral content of the tooth, calcium and phosphate

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REVIEW ARTICLE

Dental Biomaterials

Nanotechnology applications in medicine and dentistry

Jyoti Gupta

Department of Periodontics, Dr H.S.J. Institute of Dental Sciences and Research, Chandigarh, India

Keywords
biomimetic, nanodentistry, nanomedicine, nanoparticle, nanotechnology.

Correspondence
Dr Jyoti Gupta, Department of Periodontics, Dr H.S.J. Institute of Dental Sciences and Research, Sector-25, South Campus, Panjab University, Chandigarh, India.
Tel: +91-98142-53329
Fax: +91-172-2724912
Email: jyoti.guptaa@yahoo.co.in

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Abstract

Nanotechnology, or nanoscience, refers to the research and development of an applied science at the atomic, molecular, or macromolecular levels (i.e. molecular engineering, manufacturing). The prefix "nano" is defined as a unit of measurement in which the characteristic dimension is one billionth of a unit. Although the nanoscale is small in size, its potential is vast. As nanotechnology expands in other fields, clinicians, scientists, and manufacturers are working to discover the uses and advances in biomedical sciences. Applications of nanotechnology in medical and dental fields have only approached the horizon with opportunities and possibilities for the future that can only be limited by our imagination. This paper provides an early glimpse of nanotechnology applications in medicine and dentistry to illustrate their potentially far-reaching impacts on clinical practice. It also narrates the safety issues concerning nanotechnology applications.

Introduction

Nanotechnology is the engineering of molecularly precise structures. The term "nanotechnology" was coined by Professor Kerie E. Drexler, a lecturer and researcher of nanotechnology. The prefix "nano" means 10^{-9} or one billionth of a unit. The nanoscale is approximately 1000 times smaller than a microscale, which is approximately 1/80 000 the diameter of a human hair. These small scientific scales were first revolutionized by Richard Feynman at his famous speech at the Annual Meeting of the American Physical Society in 1959 entitled: "There is plenty of room at the Bottom". He proposed that machines and tools that make smaller machine tools could in turn be used to make even smaller machines and tools, right down to molecular levels.[1] He suggested that such nanomachines, nanorobots, and nanodevices could ultimately be used to develop a wide range of atomically precise microscopic instrumentation and manufacturing tools. In his historical lecture in 1959, he concluded by saying, "This is a development, which I think cannot be avoided".[2]

Nanotechnology in medicine has been recently reviewed (2002–present) from various perspectives relative to the human molecule–tissue interface,[3–5] and has led to the emergence of a new field called nanomedicine. This is the science and technology of diagnosing, treating, and preventing disease and traumatic injury in order to relieve pain and preserve and improve human health through the use of nanoscale-structured materials, biotechnology, and genetic engineering, and eventually, complex molecular machine systems and nanorobots.[6] Once one considers other potential applications of nanotechnology to medicine, it is not difficult to imagine the impact on nanodentistry. The development of nanodentistry will make possible the maintenance of near-perfect oral health through the use of nanomaterials[7] and biotechnology,[8–10] including tissue engineering[11,12] and nanorobotics.

Nanotechnology in medicine

The potential applications of nanotechnology in medicine are vast. These include imaging and diagnostics, targeted drug delivery, nano-enabled therapies, and tissue engineering.

Diagnostics

In nanodiagnostics, the ultimate goal is to identify diseases at the earliest stage possible, ideally at the level of a

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RDE
Restorative Dentistry & Endodontics

Criteria for clinical translucency evaluation of direct esthetic restorative materials

Yong-Keun Lee*

Institute for Clinical Performance of Biomaterials (ICPB) and ETN Dental Clinic, Seoul, Korea

The purpose of this review was to suggest practical criteria for the clinical translucency evaluation of direct esthetic restorative materials, and to review the translucency with these criteria. For the evaluation of reported translucency values, measuring instrument and method, specimen thickness, background color, and illumination should be scrutinized. Translucency parameter (TP) of 15 to 19 could be regarded as the translucency of 1 mm thick human enamel. Visual perceptibility threshold for translucency difference in contrast ratio (ΔCR) of 0.07 could be transformed into ΔTP value of 2. Translucency differences between direct and indirect resin composites were perceivable (ΔTP > 2). Universal and corresponding flowable resin composites did not show perceivable translucency differences in most products. Translucency differed significantly by the product within each shade group, and by the shade group within each product. Translucency of human enamel and perceptibility threshold for translucency difference may be used as criteria for the clinical evaluation of translucency of esthetic restorative materials. (*Restor Dent Endod* 2016;41(3):159-166)

Key words: Esthetics; Evaluation; Restorative material; Translucency

Introduction

Translucency in esthetic restorative materials induces the depth of color in restorations, and also influences the color harmonization with surrounding or adjacent teeth/restorations.[1-3] Optical performance of restorations may be compromised by poor shade blending of opaque restorative materials at the tooth interface.[4] For the measurements of optical properties, the Commission Internationale de I'Eclairage (CIE) color coordinates and the CIE standard illuminants are generally used.[5] For the determination of translucency, two indices such as translucency parameter (TP) and contrast ratio (CR) have been widely used.[6,7] TP is obtained by calculating the color difference of a specimen over two backgrounds: $TP = [(L_W^* - L_B^*)^2 + (a_W^* - a_B^*)^2 + (b_W^* - b_B^*)^2]^{1/2}$, where subscript W refers to the color coordinates over an ideal white background and subscript B refers to those over an ideal black background.[6] CR is calculated from the spectral reflectance (Y) of the specimens over black (Y_b) and white (Y_w) backgrounds to give Y_b/Y_w.[7] Mean CR is calculated as the averaged CR values at each wavelength (10 nm intervals) in the range of 400 to 700 nm.[8,9] Since it has been confirmed that TP and CR values are highly correlated,[8,9] they might be used interchangeably.

Care must be taken when comparing the translucency values based on different studies because technical details for measurements must be matched, or adjustments

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Lee YK
*Correspondence to
Yong-Keun Lee, DDS, PhD.
Director, Institute for Clinical Performance of Biomaterials (ICPB) and ETN Dental Clinic, 106-B101, 27 Heukseokhangang-ro, Dongjak-gu, Seoul, Korea 06981
TEL, +82-2-816-1616; FAX, + 82-2-816-0606; E-mail, ykleedm@gmail.com

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Optical behavior of one-shaded resin-based composites

Cristina Lucena[a], Javier Ruiz-López[b], Rosa Pulgar[a], Alvaro Della Bona[c], María M. Pérez[b,*]

[a] Department of Stomatology, Faculty of Dentistry, Colegio Máximo, University of Granada, Campus de Cartuja s/n, 18071, Granada, Spain

[b] Department of Optics, Faculty of Science, University of Granada, Campus Fuentenueva, Edificio Mecenas, s/n, 18071, Granada, Spain

[c] Post-graduate Program in Dentistry, Dental School, University of Passo Fundo, Brazil

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ABSTRACT

Objective. To evaluate optical properties, and translucency and opalescence parameters of one-shaded resin-based composites.

Methods. Three one-shaded resin composites (OM — Omnichroma; VP — Venus Pearl; and VD — Venus Diamond) and a group-shaded resin composite (FU- Filtek Universal A2) were used. Three composite discs from each material were fabricated for each of the following thickness: 0.5, 1.0 and 2.0 mm. Diffuse reflectance was measured against white and black backgrounds using a calibrated spectroradiometer, CIE D65 illuminant and the CIE 45°/0° geometry. Translucency parameter (TP) was calculated using $\Delta E'_{ab}$ and ΔE_{00}. Scattering (S) and absorption (K) coefficients and transmittance (T%) were calculated using Kubelka-Munk's equations, and a reflection spectrophotometer was used to measure the opalescence parameter (OP). Data was statistically analyzed using Kruskal–Wallis, Mann–Whitney tests, and VAF coefficient.

Results. Spectral distributions of S, K and T were wavelength dependent, showing significant differences between materials of the same thickness and for different thicknesses of the same material ($p < 0.001$). OM showed the greatest translucency values for all thicknesses. Translucency decreased as thickness increased with statistically significant differences ($p < 0.005$). Values of ΔTP_{ab} and ΔTP_{00} between thicknesses were above of translucency thresholds for all materials. VP and VD showed the lowest OP values.

Significance. One-shaded resin-based composites showed different optical behavior than the group-shaded resin-based composite. Understanding the optical behavior of the one-shaded resin-based composites is essential to optimize their clinical performance.

1. Introduction

Resin-based composites are widely used in restorative dentistry. Structural and optical harmonization of the composite restoration within the tooth structure and with the adja-

* Corresponding author.
E-mail address: mmperez@ugr.es (M.M. Pérez).

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RESEARCH ARTICLE

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Analysis of the color matching of universal resin composites in anterior restorations

João Luiz Bittencourt de Abreu DDS, MS[1,2,3] | Camila Sobral Sampaio DDS, MS, PhD[4] | Ernesto Byron Benalcázar Jalkh DDS, MS[2,5] | Ronaldo Hirata DDS, MS, PhD[2]

[1]Analytical Laboratory of Restorative Biomaterials - LABiom-R, Federal Fluminense University, School of Dentistry, Niteroi, Rio de Janeiro, Brazil

[2]Department of Biomaterials and Biomimetics, New York University College of Dentistry, New York, New York

[3]Department of Clinical Dentistry, Federal University of Rio de Janeiro, School of Dentistry, Rio de Janeiro, Rio de Janeiro, Brazil

[4]Department of Biomaterials, School of Dentistry, Universidad de los Andes, Santiago, Chile

[5]Department of Prosthodontics and Periodontology, University of São Paulo - Bauru School of Dentistry, Bauru, São Paulo, Brazil

Correspondence
João Luiz Bittencourt de Abreu, Department of Clinical Dentistry, Federal University of Rio de Janeiro, School of Dentistry, Rua do Catete, 311 Room 309, Catete, Rio de Janeiro 22220-001, RJ, Brazil.
Email: joaolbabreu@gmail.com

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Abstract

Objective: To evaluate color matching of universal composite restorations performed in anterior teeth using two evaluation methods.

Materials and Methods: Sixty class III preparations were made on denture central incisors with different shades (A1-A3) and restored with multishade (Tetric Evoceram, Filtek Universal, and TPH Spectra Universal) and single-shade (Omnichroma) universal composites ($n = 5$). For photographic analysis, a digital photograph of each specimen was taken under standardized set-up. Color measurements were taken in the center of the restoration, and in the tooth surface 1.0 mm adjacent from the tooth/restoration margin. CIELab coordinates were recorded and color difference analysis (ΔE) was made using the CIEDE-2000 formula. For visual analysis, calibrated observers performed visual scoring of color matching and differences were graded as 0:excellent match; 1:very good match; 2:not so good match; 3:obvious mismatch; 4:huge mismatch. All data were statistically analyzed using a linear mixed model analysis with a confidence interval of 95%.

Results: For photographic analysis, Omnichroma showed the highest ΔE compared to the other composites for all shades ($P < .05$), without difference among experimental groups regarding tooth shade. For visual analysis, Omnichroma showed the highest scores ($P < .05$) for all teeth shades, without differences between the other groups. Furthermore, there were no differences between visual scores for different shades of a same resin composite group.

Conclusions: Multishade universal composites presented higher color matching than the single shade universal composite. There were no differences of color matching for different tooth shades for all composites.

Clinical significance: Universal composites with increased color matching may be helpful to simplify anterior restorations, minimizing clinical errors.

KEYWORDS
blending, color, color matching, optical properties, resin composite

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RESEARCH ARTICLE

Color, lightness, chroma, hue, and translucency adjustment potential of resin composites using CIEDE2000 color difference formula

Leticia B. Durand, Associate Professor[1] | Javier Ruiz-López, PhD Student[2] | Bibiana G. Perez, PhD Student[1] | Ana M. Ionescu, Associate Professor[2,4] | Francisco Carrillo-Pérez, PhD Student[3] | Razvan Ghinea, Associate Professor[2,4] | María M. Pérez, Professor[2]

[1]Department of Restorative Dentistry, Federal University of Santa Maria, Santa Maria, Brazil
[2]Department of Optics, Faculty of Science, University of Granada, Granada, Spain
[3]Department of Computer Architecture and Computer Technology, E.T.S.I.I.T, University of Granada, Granada, Spain
[4]Research Associate, Department of Physics, Faculty of Sciences, University of Craiova, Craiova, Romania

Correspondence
Razvan Ghinea, Associate Professor, Department of Optics, Faculty of Science, University of Granada, Campus de Fuentenueva, 18071 Granada, Spain.
Email: rghinea@ugr.es

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Abstract

Objective: To evaluate color, lightness, chroma, hue, and translucency adjustment potential of resin composites using CIEDE2000 color difference formula.

Methods: Three resin composites (Filtek Universal, Harmonize, and Omnichroma) were tested. Two types of specimens were prepared: an outer base shade with an inner hole filled with test shades and single-composite specimens of all shades. Spectrorradiometric reflectances measurements and subsequent CIELAB color coordinates and translucency parameter (TP) were performed. Color (CAP_{00}), lightness, chroma, hue, and translucency (TAP_{00}) adjustment potential using CIEDE2000 color difference were computed. Color and transparency differences among composite materials and shades were statistically tested ($P < 0.05$).

Results: Positive CAP_{00} and TAP_{00} values were found for majority of tested materials. CAP_{00} values ranged from −0.14 to 0.89, with the highest values found for Omnichroma (>0.75 in all cases). TAP_{00} values ranged from −0.06 to 0.86 with significant translucency differences among dual and single specimens. Omnichroma exhibited the highest adjustment potential for all color dimensions studied.

Conclusions: Lightness, hue, chroma, and translucency adjustment potential have been introduced using CIEDE2000 color difference formula, and have shown their usefulness to evaluate blending effect in dentistry. Color coordinates and translucency adjustment potential were dependent on dental material. Omnichroma exhibited the most pronounced blending effect.

Clinical significance: Resin composites with increased color and translucency adjustment may simplify shade selection, making this process easier and less time consuming. Furthermore, these materials might facilitate challenging and complex color matching situations.

KEYWORDS
blending, CIEDE2000, color adjustment potential, resin composite, translucency adjustment potential

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Research Article

Color-Matching and Blending-Effect of Universal Shade Bulk-Fill-Resin-Composite in Resin-Composite-Models and Natural Teeth

Rasha M. Abdelraouf and Nour A. Habib

Faculty of Oral and Dental Medicine, Cairo University, Cairo, Egypt

Correspondence should be addressed to Rasha M. Abdelraouf; rasha.abdelraouf@dentistry.cu.edu.eg

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Objectives. To assess visually color-matching and blending-effect (BE) of a universal shade bulk-fill-resin-composite placed in resin-composite-models with different shades and cavity sizes and in natural teeth (extracted and patients' teeth). *Materials and Methods.* Resin-composite-discs (10 mm × 1 mm) were prepared of universal shade composite and resin-composite of shades: A1, A2, A3, A3.5, and A4. Spectrophotometric-color-measurement was performed to calculate color-difference (ΔE) between the universal shade and shaded-resin-composites discs and determine their translucency-parameter (TP). Visual assessment was performed by seven normal-color-vision-observers to determine the color-matching between the universal shade and each shade, under Illuminant D65. Color-matching visual scoring (VS) values were expressed numerically (1–5): 1: mismatch/totally unacceptable, 2: Poor-Match/hardly acceptable, 3: Good-Match/acceptable, 4: Close-Match/small-difference, and 5: Exact-Match/no-color-difference. Occlusal cavities of different sizes were prepared in teeth-like resin-composite-models with shades A1, A2, A3, A3.5, and A4. The cavities were filled by the universal shade composite. The same scale was used to score color-matching between the fillings and composite-models. BE was calculated as difference in mean-visual-scores in models and that of discs. Extracted teeth with two different class I-cavity sizes as well as ten patients' lower posterior molars with occlusal caries were prepared, filled by universal shade composite, and assessed similarly. *Results.* In models, the universal shade composite showed close matching in the different cavity sizes and surrounding shades ($4 \leq VS < 5$) (BE = 0.6–2.9 in small cavities and 0.5–2.8 in large cavities). In extracted teeth, there was good-to-close color-matching (VS = 3.7–4.4 in small cavities, BE = 2.5–3.2) (VS = 3–3.5, BE = 1.8–2.3 in large cavities). In patients' molars, the universal shade composite showed good-matching (VS = 3–3.3, BE = −0.9–2.1). *Conclusions.* Color-matching of universal shade resin-composite was satisfactory rather than perfect in patients' teeth.

1. Introduction

Blending-effect (BE) of a restorative dental material refers to its ability to acquire a color resembling that of the adjacent structure [1]. Some manufacturers describe their dental products with this blending potential by having a chameleon effect [2].

A main previous research by Paravina et al. [3] investigated the blending-effect of shaded resin-composites related to restoration size. The authors used two main specimens' designs; one was composite ring (shade C2) with a central hole (2, 4, or 6 mm) filled with resin-composite (shades A2 and B2 of two different brands). This combined specimens design resembled teeth cavity walls filled by restorations. The other design was single composite discs from the same materials. Visual assessments were performed using a scale from 1 to 5, where score "1" was total mismatch while score "5" was Exact-Match. Visual scoring (VS) was performed twice; the first assessment was performed for the degree of color-matching between two single resin-composite separate discs: the surrounding shade composite discs (shade C2) versus the restoration shade discs (either shade A2 or B2). Meanwhile, the other assessment was performed for the combined specimens, where VS was performed for the filling (shades A2 and B2) within the composite ring (shade C2) with the different cavity sizes. BE was calculated as the difference

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REVIEW ARTICLE

WILEY

Adhesive dentistry: Current concepts and clinical considerations

Jorge Perdigão DMD, MS, PhD, Professor[1] |
Edson Araujo DDS, MS, PhD, Associate Professor[2] |
Renato Q. Ramos DDS, MS, Graduate Student[3] |
George Gomes DDS, MSD, Private Practice[4] |
Lucas Pizzolotto DDS, MS, Graduate Student[5]

[1]Department of Restorative Sciences, Division of Operative Dentistry, University of Minnesota, Minneapolis, Minnesota, USA
[2]Department of Comprehensive Care, School of Dentistry, Federal University of Santa Catarina, Florianópolis, Santa Catarina, Brazil
[3]Department of Operative Dentistry, School of Dentistry, Federal University of Santa Catarina, Florianópolis, Santa Catarina, Brazil
[4]George Gomes Dental Center, Oeiras, Lisbon, Portugal
[5]Department of Dental Materials, Faculty of Dental Sciences, Federal University of Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil

Correspondence
*Jorge Perdigão, School of Dentistry, University of Minnesota, 515 SE Delaware Street, 8-450 Moos Tower Minneapolis, MN, USA.
Email: perdi001@umn.edu

Abstract

Objectives: To address contemporary concepts in adhesive dental materials with emphasis on the evidence behind their clinical use.

Overview: Adhesive dentistry has undergone major transformations within the last 20 years. New dental adhesives and composite resins have been launched with special focus on their user-friendliness by reducing the number of components and/or clinical steps. The latest examples are universal adhesives and universal composite resins. While clinicians prefer multipurpose materials with shorter application times, the simplification of clinical procedures does not always result in the best clinical outcomes. This review summarizes the current evidence on adhesive restorative materials with focus on universal adhesives and universal composite resins.

Conclusions: (a) Although the clinical behavior of universal adhesives has exceeded expectations, dentists still need to etch enamel to achieve durable restorations; (b) there is no clinical evidence to back some of the popular adjunct techniques used with dental adhesives, including glutaraldehyde-based desensitizers and matrix metalloproteinase inhibitors; and (c) the color adaptation potential of new universal composite resins has simplified their clinical application by combining multiple shades without using different translucencies of the same shade.

Clinical Significance: New adhesive restorative materials are easier to use than their predecessors, while providing excellent clinical outcomes without compromising the esthetic quality of the restorations.

KEYWORDS
dental adhesion, dental bonding, dental materials, universal adhesives, universal composite resins

1 | INTRODUCTION

Establishing durable adhesion to dentin with resin monomer solutions has been an arduous task since the pioneering work of several research teams in the 1950s using the phosphate monomer glycerol phosphoric acid dimethacrylate (GPDM). This monomer, patented by Oskar Hagger in 1951, was included in the composition of Sevitron Cavity Seal (Amalgamated Dental Trade Distribution, Ltd., London, UK).[1-4]

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RESEARCH ARTICLE

WILEY

Evaluation of shade matching of a novel supra-nano filled esthetic resin composite employing structural color using simplified simulated clinical cavities

Fei Chen DDS, MDS[1] | Yu Toida DDS, Ph.D.[1] | Rafiqul Islam BDS, MS.c.[1] | Arefin Alam BDS[1] | Abu Faem Mohammad Almas Chowdhury BDS, DDS, FCPS, Ph.D.[1,2] | Monica Yamauti DDS, MS, Ph.D.[1] | Hidehiko Sano DDS, Ph.D.[1]

[1]Department of Restorative Dentistry, Division of Oral Health Science, Hokkaido University Graduate School of Dental Medicine, Sapporo, Japan

[2]Department of Conservative Dentistry and Endodontics, Sapporo Dental College and Hospital, Dhaka, Bangladesh

Correspondence
Fei Chen, Department of Restorative Dentistry, Division of Oral Health Science, Hokkaido University Graduate School of Dental Medicine, Sapporo, Japan. 060-8586.
Email: chenfei0806@den.hokudai.ac.jp

Abstract

Objective: To evaluate the shade matching ability of a novel supra-nano filled esthetic resin composite employing structural color technology using simplified simulated clinical cavities. Filler morphology and light transmittance characteristics were also evaluated.

Materials and Methods: One-hundred and twenty frames of resin composite were built in A1, A2, A3, and A4 shades to simulate Class I cavities (diameter = 4 mm, height = 2 mm). For each shaded frame, cavities were filled with three different types of filler containing resin composites (n = 10): supra-nano filled (SN filled) resin composite, microhybrid filled (MH filled) resin composite, and clustered-nano filled (CN filled) resin composite. Color parameters were calculated using CIELAB ($\triangle E_{ab}$) and CIEDE2000 ($\triangle E_{00}$). Data were analyzed using one-way analysis of variance (ANOVA), followed by Duncan's test (α = .05). Filler morphology and light transmittance characteristics were measured to explore the role of structural color on shade matching.

Results: $\triangle E_{ab}$ and $\triangle E_{00}$ of SN filled resin composite were significantly lower in A2, A3, and A4 shades ($P < .05$).

Conclusions: The SN filled resin composite showed better shade matching with A2, A3, and A4 shades of resin composite frames compared to MH filled resin composite, and CN filled resin composite.

Clinical Significance: Universal-shade resin composites, which were expected to match nearly all shades, simplify the restorative procedure. Resin composite, which contained spherical supra-nano filler particles, could contribute most to its shade matching by stimulating structural color. Structural color technology may provide additional benefits for shade matching of resin composites.

KEYWORDS
esthetic resin restoration, filler morphology, resin composite, shade matching, structural color

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RESEARCH ARTICLE

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Color match using instrumental and visual methods for single, group, and multi-shade composite resins

Rubinya Sundar Iyer BDS | Vinti Rajendra Babani BDS | Peter Yaman DDS, MS | Joseph Dennison DDS, MS

Department of Cariology, Restorative Sciences and Endodontics, School of Dentistry, University of Michigan, Ann Arbor, Michigan

Correspondence
Joseph Dennison, School of Dentistry, University of Michigan, 1011, N. University, Ann Arbor, MI 48109.
Email: dennison@umich.edu

Abstract

Objective: To evaluate the shade match of three composite resin restorative materials to bi-layered acrylic teeth instrumentally and visually.

Materials and methods: Three composite materials—Omnichroma [OM], Tetric EvoCeram [TE], and TPH Spectra ST [TS] were placed into occlusal preparations (5 mm diameter, 2 mm depth) on 15 bi-layered acrylic teeth per each shade A2, B1, B2, C2, and D3. The composites were placed in a single increment and cured using Bluephase G2 light. The L^*, a^*, and b^* readings were obtained using VITA Easyshade V for the teeth and restorations; mean ΔE_{00} values were calculated and assessed using two-way analysis of variance with a test of simple effects with multiple comparisons for significance ($P < .05$). Three teeth were restored to anatomical form with each of the composites for the five shades and were subjectively graded by 30 evaluators as 1—best match, 2—intermediate, and 3—poorest match.

Results: In the instrumental evaluation, OM and TS showed lower ΔE_{00} values for lighter shades, whereas TE showed lower and similar ΔE_{00} values for all shades. In the visual evaluation, TE exhibited the best shade match for darker shades C2 and D3. OM and TS matched better with lighter shades.

Conclusion: Shade matching is composite and shade-dependent. Overall, TE matched the multiple shades better than the other two materials.

Clinical significance: Single and group shade composites displayed shade matching ability inferior to a multi-shade composite material, which may limit their use in highly esthetic clinical situations.

KEYWORDS
blending, color, composite resin, esthetics, shade match

1 | INTRODUCTION

In the replacement of missing tooth structure, it is a primary objective to restore proper tooth form, function, and esthetics. To ensure an esthetic outcome, an imperceptible match of the color of the restorative material to that of the tooth is of utmost importance. The polychromatic nature of natural teeth makes shade selection more challenging.[1] Composite resins have been developed commercially in multiple enamel and dentin shades of differing translucencies and opacities,[2,3] as measured according to the VITA Classical shade guide. This complicates the shade matching procedure, requires more inventory, and results in an increase in cost and chairside time. "Blending effect" (BE) or "chameleon effect" describes the ability of a material to acquire a color similar to that of its surrounding tooth structure.[4,5] This has enabled the introduction of composite materials with modified optical properties and thus, a reduced number of shades.

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BIOMATERIALS SYNTHESIS AND CHARACTERIZATION

Original Research

Evaluation of degree of conversion, rate of cure, microhardness, depth of cure, and contraction stress of new nanohybrid composites containing pre-polymerized spherical filler

Lidia Fanfoni[1] · Matteo De Biasi[1] · Gabriele Antollovich[1] · Roberto Di Lenarda[1] · Daniele Angerame[1]

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Abstract

The aim of the present study was to characterize nanohybrid and nanofilled composites in terms of degree of conversion (DC), rate of cure (RC), microhardness (Vickers hardness number; VHN), depth of cure, and contraction stress (CS). Ceram.X® universal- A3, duo enamel E2, and duo dentin D3 composites were compared to Tetric EvoCeram® and FiltekTMSupreme XTE composites of equivalent dentin and enamel shades under a 40 s photopolymerization protocol. DC was measured by infrared spectroscopy, calculating RC from the kinetic curve. Top and bottom VHN were determined using a Vickers indenter, and bottom/top surface ratio (Vickers hardness ratio; VHR) calculated. CS vs. time was assessed by a universal testing machine and normalized for the specimen bonding area. All materials showed DC < 60%, Ceram.X® composites reaching higher values than the other composites of corresponding shades. RC at 5 s of photopolymerization was always higher than that at 10 s. All the Ceram.X® composites and the lighter-shaded Tetric EvoCeram® and FiltekTMSupreme XTE composites reached the RC plateau after 25 s, the remaining materials showed a slower kinetic trend. Tetric EvoCeram® and FiltekTMSupreme XTE composites displayed the softest and the hardest surfaces, respectively. Differently from darker-shaded materials, the universal and the three enamel-shaded composites resulted optimally cured (VHR > 80%). The tested composites differed in CS both during and after light cure, Tetric EvoCeram® and FiltekTMSupreme XTE composites displaying the highest and the lowest CS, respectively. Only the Ceram.X® universal-A3 reached a CS plateau value. The tested composites exhibited material-dependent chemo-mechanical properties. Increasing the curing time and/or reducing the composite layer thickness for dentin-shaded composites appears advisable.

Graphical Abstract

1 Introduction

Composite restorative materials represent one of the many successes of modern biomaterials research since they replace biological tissue in both appearance and function. At least half of posterior direct restoration placements now rely on composite materials [1]. Composites consist of three distinct

✉ Daniele Angerame
d.angerame@fmc.units.it

[1] University Clinical Department of Medical, Surgical, and Health Sciences, University of Trieste, Trieste, Italy

The Visual and Spectrophotometric Effect of External Bleaching on OMNiCHROMA Resin Composite and Natural Teeth

Michael Brian Evans
West Virginia University, mevans11@mix.wvu.edu

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ORIGINAL ARTICLE

Effects of quaternary ammonium chain length on the antibacterial and remineralizing effects of a calcium phosphate nanocomposite

Ke Zhang[1,2], Lei Cheng[2,3], Michael D Weir[2], Yu-Xing Bai[1] and Hockin HK Xu[2,4,5]

Composites containing nanoparticles of amorphous calcium phosphate (NACP) remineralize tooth lesions and inhibit caries. A recent study synthesized quaternary ammonium methacrylates (QAMs) with chain lengths (CLs) of 3–18 and determined their effects on a bonding agent. This study aimed to incorporate these QAMs into NACP nanocomposites for the first time to simultaneously endow the material with antibacterial and remineralizing capabilities and to investigate the effects of the CL on the mechanical and biofilm properties. Five QAMs were synthesized: DMAPM (CL3), DMAHM (CL6), DMADDM (CL12), DMAHDM (CL16), and DMAODM (CL18). Each QAM was incorporated into a composite containing 20% NACP and 50% glass fillers. A dental plaque microcosm biofilm model was used to evaluate the antibacterial activity. The flexural strength and elastic modulus of nanocomposites with QAMs matched those of a commercial control composite ($n = 6$; $P > 0.1$). Increasing the CL from 3 to 16 greatly enhanced the antibacterial activity of the NACP nanocomposite ($P < 0.05$); further increasing the CL to 18 decreased the antibacterial potency. The NACP nanocomposite with a CL of 16 exhibited biofilm metabolic activity and acid production that were 10-fold lesser than those of the control composite. The NACP nanocomposite with a CL of 16 produced 2-log decreases in the colony-forming units (CFU) of total microorganisms, total streptococci, and mutans streptococci. In conclusion, QAMs with CLs of 3–18 were synthesized and incorporated into an NACP nanocomposite for the first time to simultaneously endow the material with antibacterial and remineralization capabilities. Increasing the CL reduced the metabolic activity and acid production of biofilms and caused a 2-log decrease in CFU without compromising the mechanical properties. Nanocomposites exhibiting strong anti-biofilm activity, remineralization effects, and mechanical properties are promising materials for tooth restorations that inhibit caries.
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Keywords: antibacterial nanocomposite; calcium phosphate nanoparticles; caries inhibition; human saliva microcosm biofilm; quaternary ammonium chain length

INTRODUCTION

Many recent studies have indicated the worldwide prevalence of dental caries, which is a biofilm-dependent oral disease.[1–2] Due to their aesthetics and direct-filling capability, resin composites along with bonding agents are the principal materials for tooth cavity restorations.[3–8] However, composites tend to accumulate more biofilm than other restorative materials,[9] and secondary caries at the restoration margins promoted by acid production from biofilms is a major cause of composite restoration failure.[10–12] Therefore, the development of composites that can fight biofilms has become increasingly necessary.[13] To this end, quaternary ammonium methacrylates (QAMs) have been developed and incorporated into dental resins that exhibit anti-biofilm activities.[14–21]

Quaternary ammonium materials can cause bacteria lysis by binding to the bacterial membranes.[22] A previous study revealed that hydrophobic, positively charged long polymeric chains can effectively kill bacteria.[23] Furthermore, the alkyl chain length (CL) directly correlated with the hydrophobicity and consequently the ability to penetrate the hydrophobic bacterial membrane.[24] Specifically, these long cationic polymers can penetrate bacterial cells similar to the way a needle can burst a balloon.[24–25] Therefore, the CL of QAMs is important. A recent study synthesized a series of new QAMs with CLs ranging from 3 to 18, incorporated them into a bonding agent, and achieved strong antibacterial efficacy.[26] However, the effects of the CL on the antibacterial efficacy of dental composites have not yet been systematically studied.

[1]Department of Orthodontics, School of Stomatology, Capital Medical University, Beijing, China; [2]Biomaterials & Tissue Engineering Division, Department of Endodontics, Periodontics and Prosthodontics, School of Dentistry, University of Maryland, Baltimore, USA; [3]State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu, China; [4]Center for Stem Cell Biology & Regenerative Medicine, School of Medicine, University of Maryland, Baltimore, USA and [5]Department of Mechanical Engineering, University of Maryland, Baltimore County, USA
Correspondence: Professor HHK Xu, Biomaterials & Tissue Engineering Division, Department of Endodontics, Periodontics and Prosthodontics, Dental School, University of Maryland, Baltimore MD 21201, USA
E-mail: hxu@umaryland.edu
Professor YX Bai, Department of Orthodontics, School of Stomatology, Capital Medical University, Beijing 100050, China
E-mail: byuxing@263.net
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dental materials

In vitro evaluation of composite containing DMAHDM and calcium phosphate nanoparticles on recurrent caries inhibition at bovine enamel-restoration margins

Wen Zhou[a,b,c], *Xian Peng*[a], *Xuedong Zhou*[a], *Michael D. Weir*[b], *Mary Anne S. Melo*[b], *Franklin R. Tay*[d], *Satoshi Imazato*[e], *Thomas W. Oates*[b], *Lei Cheng*[a,b,*], *Hockin H.K. Xu*[b,f,g,*]

[a] *State Key Laboratory of Oral Diseases, Department of Operative Dentistry and Endodontics, West China Hospital of Stomatology, National Clinical Research Centre for Oral Diseases, Sichuan University, Chengdu, 610041, China*
[b] *Department of Advanced Oral Sciences and Therapeutics, University of Maryland Dental School, Baltimore, MD 21201, USA*
[c] *Fujian Key Laboratory of Oral Diseases & Fujian Provincial Engineering Research Center of Oral Biomaterial & Stomatological Key lab of Fujian College and University, School and Hospital of Stomatology, Fujian Medical University, China*
[d] *The Dental College of Georgia, Augusta University, Augusta, GA, USA*
[e] *Department of Biomaterials Science, Osaka University Graduate School of Dentistry, Osaka, Japan*
[f] *Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA*
[g] *Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA*

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ABSTRACT

Objective. Recurrent caries is a primary reason for restoration failure caused by biofilm acids. The objectives of this study were to: (1) develop a novel multifunctional composite with antibacterial function and calcium (Ca) and phosphate (P) ion release, and (2) investigate the effects on enamel demineralization and hardness at the margins under biofilms.

Methods. Dimethylaminohexadecyl methacrylate (DMAHDM) and nanoparticles of amorphous calcium phosphate (NACP) were incorporated into composite. Four groups were tested: (1) Commercial control (Heliomolar), (2) Experimental control (0% DMAHDM + 0% NACP), (3) antibacterial group (3% DMAHDM + 0% NACP), (D) antibacterial and remineralizing group (3% DMAHDM + 30% NACP). Mechanical properties and Ca and P ion release were measured. Colony-forming units (CFU), lactic acid and polysaccharide of *Streptococcus mutans* (*S. mutans*) biofilms were evaluated. Demineralization of bovine enamel with restorations was induced via *S. mutans*, and enamel hardness was measured. Data were analyzed via one-way and two-way analyses of variance and Tukey's multiple comparison tests.

Results. Adding DMAHDM and NACP into composite did not compromise the mechanical properties ($P > 0.05$). Ca and P ion release of 3% DMAHDM + 30% NACP was increased at

* Corresponding author.
E-mail addresses: chenglei@scu.edu.cn (L. Cheng), hxu@umaryland.edu (H.H.K. Xu).
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Novel Nanocomposite Inhibiting Caries at the Enamel Restoration Margins in an In Vitro Saliva-Derived Biofilm Secondary Caries Model

Wen Zhou [1,2,3,†], Xinyu Peng [1,†], Xuedong Zhou [1], Andrea Bonavente [2], Michael D. Weir [2], Mary Anne S. Melo [2], Satoshi Imazato [4], Thomas W. Oates [2], Lei Cheng [1,2,*] and Hockin H. K. Xu [2,5,6,*]

1 State Key Laboratory of Oral Diseases, Department of Operative Dentistry and Endodontics, West China School of Stomatology, National Clinical Research Centre for Oral Diseases, Sichuan University, Chengdu 610041, China; zhouwendentist@139.com (W.Z.); pengxinyu@stu.scu.edu.cn (X.P.); zhouxd@scu.edu.cn (X.Z.)
2 Department of Advanced Oral Sciences and Therapeutics, University of Maryland Dental School, Baltimore, MD 21201, USA; andreamarie899@gmail.com (A.B.); MWeir@umaryland.edu (M.D.W.); MMelo@umaryland.edu (M.A.S.M.); toates@umaryland.edu (T.W.O.)
3 Fujian Key Laboratory of Oral Diseases & Fujian Provincial Engineering Research Center of Oral Biomaterial & Stomatological Key Lab of Fujian College and University, School of Stomatology, Fujian Medical University, Fuzhou 350002, China
4 Department of Biomaterials Science, Osaka University Graduate School of Dentistry, Osaka 565-0871, Japan; imazato@dent.osaka-u.ac.jp
5 Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA
6 Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA
* Correspondence: chenglei@scu.edu.cn (L.C.); hxu@umaryland.edu (H.H.K.X.)
† These authors contributed equally to this work.

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Abstract: Secondary caries often occurs at the tooth-composite margins. This study developed a novel bioactive composite containing DMAHDM (dimethylaminohexadecyl methacrylate) and NACP (nanoparticles of amorphous calcium phosphate), inhibiting caries at the enamel restoration margins in an in vitro saliva-derived biofilm secondary caries model for the first time. Four composites were tested: (1) Heliomolar nanocomposite, (2) 0% DMAHDM + 0% NACP, (3) 3% DMAHDM + 0% NACP, (D) 3% DMAHDM + 30% NACP. Saliva-derived biofilms were tested for antibacterial effects of the composites. Bovine enamel restorations were cultured with biofilms, Ca and P ion release of nanocomposite and enamel hardness at the enamel restoration margins was measured. Incorporation of DMAHDM and NACP into composite did not affect the mechanical properties ($p > 0.05$). The biofilms' CFU (colony-forming units) were reduced by 2 logs via DMAHDM ($p < 0.05$). Ca and P ion release of the nanocomposite was increased at cariogenic low pH. Enamel hardness at the margins for DMAHDM group was 25% higher than control ($p < 0.05$). With DMAHDM + NACP, the enamel hardness was the greatest and about 50% higher than control ($p < 0.05$). Therefore, the novel composite containing DMAHDM and NACP was strongly antibacterial and inhibited enamel demineralization, resulting in enamel hardness at the margins under biofilms that approached the hardness of healthy enamel.

Keywords: secondary caries; remineralization; antibacterial; nanocomposite; saliva-derived biofilms; enamel hardness

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Antibacterial and remineralizing nanocomposite inhibit root caries biofilms and protect root dentin hardness at the margins

Short title: Antibacterial and remineralizing nanocomposite inhibit root caries

Wen Zhou[1,2], Xuedong Zhou[1], Xiaoyu Huang[1,2], Chenyu Zhu[3], Michael D. Weir[2], Mary A. S. Melo[2], Andrea Bonavente[2], Christopher D. Lynch[4], Satoshi Imazato[5], Thomas W. Oates[2], Lei Cheng[1*], Hockin H. K. Xu[2,6,7*]

[1] State Key Laboratory of Oral Diseases & West China Hospital of Stomatology & National Clinical Research Center for Oral Diseases, Sichuan University, Chengdu 610041, China

[2] Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA

[3] School of Traditional Chinese Medicine, Shijiazhuang Medical College, Shijiazhuang 621000, China

[4] Restorative Dentistry, University Dental School and Hospital, University College Cork, Wilton, Cork, Ireland

[5] Department of Biomaterials Science, Osaka University Graduate School of Dentistry, Osaka 565-0871, Japan

[6] Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA

[7] Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA

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Novel antibacterial calcium phosphate nanocomposite with long-term ion recharge and re-release to inhibit caries

Ghalia BHADILA[1-3], Bashayer H. BARAS[1,2,4], Michael D. WEIR[2], Haohao WANG[2,5], Mary Ann S. MELO[6], Gary D. HACK[2], Yuxing BAI[7] and Hockin H. K. XU[2,8,9]

[1] *Biomedical Sciences, Biomaterials and Tissue Engineering Division, University of Maryland School of Dentistry, Baltimore, MD 21201, USA*
[2] *Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA*
[3] *Department of Pediatric Dentistry, Faculty of Dentistry, King AbdulAziz University, Jeddah 21589, Saudi Arabia*
[4] *Department of Restorative Dental Science, College of Dentistry, King Saud University, Riyadh 11451, Saudi Arabia*
[5] *State Key Laboratory of Oral Diseases, National Clinical Research Center for Oral Diseases, West China Hospital of Stomatology, Chengdu 610041, China*
[6] *Division of Operative Dentistry, Department of General Dentistry, University of Maryland School of Dentistry, Baltimore, MD 21201, USA*
[7] *Department of Orthodontics, School of Stomatology, Capital Medical University, Beijing, China*
[8] *Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA*
[9] *Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA*
Corresponding authors, Hockin H. K. XU; E-mail: hxu@umaryland.edu, Yuxing BAI; E-mail: byuxing@263.net

Short-term studies on calcium-phosphate (CaP) ion-rechargeable composites were reported. The long-term rechargeability is important but unknown. The objectives of this study were to investigate nanocomposite with strong antibacterial and ion-recharge capabilities containing dimethylaminododecyl methacrylate (DMAHDM) and nanoparticles of amorphous calcium phosphate (NACP), and evaluate long-term ion-recharge by testing for 12 cycles (taking 6 months to complete) for the first time. Three groups were tested: (1) Heliomolar control; (2) Resin+20%NACP+50%glass; (3) Resin+3%DMAHDM+20%NACP+50%glass. Biofilm acid and colony-forming units (CFU) were measured. Ion-recharge was tested for 12 cycles. NACP-DMAHDM composite reduced biofilm acid, and reduced CFU by 4 logs. High levels of ion releases were maintained throughout 12 cycles of recharge, maintaining steady-state releases without reduction in 6 months ($p>0.1$), representing long-term remineralization potential. Bioactive nanocomposite demonstrated long-term ion-rechargeability for the first time, showed remineralization and potent anti-biofilm functions, with promise for tooth restorations to combat caries.

Keywords: Dental composite, Calcium phosphate nanoparticles, Ion recharge and re-release, Dimethylaminododecyl methacrylate, Dental caries

INTRODUCTION

Resin composites are the most frequently used direct restorative material due to their conservative removal of tooth structure, improved esthetics, and direct-filling capabilities[1,2]. However, composites still present some serious drawbacks, including recurrent caries, restoration fracture, and marginal leakage[3]. Marginal leakage allows for bacterial entry, proliferation, and production of acids, subsequently resulting in recurrent caries. Moreover, composites favor the accumulation of biofilms/plaque[4,5] when compared to other restorative materials[6]. Previous studies have shown that plaque associated with composite restorations tends to favor the adherence of the more cariogenic bacteria, including mutans streptococci and lactobacilli[6]. Composites can accumulate more biofilm leading to tooth structure demineralization and recurrent caries at the tooth-restoration interface, which is 3.5 times more common with composites than with amalgam[7]. Recurrent caries is considered one of the two main reasons to replace an existing restoration[3,8], followed by restoration fracture[9,10]. The replacement of failed dental restorations constitutes approximately 50 to 70% of performed operative dental procedures[8,11], which involves removal of additional tooth structure, resulting in a weaker tooth that is more susceptible to fracture[12].

Therefore, there is a strong need to develop a new generation of bioactive dental composites with antibacterial and remineralization abilities[8,13]. Quaternary ammonium methacrylates (QAMs) were synthesized and incorporated into resins to produce antibacterial effects[14-16]. QAMs are a class of cationic compounds with a broad-spectrum antimicrobial effect[17,18]. The alkyl chain length (CL) of quaternary ammonium compounds has been correlated with their antibacterial effectiveness[19-22]. Recently, dimethylaminohexadecyl methacrylate (DMAHDM) with a CL of 16 was synthesized and shown to have stronger antibacterial properties than QAMs with shorter CLs[20]. DMAHDM has been incorporated into composites and adhesives that showed potent antibacterial properties against a wide range of oral pathogens[20,21,23-26].

Another way to combat dental caries is through the application of remineralizing materials that can release calcium (Ca) and phosphate (P) ions, which constitute

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ORIGINAL RESEARCH REPORT

WILEY

Low-shrinkage-stress nanocomposite: An insight into shrinkage stress, antibacterial, and ion release properties

Ghalia Bhadila[1,2,3] | Xiaohong Wang[4] | Michael D. Weir[2] | Mary Ann S. Melo[5] | Frederico Martinho[2] | Guadalupe Garcia Fay[2] | Thomas W. Oates[2] | Jirun Sun[4] | Hockin H. K. Xu[2,6,7]

[1]Biomaterials and Tissue Engineering Division, University of Maryland School of Dentistry, Baltimore, Maryland

[2]Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, Maryland

[3]Department of Pediatric Dentistry, King AbdulAziz University, Jeddah, Saudi Arabia

[4]Volpe Research Center, American Dental Association Foundation, Frederick, Maryland

[5]Division of Operative Dentistry, Department of General Dentistry, University of Maryland School of Dentistry, Baltimore, Maryland

[6]Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, Maryland

[7]Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, Maryland

Correspondence
Hockin H. K. Xu, Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA.
Email: hxu@umaryland.edu

Jirun Sun, Volpe Research Center, American Dental Association Foundation, Frederick, MD 21704, USA.
Email: sunj@ada.org

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Abstract

The aims are: (a) To develop the first low-shrinkage-stress nanocomposite with antibacterial and remineralization capabilities through the incorporation of dimethylaminododecyl methacrylate (DMAHDM) and nanoparticles of amorphous calcium phosphate (NACP); (b) to investigate the effects of the new composite on biofilm inhibition, mechanical properties, shrinkage stress, and calcium (Ca) and phosphate (P) ion releases. The low-shrinkage-stress resin consisted of urethane dimethacrylate and triethylene glycol divinylbenzyl ether. Composite was formulated with 3% DMAHDM and 20% NACP. Mechanical properties, shrinkage stress, and degree of conversion were evaluated. *Streptococcus mutans* biofilm growth on composites was assessed. Ca and P ion releases were measured. The shrinkage stress of the low-shrinkage-stress composite containing 3% DMAHDM and 20% NACP was 36% lower than that of traditional composite control ($p < 0.05$), with similar degrees of conversion of 73.9%. The new composite decreased the biofilm colony-forming unit by 4 log orders and substantially reduced biofilm lactic acid production compared to control composite ($p < 0.05$). Incorporating DMAHDM to the low-shrinkage-stress composite did not adversely affect the Ca and P ion release. A novel bioactive nanocomposite was developed with low shrinkage stress, strong antibiofilm activity, and high levels of ion release for remineralization, without undermining the mechanical properties and degree of conversion.

KEYWORDS
antibiofilm, calcium phosphate nanoparticles, ion release, low shrinkage stress, nanocomposite

1 | INTRODUCTION

Dental resin composites are popular for restoring carious lesions,[1] however, polymerization shrinkage and secondary caries remain as major unresolved issues for resin composites, limiting the longevity of the restorations.[2,3] Replacement of a failed restoration results in more tooth structure removal and hence a higher susceptibility for the tooth to fracture.

Polymerization shrinkage stresses of composites at the tooth-restoration interface play an important role in secondary caries formation.[4] These stresses can cause restoration debonding, interfacial microcracks, and gaps.[5] Therefore, the selection of composite monomers and the principal polymerization mechanisms highly influence the polymerization stress and, consequently, the longevity of the restoration.[6]

Bioactive Low-Shrinkage-Stress Nanocomposite Suppresses *S. mutans* Biofilm and Preserves Tooth Dentin Hardness

Ghalia Bhadila[1-3], Hanan Filemban[1-2], Xiaohong Wang[4], Mary Ann S. Melo[5], Dwayne D. Arola[6], Franklin R. Tay[7], Thomas W. Oates[2], Michael D. Weir[2], Jirun Sun[4], Hockin H. K. Xu[2,8,9]

[1]Ph.D. Program in Dental Biomedical Sciences, Biomaterials and Tissue Engineering Division, University of Maryland School of Dentistry, Baltimore, MD 21201, USA;
[2]Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA;
[3]Department of Pediatric Dentistry, Faculty of Dentistry, King AbdulAziz University, Jeddah 21589, Saudi Arabia;
[4]Volpe Research Center, American Dental Association Foundation, Frederick, MD 21704, USA;
[5]Division of Operative Dentistry, Department of General Dentistry, University of Maryland School of Dentistry, Baltimore, MD 21201, USA;
[6]Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA;
[7]Department of Endodontics, Dental College of Georgia, Augusta University, Augusta, GA 30912, USA;
[8]Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA;
[9]Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA

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Correspondence: Dr. Hockin Xu, email: hxu@umaryland.edu; Dr. Michael D. Weir, email: michael.weir@umaryland.edu; Dr. Jirun Sun, email: sunj@ada.org.

Short title: Bioactive low-shrinkage nanocomposite protects dentin hardness under biofilms.

Keywords: Bioactive nanocomposite; low polymerization stress; calcium phosphate nanoparticles; dental caries; dentin hardness; oral biofilm.

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Novel low-shrinkage-stress nanocomposite with remineralization and antibacterial abilities to protect marginal enamel under biofilm

Ghalia Bhadila[a,b,c], Xiaohong Wang[d], Wen Zhou[b,e], Deepak Menon[f], Mary Ann S. Melo[g], Silvia Montaner[f], Thomas W. Oates[b], Michael D. Weir[b,*], Jirun Sun[d,*], Hockin H.K. Xu[b,h,i,*]

[a] Ph.D. Program in Dental Biomedical Sciences, Biomaterials and Tissue Engineering Division, University of Maryland School of Dentistry, Baltimore, MD 21201, USA
[b] Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA
[c] Department of Pediatric Dentistry, Faculty of Dentistry, King AbdulAziz University, Jeddah 21589, Saudi Arabia
[d] Volpe Research Center, American Dental Association Foundation, Frederick, MD 21704, USA
[e] State Key Laboratory of Oral Diseases, Department of Operative Dentistry and Endodontics, West China Hospital of Stomatology, National Clinical Research Centre for Oral Diseases, Sichuan University, Chengdu, 610041, China
[f] Department of Oncology and Diagnostic Sciences, University of Maryland School of Dentistry, Baltimore, MD 21201, USA
[g] Division of Operative Dentistry, Department of General Dentistry, University of Maryland School of Dentistry, Baltimore, MD 21201, USA
[h] Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA
[i] Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA

A R T I C L E   I N F O

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Calcium phosphate nanoparticles
Enamel remineralization
Monomers cytotoxicity

A B S T R A C T

Objectives: Polymerization shrinkage stress may lead to marginal damage, microleakage and failure of composite restorations. The objectives of this study were to : (1) develop a novel nanocomposite with low-shrinkage-stress, antibacterial and remineralization properties to reduce marginal enamel demineralization under biofilms; (2) evaluate the mechanical properties of the composite and calcium (Ca) and phosphate (P) ion release; and (3) investigate the cytotoxicity of the new low-shrinkage-stress monomer in vitro.
Methods: The low-shrinkage-stress resin consisted of urethane dimethacrylate (UDMA) and triethylene glycol divinylbenzyl ether (TEG-DVBE), and 3 % dimethylaminohexadecyl methacrylate (DMAHDM) and 20 % calcium phosphate nanoparticles (NACP) were added. Mechanical properties, polymerization shrinkage stress, and degree of conversion were evaluated. The growth of *Streptococcus mutans* (*S. mutans*) on enamel slabs with different composites was assessed. Ca and P ion releases and monomer cytotoxicity were measured.
Results: Composite with DMAHDM and NACP had flexural strength of 84.9 ± 10.3 MPa ($n = 6$), matching that of a commercial control composite. Adding 3 % DMAHDM did not negatively affect the composite ion release. Under *S. mutans* biofilm, the marginal enamel hardness was 1.2 ± 0.1 GPa for the remineralizing and antibacterial group, more than 2-fold the 0.5 ± 0.07 GPa for control ($p < 0.05$). The polymerization shrinkage stress of the new composite was 40 % lower than that of traditional composite control ($p < 0.05$). The new monomers had fibroblast viability similar to that of traditional monomer control ($p > 0.1$).
Conclusion: A novel low-shrinkage-stress nanocomposite was developed with remineralizing and antibacterial properties. This new composite is promising to inhibit recurrent caries at the restoration margins by reducing polymerization stress and protecting enamel hardness.

1. Introduction

Dental caries is a prevalent dental disease affecting as much as 35 % of the entire global population [1], and costing the United States $298 billion annually [2]. Polymeric composites are a popular material in restoring carious teeth [3]. However, recurrent caries at the composite-tooth interface has been a main reason for restoration failures [4]. Resinous materials tend to accumulate more plaque and bacterial biofilm than other restorative materials [5]. The replacement of failed dental restorations accounted for 57 % of all operative dental procedures [4]. A main drawback of dental composites is their polymerization shrinkage stresses, which have been linked to adverse clinical outcomes such as internal and marginal gap formation, cusp deflection, enamel crack propagation and reduced bond strength [6]. Therefore,

* Corresponding authors at: Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA and Volpe Research Center, American Dental Association Foundation, Frederick, MD 21704, USA.
E-mail addresses: Michael.weir@umaryland.edu (M.D. Weir), sunj@ada.org (J. Sun), hxu@umaryland.edu (H.H.K. Xu).

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Novel rechargeable calcium phosphate nanocomposite with antibacterial activity to suppress biofilm acids and dental caries

Short title: Rechargeable calcium phosphate nanocomposite with antibacterial activity

Yousif A. Al Dulaijan[1,2], Lei Cheng[1,3], Michael D. Weir[1], Mary Anne S. Melo[1], Huaibing Liu[4], Thomas W. Oates[1], Lin Wang[1,5], Hockin H. K. Xu[1,6,7]

[1]Department of Advanced Oral Sciences and Therapeutics, University of Maryland School of Dentistry, Baltimore, MD 21201, USA;
[2]Department of Substitutive Dental Sciences, College of Dentistry, Imam Abdulrahman bin Faisal University, Dammam, Saudi Arabia;
[3]State Key Laboratory of Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu 610041, China
[4]L.D. Caulk Division, Dentsply Sirona Restorative, Milford, DE 19963, USA
[5]VIP Integrated Department, Stomatological Hospital of Jilin University, Changchun, China
[6]Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA;
[7]Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA

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Correspondence:
Hockin Xu, Director of Biomaterials & Tissue Engineering Division, Department of Advanced Oral Sciences and Therapeutics, University of Maryland Dental School, Baltimore, MD 21201, USA, email: hxu@umaryland.edu. Lin Wang, Stomatological Hospital of Jilin University, Changchun, China, email: dentistwanglin@126.com.

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Article

Novel CaF_2 Nanocomposites with Antibacterial Function and Fluoride and Calcium Ion Release to Inhibit Oral Biofilm and Protect Teeth

Heba Mitwalli [1,2], Abdulrahman A. Balhaddad [1,3], Rashed AlSahafi [1,4], Thomas W. Oates [5], Mary Anne S. Melo [5,6], Hockin H. K. Xu [5,7,8] and Michael D. Weir [5,*]

1 Program in Dental Biomedical Sciences, University of Maryland School of Dentistry, Baltimore, MD 21201, USA; hmitwalli@umaryland.edu (H.M.); aabalhaddad@umaryland.edu (A.A.B.); rashed.alsahafi@umaryland.edu (R.A.)
2 Department of Restorative Dental Science, College of Dentistry, King Saud University, Riyadh 11451, Saudi Arabia
3 Department of Restorative Dental Sciences, College of Dentistry, Imam Abdulrahman bin Faisal University, Dammam 31441, Saudi Arabia
4 Department of Restorative Dental Sciences, College of Dentistry, Umm Al-Qura University, Makkah 24211, Saudi Arabia
5 Department of Advanced Oral Sciences and Therapeutics, School of Dentistry, University of Maryland, Baltimore, MD 21201, USA; TOates@umaryland.edu (T.W.O.); MMelo@umaryland.edu (M.A.S.M.); HXu2@umaryland.edu (H.H.K.X.)
6 Division of Operative Dentistry, Department of General Dentistry, University of Maryland School of Dentistry, Baltimore, MD 21201, USA
7 Center for Stem Cell Biology & Regenerative Medicine, University of Maryland School of Medicine, Baltimore, MD 21201, USA
8 Marlene and Stewart Greenebaum Cancer Center, University of Maryland School of Medicine, Baltimore, MD 21201, USA
* Correspondence: michael.weir@umaryland.edu

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Abstract: (1) Background: The objective of this study was to develop a novel dental nanocomposite containing dimethylaminohexadecyl methacrylate (DMAHDM), 2-methacryloyloxyethyl phosphorylcholine (MPC), and nanoparticles of calcium fluoride ($nCaF_2$) for preventing recurrent caries via antibacterial, protein repellent and fluoride releasing capabilities. (2) Methods: Composites were made by adding 3% MPC, 3% DMAHDM and 15% $nCaF_2$ into bisphenol A glycidyl dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (denoted BT). Calcium and fluoride ion releases were evaluated. Biofilms of human saliva were assessed. (3) Results: $nCaF_2$+DMAHDM+MPC composite had the lowest biofilm colony forming units (CFU) and the greatest ion release; however, its mechanical properties were lower than commercial control composite ($p < 0.05$). $nCaF_2$+DMAHDM composite had similarly potent biofilm reduction, with mechanical properties matching commercial control composite ($p > 0.05$). Fluoride and calcium ion releases from $nCaF_2$+DMAHDM were much more than commercial composite. Biofilm CFU on composite was reduced by 4 logs ($n = 9$, $p < 0.05$). Biofilm metabolic activity and lactic acid were also substantially reduced by $nCaF_2$+DMAHDM, compared to commercial control composite ($p < 0.05$). (4) Conclusions: The novel nanocomposite $nCaF_2$+DMAHDM achieved strong antibacterial and ion release capabilities, without compromising the mechanical properties. This bioactive nanocomposite is promising to reduce biofilm acid production, inhibit recurrent caries, and increase restoration longevity.

Keywords: dental nanocomposite; calcium fluoride nanoparticles; remineralization; antibacterial; protein repellent; oral biofilm

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Design, synthesis and applications of core–shell, hollow core, and nanorattle multifunctional nanostructures

Ahmed Mohamed El-Toni,*[a,b] Mohamed A. Habila,[c] Joselito Puzon Labis,[a,d] Zeid A. ALOthman,[c] Mansour Alhoshan,[e] Ahmed A. Elzatahry[f] and Fan Zhang[g]

With the evolution of nanoscience and nanotechnology, studies have been focused on manipulating nanoparticle properties through the control of their size, composition, and morphology. As nanomaterial research has progressed, the foremost focus has gradually shifted from synthesis, morphology control, and characterization of properties to the investigation of function and the utility of integrating these materials and chemical sciences with the physical, biological, and medical fields, which therefore necessitates the development of novel materials that are capable of performing multiple tasks and functions. The construction of multifunctional nanomaterials that integrate two or more functions into a single geometry has been achieved through the surface-coating technique, which created a new class of substances designated as core–shell nanoparticles. Core–shell materials have growing and expanding applications due to the multifunctionality that is achieved through the formation of multiple shells as well as the manipulation of core/shell materials. Moreover, core removal from core–shell-based structures offers excellent opportunities to construct multifunctional hollow core architectures that possess huge storage capacities, low densities, and tunable optical properties. Furthermore, the fabrication of nanomaterials that have the combined properties of a core–shell structure with that of a hollow one has resulted in the creation of a new and important class of substances, known as the rattle core–shell nanoparticles, or nanorattles. The design strategies of these new multifunctional nanostructures (core–shell, hollow core, and nanorattle) are discussed in the first part of this review. In the second part, different synthesis and fabrication approaches for multifunctional core–shell, hollow core–shell and rattle core–shell architectures are highlighted. Finally, in the last part of the article, the versatile and diverse applications of these nanoarchitectures in catalysis, energy storage, sensing, and biomedicine are presented.

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1. Introduction

Recently, nanoparticles have increasingly gained attention because of their remarkable properties that result from their nano-dimensions. Continuous development in nanoparticle research has been motivated by the search for new applications, performance improvement, and combined nanomaterial functions (*i.e.*, developing multifunctional nanomaterials). One method to accomplish these objectives is through the coating of nanoparticles with one or more layers of other materials that have interesting properties. The surrounding layer is called the shell, and the original nanoparticle is named as the core. It has been discovered that the constructed layer, or shell, can change the function and properties of the original core. In other words, the core can exhibit new chemical or catalytic reactivity with shell formation. In addition, thermal stability or dispersibility can be improved by growing such shells. In fact, novel optical, magnetic and

[a] *King Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11451, Saudi Arabia. E-mail: aamohammad@ksu.edu.sa, ahmedtoni@yahoo.com*
[b] *Central Metallurgical Research and Development Institute, CMRDI, Helwan 11421, Cairo, Egypt*
[c] *Advanced Materials Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
[d] *Math-Physics Dept., Mindanao State University, Fatima, General Santos City 9500, Philippines*
[e] *Department of Chemical Engineering, King Saud University, Riyadh 11451, Saudi Arabia*
[f] *Materials Science and Technology Program, College of Arts and Sciences, Qatar University, P. O. Box 2713, Doha, Qatar*
[g] *Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China*

Vesicle Templated Polymerization, a Review

Alexander M. van Herk
Institute of Chemical and Engineering Sciences, Singapore
Email: alexander_herk@ices.a-star.edu.sg

Abstract

Vesicle templated polymerization has developed into a mature research area over the last 35 years. The main purpose of this approach was to produce hollow polymeric nanocapsules from low-cost chemicals, utilizing a simple emulsion polymerization like process. Over the years understanding of the different varieties of the approach has grown. In retrospect, the characterization methods utilized to determine the morphologies are essential to draw the right conclusions. In this review, first, an overview of the earlier attempts to produce nanocapsules with uniformous wall thickness will be given, looking at the results with the current understandings, greatly enhanced by quantification of the different morphologies through cryo-TEM images. The latest approach, reactive oligomer assisted transcriptive synthesis, seems to be able to fulfill the initial purpose and almost 100% of nanocapsule morphologies can be formed under the right conditions.

Introduction

Vesicle templated polymerization has been studied for over 35 years now, starting with the work of Murtagh and Thomas[1] (starting in 1986) and the group of German[2] (starting in 1993). The purpose of these studies in terms of applications would be to prepare nanocapsules that could be used in controlled release of drugs and fragrances for example. Utilizing readily available synthetic chemicals like vesicle forming surfactants (e.g. dioctadecyldimethyl ammonium bromide or chloride, DODAB, DODAC) and simple monomers (e.g. styrene, acrylics etc.), deploying an emulsion polymerization like process would open an avenue to large scale and low costs production of polymeric nanocapsules. In this review we focus on this particular route. With the recent insights in factors influencing the outcome of these polymerizations and systematic studies of the resulting particle morphologies, in retrospect, a lot of the results can now be better understood. Utilizing the vesicle templates as reaction media, polymerizing inside the hydrophobic domain, is called **morphosynthesis**. Morphosynthesis has been studied through free radical polymerization[3] and silica formation inside the bilayer[4].

Besides utilizing vesicles as a template, also solids particles and other structures can be utilized[5]. The main reason why vesicle templated polymerization are attractive is that the template itself does not need to be removed after polymerization[5].

Utilizing the interface between the vesicle template and the solution as a specific site for the growth of material from solution is called **transcriptive synthesis**. Besides organic polymerizations[6], also inorganic polymerizations, in the form of deposition of silica during hydrolysis and condensation from silicon alkoxides has been performed onto vesicles[7]. Furthermore, transcriptive synthesis has been performed through the RAFT oligomer approach[6]. We coined these latter two approaches **reactive oligomer assisted transcriptive synthesis** (ROATS).

Over the years it has become more and more evident that the characterization of the resulting morphologies is often challenging, both from the very first papers[2] and the more recent papers[8]. Furthermore, the preparation of the vesicle template[9] itself and intermediates in the case of transcriptive synthesis via the RAFT-oligomer approach[10] and its relation to the final particle morphology only now seem to be better understood[9-11].

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Novel core–shell CHX/ACP nanoparticles effectively improve the mechanical, antibacterial and remineralized properties of the dental resin composite

Yanwei Yang[a,1], *Zexian Xu*[b,1], *Yuqing Guo*[b,1], *Hongchen Zhang*[c], *Yinong Qiu*[a], *Jianxue Li*[a], *Dongyang Ma*[a], *Zhiqiang Li*[d], *Ping Zhen*[e,*], *Bin Liu*[b,*], *Zengjie Fan*[b,*]

[a] *Department of Stomatology, The 940th Hospital of Joint Logistic Support Force of the Chinese People's Liberation Army, Lanzhou, 730050, PR China*
[b] *School of Stomatology, Lanzhou University, Lanzhou, 730000, PR China*
[c] *School of Nursing, Lanzhou University, Lanzhou, 730000, PR China*
[d] *Key Lab of Stomatology of State Ethnic Affairs Commission, Key Lab of Oral Diseases of Gansu Province, School of Stomatology, Northwest Minzu University, Lanzhou, 730030, PR China*
[e] *Orthopedic Center, The 940th Hospital of Joint Logistic Support Force of the Chinese People's Liberation Army, Lanzhou 730050, PR China*

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ABSTRACT

Objective. The core–shell chlorhexidine/amorphous calcium phosphate (CHX/ACP) nanoparticles were synthesized and used to modify the dental resin composite, aiming to improve its remineralized and antibacterial properties.

Methods. The core–shell CHX/ACP nanoparticles were synthesized by vesicle-templating technology and characterized, and their sustained release and antibacterial properties were also evaluated. Subsequently, the synthesized nanoparticles were incorporated into the dental resin composite at 1 wt.%, 5 wt.% or 10 wt.% to obtain different experimental groups. The physical properties, including curing depth, double bond conversion rate, water absorption and solubility, the sustained-release effects, and mechanical properties of the modified resin composite were evaluated. The remineralization ability was also measured by SEM. The antibacterial experiment of the modified resin composite with fresh preparation or aging in water for 28 days was carried out by a plate count method.

Results. The physical and chemical characterizations showed that the synthesized nanoparticles presented a core–shell structure, and their diameter was about 98.5 nm. The shell was composed of ACP with the core full of CHX. These nanoparticles had a release effect on calcium, phosphate ions, and CHX. The nanoparticles could effectively inhibit the growth of *S. mutan* at a lower concentration ($\geq$50 μg/mL). The curing depth, the double bond conversion, the water absorption, the solubility, the flexural strength, the flexural modulus, and

* *Corresponding authors.*
E-mail addresses: zhenpingok@163.com (P. Zhen), liubkq@lzu.edu.cn (B. Liu), zjfan@lzu.edu.cn (Z. Fan).
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Synthesis and characterization of silver phosphate/calcium phosphate mixed particles capable of silver nanoparticle formation by photoreduction

Livia C. Natale [a], Yvette Alania [a], Marcela C. Rodrigues [a], Alyne Simões [a], Douglas N. de Souza [a], Erick de Lima [a], Victor E. Arana-Chavez [a], Thiago L.R. Hewer [b], Rochelle Hiers [d], Fernando L. Esteban-Florez [d], Giancarlo E.S. Brito [c], Sharukh Khajotia [d], Roberto R. Braga [a,*]

[a] Department of Biomaterials and Oral Biology, School of Dentistry, University of São Paulo School of Dentistry, São Paulo, Brazil
[b] Department of Chemical Engineering, Polytechnic School, University of São Paulo, São Paulo, Brazil
[c] Department of Applied Physics, Institute of Physics, University of São Paulo, São Paulo, Brazil
[d] Department of Dental Materials, University of Oklahoma Health Sciences Center, Oklahoma City, USA

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ABSTRACT

Silver phosphate is a semi-conductor sensitive to UV-Vis radiation (<530 nm). Exposure to radiation removes electrons from the oxygen valence shell, which are scavenged by silver cations (Ag^+), forming metallic silver (Ag^0) nanoparticles. The possibility of silver nanoparticle formation *in situ* by a photoreduction process was the basis for the application of mixed calcium phosphate/silver phosphate particles as remineralizing and antibacterial fillers in resin-based dental materials. Mixed phosphate particles were synthesized, characterized and added to a dimethacrylate resin in 20% or 30% mass fractions to investigate their efficacy as ion-releasing fillers for dental remineralization and antibacterial activity. The formation of metallic silver nanoparticles after exposure to visible radiation from a dental curing unit (peak emission: 470 nm) was demonstrated by particle X-ray diffraction and scanning electron microscopy analysis of the composite fractured surface. Calcium and phosphate release from materials containing the mixed particles were similar to those containing pure CaP particles, whereas *Streptococcus mutans* colonies were reduced by three orders of magnitude in relation to the control, which can be attributed to silver release. As expected, the optical properties of the materials containing mixed phosphate particles were compromised by the presence of silver. Nevertheless, materials containing mixed phosphate particles presented higher fracture strength and elastic modulus than those with pure CaP particles.

1. Introduction

Dental caries is a multi-factorial infectious disease that leads to irreversible loss of the mineralized tooth structure. Its treatment includes the removal of affected tooth structure and subsequent restoration of cavitated lesions to arrest their progression and re-establish both the original tooth anatomy and its masticatory function. In some cases, it is also important that the restorative material mimics the optical behavior of the surrounding tooth structure for aesthetic reasons. Recent epidemiological data shows that untreated caries lesions in permanent teeth represent the most prevalent health condition worldwide, affecting 2.4 billion people [1].

Dimethacrylate-based composites have become the material of choice for cavity restorations due to their handling characteristics, mechanical properties and optical behavior. However, these materials have a higher tendency to accumulate biofilm in comparison to natural enamel, ceramics and silver amalgam [2,3], which increases the risk of new caries lesions at the tooth/restoration interface and, consequently, restoration failure [4–6]. In order to reduce the incidence of secondary caries around composite restorations and extend their service life, several research groups have investigated ways to introduce remineralizing and/or antibacterial capabilities into resin-based composites [7–13].

Calcium orthophosphate particles used as bioactive fillers in resin-based composites were shown to remineralize non-cavitated enamel lesions [8,14,15] and demineralized dentin [16–18], and postpone the development of caries lesions in the presence of biofilm [19]. Unfortunately, the incorporation of calcium orthophosphate particles in resin matrices has drawbacks. First, the resulting materials have poor

* Corresponding author at: Departamento de Biomateriais e Biologia Oral da FOUSP, Av. Prof. Lineu Prestes, 2227, São Paulo SP 05508-000, Brazil.
E-mail address: rrbraga@usp.br (R.R. Braga).

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Bactericidal and Bioactive Dental Composites

Xanthippi Chatzistavrou[1*†], Anna Lefkelidou[1,2†], Lambrini Papadopoulou[3], Eleni Pavlidou[4], Konstantinos M. Paraskevopoulos[4], J. Christopher Fenno[5], Susan Flannagan[6], Carlos González-Cabezas[6], Nikos Kotsanos[2] and Petros Papagerakis[1*]

[1] Department of Orthodontics and Pediatric Dentistry, University of Michigan, Ann Arbor, MI, United States, [2] Department of Pediatric Dentistry, Aristotle University of Thessaloniki, Thessaloniki, Greece, [3] Department of Geology, Aristotle University of Thessaloniki, Thessaloniki, Greece, [4] Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece, [5] Biologic and Materials Sciences, School of Dentistry, University of Michigan, Ann Arbor, MI, United States, [6] Cariology, Restorative Sciences and Endodontics, University of Michigan, Ann Arbor, MI, United States

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Thomas G. H. Diekwisch, Texas A&M University College of Dentistry, United States
Andrea Santarelli, Università Politecnica delle Marche, Italy

***Correspondence:**
Xanthippi Chatzistavrou
chatzist@msu.edu
Petros Papagerakis
petros.papagerakis@usask.ca

† *These authors have contributed equally to this work.*

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Aim: Antimicrobial and bioactive restorative materials are needed to develop a bacteria free environment and tight bond with the surrounding tissue, preventing the spread of secondary caries and thus extending the lifetime of dental restorations. The characteristic properties of new dental bioactive and antibacterial composites are presented in this work. The new composites have been microstructurally characterized and both long and short term properties have been studied.

Methods: The Ag-doped sol-gel derived bioactive glass (Ag-BG) was incorporated into resin composite in concentrations 5, 10, and 15 wt.%, to fabricate new Ag-doped bioactive and antibacterial dental composites (Ag-BGCOMP). The microstructural properties and elemental analysis of the developed Ag-BGCOMP was observed. The total bond strength (TBS) was measured immediately and after long term of immersion in medium using microtensile testing. The capability of Ag-BGCOMPs to form apatite layer on their surface after immersion in Simulated Body Fluid (SBF) as well as the bacteria growth inhibition in a biofilm formed by *Streptococcus mutans* (*S. mutans*) were evaluated.

Results: Homogeneous distribution of Ag-BG particles into the resin composite was observed microstructurally for all Ag-BGCOMPs. The TBS measurements showed non-statistically significant difference between control samples (Ag-BG 0 wt.%) and Ag-BGCOMP specimens. Moreover, the total bond strength between the surrounding tooth tissue and the material of restoration does not present any statistically significant change for all the cases even after 3 months of immersion in the medium. The bioactivity of the Ag-BGCOMPs was also shown by the formation of a calcium-phosphate layer on the surface of the specimens after immersion in SBF. Antibacterial activity was observed for all Ag-BGCOMPs, statistically significant differences were observed between control samples and Ag-BGCOMPs. Accordingly, the number of dead bacteria in the biofilm found to increase significantly with the increase of Ag-BG concentration in the Ag-BGCOMPs.

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Article

Development of a Bioactive Flowable Resin Composite Containing a Zinc-Doped Phosphate-Based Glass

Myung-Jin Lee [1,†], Young-Bin Seo [2,3,†], Ji-Young Seo [4], Jeong-Hyun Ryu [2], Hyo-Ju Ahn [2], Kwang-Mahn Kim [2], Jae-Sung Kwon [2,3,*] and Sung-Hwan Choi [3,4,*]

1 Department of Dental Hygiene, Division of Health Science, Baekseok University, Cheonan 31065, Korea; dh.mjlee@bu.ac.kr
2 Department and Research Institute of Dental Biomaterials and Bioengineering, Yonsei University College of Dentistry, Seoul 03722, Korea; youngbin@yuhs.ac (Y.-B.S.); sweetden623@gmail.com (J.-H.R.); hjan505@yuhs.ac (H.-J.A.); kmkim@yuhs.ac (K.-M.K.)
3 BK21 FOUR Project, Yonsei University College of Dentistry, Seoul 03722, Korea
4 Department of Orthodontics, Institute of Craniofacial Deformity, Yonsei University College of Dentistry, Seoul 03722, Korea; jyseo13@yuhs.ac
* Correspondence: jkwon@yuhs.ac (J.-S.K.); selfexam@yuhs.ac (S.-H.C.); Tel.: +82-2-2228-3081 (J.-S.K.); +82-2-2228-3102 (S.-H.C.)
† These authors contributed equally to this work.

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Abstract: Flowable resins used for dental restoration are subject to biofilm formation. Zinc has antibacterial properties. Thus, we prepared a zinc-doped phosphate-based glass (Zn-PBG) to dope a flowable resin and evaluated the antibacterial activity of the composite against *Streptococcus mutans* (*S. mutans*) to extrapolate the preventative effect toward secondary caries. The composites were prepared having 0 (control), 1.9, 3.8, and 5.4 wt.% Zn-PBG. The flexural strength, elastic modulus, microhardness, depth of cure, ion release, inhibition zone size, and number of colony-forming units were evaluated and analyzed using ANOVA. The flexural strength of the control was significantly higher than those of Zn-PBG samples ($p < 0.05$). However, all samples meet the International Standard, ISO 4049. The microhardness was not significantly different for the control group and 1.9 and 3.8 wt.% groups, but the 5.4 wt.% Zn-PBG group had a significantly lower microhardness ($p < 0.05$). Further, the composite resins increasingly released P, Ca, Na, and Zn ions with an increase in Zn-PBG content ($p < 0.05$). The colony-forming unit count revealed a significant reduction in *S. mutans* viability ($p < 0.05$) with increase in Zn-PBG content. Therefore, the addition of Zn-PBG to flowable composite resins enhances antibacterial activity and could aid the prevention of secondary caries.

Keywords: dental restoration; flowable resin composite; antibacterial; plaque prevention; biofilm; zinc; bioglass; bioactive material; tooth remineralization

1. Introduction

Flowable resin composites have been clinically proven to be an effective dental treatment over the last 60 years are a popular restorative material in dentistry because of the good flowability and color, which is similar to that of natural tooth enamel [1,2]. Flowable resin composites have a diverse variety of applications, including preventive resin restoration, pit and fissure sealing, restoration repair, and cavity lining [3]. Although flowable composite resins have shown long-term clinical success, they tend to accumulate more bacteria and dental plaque than enamel and other restorative