Tricalcium Silicate Cements with Resins and Alternative Radiopacifiers

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Abstract

Objective: The objectives of this study were the investigation of the setting mechanisms and characterization of radiopacified tricalcium silicate–based materials mixed with different liquid vehicles. **Methods:** Tricalcium silicate cement replaced with 20% of either zirconium oxide or barium zirconate radiopacifier was investigated. The cements were mixed with water, an epoxy resin, or a light-cured Bis-GMA–based resin. The setting mechanism and characterization of set materials after immersion in Hank's balanced salt solution (HBSS) for 28 days were investigated by scanning electron microscopy of polished specimens and x-ray diffraction analysis. The bioactivity and surface microstructure of cements immersed in HBSS or water were also assessed by similar techniques together with leaching in solution investigated by inductively coupled plasma emission spectroscopy. **Results:** The formation of calcium hydroxide as a by-product of cement reaction was affected by the type of radiopacifier and also by the resin vehicle used. Barium zirconate enhanced the formation of calcium hydroxide as indicated by both scanning electron microscopy and x-ray diffraction analysis. The use of resins as vehicles reduced the formation of calcium hydroxide, with the Bis-GMA–based resin being mostly affected. Calcium hydroxide was deposited on the material surface regardless of the type of vehicle used. Formation of beta calcium phosphate was observed on materials containing barium zirconate radiopacifier immersed in HBSS. Inductively coupled plasma emission spectroscopy analysis showed high levels of calcium leached from materials by using water and light-curable resin as mixing vehicles. Barium was leached in solution, with the highest amount from the water-based mixtures. Zirconium leaching was negligible in materials containing zirconium oxide as radiopacifier, but leaching of zirconium was measurable in materials by using barium zirconate with tricalcium silicate. **Conclusions:** The resin type and composition of the radiopacifier affect the calcium releasing ability and bioactivity of tricalcium silicate cements. Barium was leached in solution with barium zirconate radiopacified variants. Light-cured Bis-GMA–based resins did not exhibit cement hydration; however, they encouraged leaching of calcium ions in solution and promoted surface deposition of calcium phosphate. *(J Endod 2014;40:2030–2035)*

Key Words

Epoxy resin, hydration, light cure resin, radiopacifier, tricalcium silicate

Tricalcium silicate cements have been reported as suitable for use as root-end filling and repair materials, for pulp capping, and more recently as sealer cements. The bioactivity is an important parameter for repair materials (1, 2) and sealer cements used in gutta-percha obturations (3, 4), whereas the ability to elicit dentin bridge formation (5, 6) is mandatory for pulp-capping materials. Light-curable tricalcium silicate–based materials are indicated for use as liner under composite restorations aiming to achieve a bond between the layers of materials, thus reducing microleakage. The classic mineral trioxide aggregate (MTA) mixed with water creates a problem when layering with composite because calcium silicate–based materials have been shown to be adversely affected by acid etching, which is a necessary step in composite placement. Acid etching affected the compressive strength and surface microhardness of ProRoot MTA (7). This indicates that it may be better to postpone restorative procedures for at least 96 hours after mixing MTA (7). Biodentine exhibited microleakage and surface erosion when etched with 37% phosphoric acid used under composite resin restorations (8). Postponement of acid etching will not reduce the acid susceptibility. Etching of materials based on tricalcium silicate should be avoided.

The use of a resin vehicle with tricalcium silicate cement may prospectively improve the material properties. The main light-curing dental resin systems are Bis-GMA and a biocompatible resin (9, 10), 2-hydroxyethyl methacrylate (HEMA), tetraethylene glycol dimethacrylate (TEGDMA), camphorquinone, and ethyl-4-(dimethylamino)benzoate with and without polyacrylic co-maleic acid (11, 12), Bis-GMA, TEGDMA (13) and Bis-GMA, pyromellitic acid diethylmethacrylate, and HEMA (14). A light-curable tricalcium silicate–based material would make an ideal pulp-capping material because it will allow command cure, and also improved bonding of overlying resin composites can be anticipated. The light-curing systems proposed so far have exhibited alkaline pH, calcium ion release, formation of apatite (11, 13), and functional groups able to chelate calcium ions (11). Furthermore, therapeutic remineralization of dentin was observed (12, 14, 15). Experimental light-cured MTA formed mineralized tissue close to the materials in alveolar tissue of rats (10). It presented a moderate chronic inflammatory response at 30 days that decreased at 60 days but was more intense than with Angelus MTA and without dystrophic calcifications. Light-cured MTA was similar to MTA at 60 days, but it did not stimulate mineralization (9). Hydration did not occur by the resin-modified MTA. Reaction rims around the cement particles were absent, and the formation and leaching of calcium hydroxide were shown to be negligible (13).

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Addition of epoxy resins to MTA increases the material flow and improves handling characteristics (4). A range of sealers to be used with gutta-percha for root canal obturations similarly to AH Plus have thus been developed. One formulation marketed by Angelus (Londrina, Brazil) as MTA Fillapex is composed of MTA, methyl salicylate, butylene glycol colophony, and other additives. Other experimental resin systems based on epoxy resin have also been reported in use with MTA as a sealer cement (16).

Tricalcium silicate–based materials include radiopacifiers to be detected radiographically. MTA has bismuth oxide, whereas alternative radiopacifiers are in use by other systems. The main role of radiopacifer is for enhancement of material detection on a radiograph. However, there are few reports on the effect of radiopacifier on material properties and hydration. The aim of this research was to investigate the hydration reaction and characterize pure tricalcium silicate to which different radiopapacifiers and liquid vehicles were added.

Materials and Methods

The materials used in this study included pure tricalcium silicate cement (Mineral Research Processing, Meyzieu, France) with 20% zirconium oxide (ZrO_2; Sigma-Aldrich, Buchs, Germany); TCS-Zr and tricalcium silicate cement with 20% barium zirconate (TCS-BaZr; Mineral Research Processing) were both developed at the University of Malta. The powders were mixed with different vehicles: (1) water (water/powder ratio 0.35); (2) epoxy resin based on bisphenol A-(epichlorhydrin), oxirane, and mono[(C12-14-alkyloxy)methyl] derivatives (resin/powder ratio 0.35); and (3) Bis-GMA and TEGDMA (resin/powder ratio 0.35).

The epoxy resin was based on bisphenol A-(epichlorhydrin), oxirane, and mono[(C12-14-alkyloxy)methyl] derivatives resin and hardener components were pre-mixed in 3:2 proportion by volume. The epoxy resin was then added to the powder in a resin/powder ratio of 0.35. The Bis-GMA–based resin was light-cured with an LED light-curing unit for 20 seconds per 1-mm increment. After preparation the materials were immersed in Hank's balanced salt solution (HBSS) (H6648; Sigma-Aldrich, St Louis, MO) for 28 days at 37°C unless otherwise indicated.

Characterization of Materials and Material Surfaces

The set materials were characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and x-ray diffraction (XRD) analysis.

Microscopy and Elemental Analysis. Cylindrical specimens 10 mm in diameter and 2 mm in height were prepared and stored in HBSS for 28 days. For microscopy and elemental analysis of polished specimens, the materials were vacuum desiccated and embedded in resin (Epoxyfix; Struers GmbH, Ballerup, Denmark) and were then ground by using progressively finer diamond disks and pastes by using an automatic polishing machine (Tegramin 20; Struers GmbH). The polished specimens were attached to aluminum stubs, carbon coated, and viewed under the SEM (Zeiss MERLIN Field Emission SEM; Carl Zeiss NTS GmbH, Oberkochen, Germany). Scanning electron micrographs of the different material microstructural components at different magnifications in back-scatter electron mode were captured, and EDS was carried out. Calcium-to-silicon ratio plots of different zones were drawn from the back-scattered electron images of the polished specimens. Area 1 indicated the calcium/silicon ratio in cement particle center, Area 2 in the reaction rim, and Area 3 in the cement matrix.

Another 2 sets of specimens were prepared for surface characterization. One set was placed in water and another set in HBSS at 37°C for 28 days. For surface characterization, the cement disks were dried in vacuum desiccator and were then mounted on aluminum stubs, carbon coated, and viewed under SEM in secondary electron mode for surface characterization.

X-ray Diffraction Analysis. Specimens measuring 15 mm in diameter and 2 mm high of each material type were prepared and immersed in HBSS at 37°C for 28 days. At the end of the curing period the specimens were dried in vacuum desiccator and powdered. Powder diffractometry of the specimens was performed by using a Rigaku Ultima IV (Rigaku, Tokyo, Japan) with a Cu$K\alpha$ source set at 40 mA and 45 kV, and the detector was set to rotate between 15° and 45°, with a sampling width of 0.05° and scan speed of 1°/min at 15 revs/min.

Another 2 sets of samples of similar dimensions were prepared. Half were immersed in water and the other half in HBSS at 37°C for 28 days. The surface analysis was performed by using the same diffractometer in grazing incidence asymmetric Bragg mode with an incidence angle of 3°. The diffractometer was operated at 40 mA and 45 kV from 15° to $45°2\theta$ range, with a sampling width of 0.05° and a scan speed of 1°/min. The diffractometer slit system has divergent slits at 1 mm, divergent height slits of 10 mm, a scintillator slit of 8 mm, and a receiver slit of 13 mm. Phase identification of the powder diffractograms and glancing angle XRDs was accomplished by using a search-match software indexing the peaks against Power Diffraction Files data provided by International Centre for Diffraction Data (ICDD; Newtown Square, PA).

Assessment of Leaching

Cylindrical specimens 10 mm in diameter and 2 mm in height were prepared, weighed, and stored in 5 mL water or HBSS at 37°C for 28 days. The storage solution was tested for calcium, silicon, zirconium, and barium by using inductively coupled plasma-emission spectroscopy (ICP-ES). Ion release was calculated, taking into consideration the sample size and volume of solution used. A blank water and HBSS solution served as controls. The values for the elements present in the soaking liquids were reduced from the analyses.

Results

Characterization of Materials and Material Surfaces

The back-scattered scanning electron micrographs of polished material surfaces are shown in Figure 1. The prototype cements were composed of cement particles around which was interspersed the radiopacifier, which appeared whiter on the micrograph. The cements mixed with water and epoxy resin exhibited a darker reaction rim (labeled on micrographs) around the cement particle, indicating cement hydration. The cements that were mixed with Bis-GMA and TEGDMA did not have any reaction rims around the cement particle and no hydration product in the cement matrix.

The calcium/silicon ratio plots for the 6 experimental materials are shown in Supplemental Figure S1 (available online at www.jendodon.com). The materials mixed with water or epoxy resin showed lower calcium-to-silicon ratios moving from the center of the cement particle toward the reaction rim and material matrix. Thus, calcium ions were released into the matrix as calcium hydroxide, a well-known mechanism of tricalcium silicate cement setting. The cements mixed with the light-curable Bis-GMA/TEGDMA resin did not have a calcium-to-silicon gradient, indicating the lack of formation of calcium hydroxide.

The secondary electron micrographs of the materials immersed in water and HBSS for 28 days are shown in Supplemental Figures S2 and S3 (available online at www.jendodon.com). The surface of the