

## Modification of Glass Ionomer Restorative Material: A Review of Literature

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### Abstract

Conventional glass-ionomer (GI) cements have a large number of applications in dentistry. They are biocompatible with the dental pulp to some extent. GI is predominantly used as cements in dentistry; however, they have some disadvantages, the most important of which is lack of adequate strength and toughness. In an attempt to improve the mechanical properties of the conventional GI, resin-modified glass-ionomers have been marketed, with hydrophilic monomers, such as hydroxyethyl methacrylated (HEMA). Some recent studies have evaluated GI with modification in its structure to validate the claims that such a combination will improve tooth bioactivity, regeneration capacity and restoration. There is ever-increasing interest in the application of bioactive materials in the dental field in an attempt to remineralize affected dentin. The aim of this review article is to evaluate these materials and their characteristics and applications.

**Keywords:** Metal Reinforced Glass Ionomer; Nanoionomer; Fiber Reinforced Glass Ionomer; Titanium Dioxide Nanoparticles

### Introduction

Glass-ionomers (GIs) were first introduced to the dental field in 1972 by Wilson and Kent [1]. Their chemical adhesive potential and fluoride releasing properties have led to their widespread use as luting materials, cavity liners and bases, as well as restorative materials. Glass ionomer cements have different applications in dentistry including its use as: type I used for luting crowns, bridges and orthodontic brackets. These types are characterized by their rapid set and low film thickness. Type II a: aesthetic restorative cements, they are available in both conventional and resin modified presentation. Type II b: reinforced restorative cements. They are not necessarily stronger than type II a, however they are more wear resistant. Type III used as lining cements and base which is characterized by low viscosity and rapid set [2]. The chemistry is essentially the same for all three categories, but there are variations in powder - liquid ratio and powder particle size to accommodate the desired function [3].

### Modification of glass ionomer cements

Successive changes have been made in conventional GIC in order to overcome the deficiency of their mechanical integrity and their ability to withstand fracture loads. Thus, several materials have emerged with different composition such as glass ionomer cements reinforced with metal or modified with resin, in addition to the high viscosity ionomer cements, as well as those with incorporation of nanoparticles. All these modifications were done to meet individual clinical needs and to improve the physicochemical properties of GICs [4]. For many years, there have been attempts to incorporate fibers into the composition of these materials as reinforcing agents [5]. but there are variations in powder - liquid ratio and powder particle size to accommodate the desired function [3].

### **Metal reinforced glass ionomer cements**

Metal reinforced glass ionomer cements were first introduced in 1977 [6], in an attempt to reinforce glass ionomer cements, and to render them sufficiently radiopaque as well [7]. Silver tin metal alloys were either incorporated with glass powder, resulting in a silver alloy admix, or were sintered with glass, producing a glass cermet material [6,8]. The addition of silver amalgam alloy powder to conventional materials enhanced different mechanical properties of the cement and provided radiopacity. Subsequently, silver particles were sintered onto the glass, and a number of products then appeared where the amalgam alloy content had been fixed at a level claimed to produce optimum physical and mechanical properties for a glass cermet [9]. Cermet cements were prepared by sintering the metal and glass powders together. Strong bonding of the metal to the glass was achieved. Ion leachable calcium aluminum fluorosilicate glasses were used in the preparation of the glass powder and a number of metal powders were tried including alloys of silver and tin, pure silver, gold, titanium and palladium. Gold and silver were found to be the most suitable materials. Cermet cements have greatly improved resistance to abrasion when compared with glass ionomer cements and their flexural strength was found to be higher also. However, their strength is still insufficient to replace amalgam alloys and their use should be confined to low stress bearing cavity preparations [3].

These cements have short setting times. They can be finished five minutes after the start of mix. They lack translucency, therefore, they are used only in areas where esthetics is of no concern. This type has improved mechanical and chemical properties compared with conventional glass ionomer cements, such as higher compressive strength and better wear resistance. Fracture resistance was found to be similar to the unreinforced type [10]. However, these products have poor adhesion to tooth structure [11]. Also, the initially released appreciable amounts of fluoride decrease over time compared to the conventional GICs, a lower fluoride amount is released from the cermet cement, because a portion of the glass particles is metal coated [8]. A recent clinical study has shown that the durability of the cermet ionomer cements as posterior restorative was inferior to conventional glass ionomer cement [11,12].

### **Resin modified glass ionomer cements**

In 1980, resin modified glass ionomer cements (RMGIC) were developed to overcome the disadvantages of conventional glass ionomer cement. Resin modified glass ionomer cements are hybrid of glass ionomer and composite resin, and thus contain acid base and polymerizable components. Resin modified ionomers are usually formulated from fluoroaluminosilicate glasses, photo-initiators, polyacrylic acid, water, and a water-soluble methacrylate monomer, such as hydroxyethyl methacrylate (HEMA), which may or may not be grafted onto the polyacrylic acid [13]. Although commercial materials vary widely in composition, the essential component of resin modified glass ionomer cements are polycarboxylic acid polymer with some pendent methacrylate monomer and free radical initiators. The liquid contains methacrylate modified carboxylic acid and water miscible methacrylate monomer, as hydroxyethyl methacrylate (HEMA) or glycerol dimethacrylate (GDMA). In another type, the polymer is unmodified polycarboxylic acid. In this case, the liquid is formulated with a mixture of hydrophilic methacrylate monomers and water. The water content of these materials is lower and the monomer content is higher than for the first type, so the coefficient of thermal expansion is higher. Free radical initiators are added to trigger the curing of the methacrylate group. The powder is fluoroaluminosilicate glass similar to the glasses described for conventional glass ionomer cement [14].

In resin modified glass ionomer cement (RMGIC), the polymerizable functional groups impart more rapid curing when activated by light or chemicals and still allow the acid base reaction to take its course long after polymerization [8]. Thus, the setting reaction is said to be a dual mechanism. The usual glass ionomer acid base reaction begins on mixing the material, followed by a free radical polymerization reaction which may be generated by either photoinitiators or by chemical initiators or both. If chemical initiators are included, the polymerization reaction will begin on mixing as well. The acid base reaction in this modified cement system was found to slow down as some of the water has been replaced by HEMA [15]. Finally, two matrices are formed: Metal polyacrylate salt hydrogel and a polymer. The initial set of the resin modified glass ionomer cement is the result of the formation of polymer matrix. The resin modified glass ionomers must be capable of setting without being photocured, that is, it sets under condition where no polymerization reaction occurs, with the acid base reaction still being active [16]. This acid base reaction is essential for its setting as well as the diffusion based adhesion between the

tooth surface and the cement, in addition to the continuing fluoride release [17]. Tri-cure glass ionomer system is a resin modified glass ionomer cement with an additional curing mode. It was developed to overcome the limited depth of visible light penetration ability. Here, in addition to the photo-initiators, self-cure redox initiator are added so that the methacrylate polymerization can proceed in the absence of light. The three curing reaction are: chemically-activated polymerization, light-activated polymerization and an acid-base reaction. The chemically activated reaction, as well as the acid base reaction takes place spontaneously when the powder and liquid are mixed, while the light activated reaction is initiated by light. The redox cure is quite rapid to allow the material to be placed in bulk, if desired [14]. The resin modified glass ionomer cements (RMGICs) have some advantages over the conventional glass ionomer materials concerning its longer working time, ability for earlier finishing, better esthetics and enhanced strength characteristics [18]. However, they have not been proven to be superior to the conventional glass ionomer materials with regard to the strength of the adhesive junction, resistance to water up take, fluoride release, solubility and biocompatibility [17,19]. Addition of resin has not significantly reduced dehydration of the glass ionomer component of these cements, and dehydration shrinkage has been observed as late as 3 months after maturity [19]. A significant disadvantage of the resin ionomers is the hydrophilic nature of poly hydroxy ethyl methacrylate (polyHEMA), which results in increased water sorption and subsequently its hygroscopic expansion. This behavior is analogous to a synthetic hydrogel. Although initial water sorption has deleterious effects [20].

### Nanoionomer

Nowadays, nanotechnology, also known as molecular nanotechnology or molecular engineering, has been introduced in dental field providing a cosmetically acceptable restoration with excellent mechanical and physical properties [21]. In 2007, a new generation of resin modified glass ionomer cements (RMGICs) was introduced. Ketac nano (3M ESPE) is described by the manufactures as (nano-ionomer). Incorporation of nanotechnology in this materials enhances their physical properties [21]. Nanoionomer combines nanofillers and clusters with fluoroaluminosilicate glass particles in such a way to improve color characteristics and polishability. This new nano filled resin modified glass ionomer restorative material has been introduced for restoration of primary teeth and small cavities in permanent teeth. It is based on a prior resin modified glass ionomer from the same manufacturer (Vitremer), with a simplified dispensing and mixing system that requires the use of a priming step, but no separate conditioning step. Its primary curing mechanism is by light activation, and no redox or self-curing occurs during setting. This system allows a highly packed filler composition incorporation, of which approximately two thirds are nano fillers [22]. The fluoride release profile of the nanofilled resin modified glass ionomer cement is similar to that of the RMGIC [23].

### Fiber reinforced glass ionomer cement

In an another attempt to improve strength of the conventional GIC, incorporation of alumina fibers and others such as glass, silica and carbon has led to the development of fiber reinforced glass ionomer cement. These fiber reinforced ionomers have diametrical tensile strength and flexural strength of 1.8 and 4.5 times respectively compared with conventional GIC [4] and almost 140% increase in fracture toughness [24].

The addition of short glass fibers to glass ionomer cement was found be more effective in strengthening, if the fibers composition is similar to that of the fluoroaluminosilicate glass of the cement powder. Therefore, a glass fiber composed of  $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$  was used in an attempt to strengthen glass ionomer cement. Other studies used glass fibers of 0.1 up to 12 mm in length to reinforce polypropylene and resin composite materials [25-27]. The fibers were prepared from a glass frit of the system  $\text{SiO}_2\text{-AlO}_3\text{-CaF}_2\text{-Na}_3\text{AlF}_6$ . The clinical characteristics of these materials have been compromised due to difficulty in mixing and a lack of bonding between fiber and matrix leading to decreased abrasion resistance [3].

### Highly viscous conventional glass ionomer cement

Recently, several fast setting and high viscosity conventional GICs have been available, also called viscous or condensable glass ionomer cements [28]. To overcome early moisture sensitivity and low mechanical properties associated with conventional materials, these restorative materials were originally developed in the early 1990s to be used as a restorative material [29]. These materials set faster and are of higher viscosity because of finer glass particles, anhydrous polyacrylic acids of high molecular weight and a high p/L mixing ratio [30]. The setting reaction is the same as the acid base reaction typical of conventional glass ionomer cements [30].

### Addition of titanium dioxide nanoparticles

Adding apatite and titanium nanotubes to resin based cements was found to increase fracture toughness, flexural strength and compressive strength, as well as hardness and modulus of elasticity of the resin based cements, without changing their radiopacity or biocompatibility [31]. In 2011, Elsaka, *et al.* [32] evaluated the effect of adding titanium dioxide nanoparticles to conventional glass ionomer cement in three different ratios 3, 5 and 7 wt%. They found that, glass ionomer cement containing 3 and 5 wt% titanium dioxide nanoparticles showed improved fracture toughness, flexural strength and compressive strength compared to unmodified glass ionomer cement. However, a decrease in mechanical properties was found for glass ionomer cement containing 7wt% titanium dioxide nanoparticles. Glass ionomer containing 5 and 7 wt% titanium dioxide nanoparticles had decreased surface micro hardness. Setting time of glass ionomer containing titanium dioxide nanoparticles was accepted. The addition of titanium dioxide nanoparticles to the conventional GIC did not compromise its bond strength with dentin or its fluoride release. Glass ionomer containing TiO<sub>2</sub> nanoparticles processed the most potent antibacterial activity against streptococcus mutants compared to the unmodified glass ionomer [33].

### Conclusion

The recent studies attention that the increasing use of “smart” bioactive materials in dentistry, especially with the aim of remineralizing dentin. Modified forms of glass-ionomer are available, in the form of resin-modified glass-ionomers and glass carbomer. The former include a monomer and set in part by an addition polymerization, which augments the acid-base process and can be controlled using light activation. Physical properties of these materials are comparable with those of conventional glass-ionomers, but their biocompatibility is less good. More research is required to develop our understanding how to improve the characteristics of these materials.

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