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NEW PERSPECTIVE ARTICLE

Is Mineral Trioxide Aggregate a Bioceramic? ¿Es el agregado de trióxido mineral una biocerámica?

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ABSTRACT

Bioceramics are a subset of biomaterials and define ceramic materials, which are biocompatible. The range of biocompatibility is wide from totally inert materials to fully resorbable materials that are fully replaced with time. The first mention of Bioceramics in Endodontics referred to a study on a new material Bioaggregate, which was developed as a replacement for mineral trioxide aggregate (MTA) boasting a Portland cement free formulation. But is MTA a bioceramic?.

KEYWORDS

Mineral trioxide aggregate; Tricalcium silicate-based materials; Bioceramics; Material composition.

RESUMEN

Las biocerámicas son un subconjunto de los biomateriales y define los materiales cerámicos, los cuales son biocompatibles. La gama de biocompatibilidad es amplia y varía desde materiales totalmente inertes a los materiales totalmente reabsorbibles los cuales son reemplazados a lo largo del tiempo. La primera mención de Biocerámicas en Endodoncia se refirió a un estudio sobre un nuevo material un Bioagregado, que fue desarrollado como un reemplazo para el agregado trióxido mineral (MTA) que cuenta como un material con formulación libre de cemento Portland. Pero el MTA puede ser considerado una biocerámica?.

PALABRAS CLAVE

Agregado de Trióxido Mineral, Materiales basados en silicato tricalcico, Biocerámicas, Composición de materiales.

Bioceramic refers to a group of materials used in medicine and dentistry that are biocompatible. Ceramics is also a very broad term which encompasses inorganic, nonmetallic solids comprising metal, non-metal or metalloid atoms primarily held in ionic and covalent bonds. The crystallinity ranges from highly crystalline well ordered solids to poorly crystalline and amorphous glasses.

The first research article found on Pubmed (1) about bioceramics in Endodontics is an article about Bioaggregate (2). Bioaggregate was introduced by Verio Dental, a Canadian company as a replacement for MTA. It called the new material bioceramic. The manufacturer claimed that the material was not a mineral but ceramic based, was free of aluminium and free of heavy metals (3). Characterization of Bioaggregate shows that the

material is composed of tricalcium silicate, tantalum oxide, calcium phosphate and silicon dioxide (4). Other articles published on Bioaggregate show that it has the same composition as MTA with the only difference being the tantalum oxide, which was used to replace the bismuth oxide in MTA (5, 6). However as shown in the Camilleri *et al* 2015 (4) article Bioaggregate is a completely new concept. Although it is based on tricalcium silicate like the MTA it shows the presence of another cement type (calcium phosphate). Thus Bioaggregate is a biphasic cement. The tantalum oxide also replaces the bismuth oxide radiopacifier in MTA. However there is also the presence of an additive namely silicon oxide. What is not clear is to why Bioaggregate was marketed as a bioceramic?

To understand better the role of each component of the hydraulic tricalcium silicate-based materials one has to first investigate the original formulation then look at the other generations of materials. The first formulation of a hydraulic cement introduced to Dentistry was ProRoot MTA (Dentsply, Tulsa Dental Specialities, Tulsa OK, USA). This material although initially marketed as a calcium phosphate cement was shown to be composed of Portland cement whose components are tricalcium silicate, dicalcium silicate and tricalcium aluminate. In the grey version tetracalcium aluminoferrite is present. The ProRoot MTA also contains bismuth oxide in 1:4 proportions, added as radiopacifier (7, 8). Another material, which has the same formulation is MTA Angelus (Angelus, Londrina, Brazil). The MTA Angelus although marketed as being composed of Portland cement and bismuth oxide was shown to have excess of calcium oxide. Thus the hydration mechanisms of MTA Angelus are different as the calcium oxide reacts fast with water and this causes an exothermic peak at the start of the hydration reaction shown by isothermal calorimetry (9). It has been postulated that the excess calcium oxide in the MTA Angelus is due to the use of a cheap Portland cement in the formulation since

inadequate temperature of firing during kilning will result in high levels of hard burn lime (calcium oxide) in Portland cement which is undesirable for industrial use of this material. Another change to the material, which improved its characteristics was reduction in the particle size of the powder. This enhanced the hydration kinetics as more surface area of the cement particles is available for hydration (10). Furthermore this formulation which was marketed by Avalon Biomed (Florida, USA) as MTA Plus also incorporated a water-soluble polymer, which reduced washout considerably (11).

The second generation of hydraulic cements for dental use introduced three changes to the original formulation. These changes include modification to the cement formulation, alternative radiopacifiers and the introduction of additives. The Portland cement was replaced by tricalcium silicate, which was manufactured by a sol-gel process thus avoiding the incorporation of heavy metals (12), which are inadvertently included from the use of natural minerals and also the use of wastes to fire the kiln a measure taken to reduce costs of firing. The tricalcium silicate hydration characteristics were similar to those of Portland cement (13). The alternative radiopacifiers to replace bismuth oxide were necessary as bismuth oxide over the years was shown to cause tooth discoloration by three main mechanisms. The exposure to light and lack of oxygen resulted in darkening of materials based on bismuth oxide (14). Reaction of bismuth oxide with sodium hypochlorite also exhibited a dark brown/black discoloration (15) and bismuth oxide colour was also affected by contact with tooth structure (16). The various additives affected the material characteristics in a different way as will be reported later.

The first formulation, which included all three modifications was marketed as Biodentine (Septodont, St Maur de Fosses, France). Although Biodentine is a modification of the original MTA formulation it was marketed as a

dentine replacement material. Characterization of Biodentine shows material to be composed of tricalcium silicate, which replaces the Portland cement in MTA, zirconium oxide replacing the bismuth oxide and a number of additives. These additives include calcium carbonate, which is added to the powder and a water-soluble polymer and calcium chloride added to the liquid (9). Biodentine is also supplied in capsules. The changes in formulation resulted in a reduction in radiopacity (17), however the setting time was drastically reduced (17) and the material exhibited enhanced hydration with higher reaction rate than MTA (9). Leaching of calcium was also higher than other formulations namely MTA Angelus (9) and Theracal (Bisco, Schaumburg, IL, USA), which is a light curable tricalcium silicate-based material (18). The performance of Biodentine in contact with the pulp was shown to be optimal since the material although hydraulic in nature thus needing a wet environment could hydrate even in areas where there was a limitation with fluid availability such as that encountered when the material is used as a pulp capping material (19). Theracal is composed of Portland cement and barium zirconate radiopacifier. It also includes a glass additive in its matrix. This material replaces the water by a resin and is presented in a syringe. It is light curable. Hydration is dependent on uptake of water from environment and has been shown to be slow thus limiting hydration (19) and also exhibits no formation of calcium hydroxide and limited leaching of calcium ions in solution (18). The restricted availability of calcium indicates limits the use of Theracal as a pulp capping material.

A material, which is similar to Biodentine but maintains the original Portland cement and bismuth oxide formulation with the additives is MM MTA (Micromega, Besancon, France). The additives of the MM MTA are similar to those of Biodentine. The material hydration is however not similar to that of Biodentine. The MM MTA exhibits a shorter setting time, which is caused by the

presence of calcium chloride, which is a known accelerator to Portland cement systems even in the construction industry. In Portland cements, the addition of calcium carbonate affects the formation of ettringite during hydration, thus modifying the hydration process. This effect is not manifested in Biodentine where the calcium carbonate simply acts as a nucleation site thus enhancing hydration. Furthermore the calcium carbonate releases calcium ions in solution but impedes crystallization of calcium hydroxide (20). This highlights the role that additives have on material chemistry and setting. MM MTA is presented in a self-dispensing capsule thus facilitating the mixing and placement of the material.

The materials that are referred to as bioceramics are based on pure tricalcium silicate rather than Portland cement thus do not contain the aluminate phase. The manufacturing process is different and raw materials are laboratory grade chemicals rather than natural minerals. The first in this range as discussed was Bioaggregate. Bioaggregate root repair material has two cementitious phases consisting of both tricalcium silicate and calcium phosphate. The radiopacifier was changed to tantalum oxide. Silicon oxide is present as an additive. Once again the presence of a biphasic cement and silicon oxide changes the hydration. In the long term the calcium hydroxide, which is the main by-product necessary for these materials to remain bioactive is depleted questioning the long-term efficacy of these materials (4). This mechanism is very well documented for Portland cement in the construction industry where amorphous silicon dioxide is added to the cement to react with the calcium hydroxide producing more tricalcium silicate thus enhancing the physical properties of the material in the long term. The silicon dioxide is referred to as a latent hydraulic binder.

The bioceramic range with biphasic cement compositions was extended to the group of

materials manufactured by Brasseler (Savannah, GA, USA) known as Endosequence. The Endosequence materials are being distributed in Europe as TotalFill (FKG Dentaire, La Chaux-de-Fonds, Switzerland). These materials include a putty, a root repair material and a sealer. All of them are premixed thus they hydrate by contact with environmental moisture. For the sealer the availability of moisture using a low-pressure model showed that the fluid available was enough for the sealer to hydrate (21). The composition of the sealer is different to that of the putty and root-repair material. Both are biphasic cements consisting of tricalcium silicate and calcium phosphate. However the putty and root repair material include zirconium oxide and tantalum oxide as radiopacifiers with no additives. The sealer does not include the tantalum oxide but is made up of the two cement phases and zirconium oxide (21).

Other sealers based on tricalcium silicate with a similar formulation to the root repair materials are available. Angelus has MTA Fillapex. Besides the Portland cement and bismuth oxide in a resin matrix this formulation also incorporates silicon dioxide (22). This sealer does not release calcium hydroxide. This could be a consequence of the reaction of calcium hydroxide with the silicon dioxide as that reported for Bioaggregate (4) and also the hydrophobicity of the resin matrix, which could impede the leaching of calcium in solution. Another tricalcium silicate-based sealer has been developed which is composed of tricalcium silicate and zirconium oxide with calcium chloride and a water-soluble polymer additives (BioRoot RCS, Septodont). This sealer release double the calcium ions in solution compared to the Endosequence BC sealer (21).

There are several other products, which exhibit similar components to the original MTA formulation with some variations. More details on MTA and the various related materials both available for clinical use and experimental ones can

be found in the book Mineral Trioxide Aggregate in Dentistry; From preparation to application (23). From the literature reviewed it is clear that all these materials are based on tricalcium silicate and include a radiopacifying material. Why some are called Bioceramic seems unclear. Bioceramic is a broad term that tends to lead to confusion. Thus one can consider this as a misnomer like the term mineral trioxide aggregate since the material is not an oxide and also not an aggregate. Fancy names may attract sales but do very little to enhance the science.

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Introduction: This study aimed to compare the marginal adaptation of new bioceramic materials, EndoSequence Root Repair Material (ERRM putty and ERRM paste), to that of mineral trioxide aggregate (MTA) as root-end filling materials. Materials and Methods: Thirty-six extracted human single-rooted teeth were prepared and obturated with gutta-percha and AH-26 sealer. The roots were resected 3 mm from the apex. Root-end cavities were then prepared with an ultrasonic retrotip. The specimens were divided into three groups (n=12) and filled with MTA, ERRM putty or ERRM paste. Epoxy resin replicas for optimal cytocompatibility of a bioceramic nanoparticulate cement in primary human mesenchymal cells. *J Endod.* 2009 Oct;35 (10):1387-90. Camilleri J. Color stability of white mineral trioxide aggregate in contact with hypochlorite solution. *J Endod.* 2014 Mar;40(3):436-40. Marciano MA, Costa RM, Camilleri J, Mondelli RF, Guimarães BM, Duarte MA. Assessment of color stability of white mineral trioxide aggregate angelus and bismuth oxide in contact with tooth structure. *J Endod.* 2014 Aug;40(8):1235-40.