Available online at http://www.journalcra.com

ISSN: 0975-833X

International Journal of Current Research
Vol. 11, Issue, 04, pp.2925-2929, April, 2019

DOI: https://doi.org/10.24941/ijcr.35059.04.2019

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

REVIEW ARTICLE

CONVENTIONAL GLASS-IONOMER RESTORATIVE MATERIAL; AN OVERVIEW

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ARTICLE INFO

Article History:
Received 07th January, 2019
Received in revised form
14th February, 2019
Accepted 07th March, 2019
Published online 29th April, 2019

Key Words:
Glass Ionomer, Cement, Restorative Material, Biocompatibility.

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ABSTRACT

Glass ionomers were introduced to the profession 25 years ago and have been shown to be a very useful adjunct to restorative dentistry. Glass ionomer cement composed of a calcium – alumino – silicate glass powder and an aqueous solution of an acrylic acid homo – or copolymer. These cements possess certain unique properties that make them useful as restorative and adhesive materials, including adhesion to tooth structure and base metals, anticariogenic properties due to release of fluoride, thermal compatibility with tooth enamel, and biocompatibility.

***Citation*: *Dhafer Al shaibani et al.,* 2019.** "Conventional Glass-Ionomer Restorative Material; An overview", *International Journal of Current Research*, 11, (04), 2925-2929.

INTRODUCTION

Glass-ionomers (GIs) were first introduced to the dental field in 1972 by Wilson and Kent (Wilson, 1972). 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. In addition, the coefficient of thermal expansion for GIs is close to that of tooth structure and they are considered biocompatible with low cytotoxicity (Wilson, 1972; Anusavice, 2003; Powers, 2006). Although glass ionomers are often used as restorative materials, they cannot generally withstand the forces generated in the posterior area of the mouth because of their low mechanical properties, especially the low fracture toughness. Consequently, GI restoratives are recommended for anterior restorations, rather than posteriorly, where the stress is much lower in the anterior region of the oral cavity (Crisp, 1976; Dowling, 2006)

Glass Ionomer Cements: The term glass ionomer cements (GICs) are exclusively reserved for material that involve a significant acid base reaction as a part of its setting reaction and show a continuing fluoride release.

Glass ionomer cements were introduced by Wilson and Kent in 1969 in an effort to combine in a luting cement, the translucency and fluoride release of silicate cement with the adhesion to tooth structure of polycarboxylate cement (Finch, 1994). 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. (Tyas, 2004). 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 (Upadhya, 2005).

Conventional glass ionomer cements: Conventional glass ionomer cements (GICs) consists of finely ground fluoroaluminosilicate glass filler that is ion leachable. It has no susceptibility to dissolution which is a disadvantage in silicates by substituting phosphoric acid with the polymeric carboxylic acids of zinc polycarboxylate materials (Greig, 2012). The liquid is typically a mixture of polyacrylic acid and may contain itaconic and maleic acids. Depending on the product, the liquid component does not necessarily contain all of the acid, since in some products the polyacrylic acid is incorporated into the powder in its dehydrated form leaving the liquid to consist of water or an aqueous solution of tartaric acid. (An atlas of glass-ionomer cement, 2002). The main glasses are based on the systems; SiO_2-AL_2O3-CaF_2 or SiO_2-AL_2O3-CaO. These are similar to those used in the former dental silicate cement but the alkalinity of glass ionomer should be greater, to compensate for the reduced acidity of polyacrylic acid compared to phosphoric acid in silicate cement (Kent, 1979). When ratio of Si-Al atoms in the network is between 2:3 to 1:1, these glasses are somewhat alkaline and susceptible to acid attack and are able to leach ions. Later glasses in commercial materials contained more sodium and less fluoride, (Mathis, 1989; Culbertson, 2001) sodium has a deleterious influence on the solubility, hydrolytic stability and mechanical properties of the cement. It is likely to be released from the glass in greater proportions relative to the other cations present in the glass, as it is known to be relatively mobile at low temperatures in silicate glasses and can be easily exchanged for hydrogen ions (De Barra, 1998). Sodium ions compete with calcium and aluminum cations for carboxylate groups in the polyacid chains and therefore inhibit the cross-linking process. There are advantages in the use of either strontium or lanthanum to replace some or all of the calcium, in as much as these elements introduce a degree of radiopacity. Fluoride is present at some level and this is to lower the temperature of glass fusion, to improve the handling properties of the cement mix, to increase the strength and translucency of the set cement and to enhance the fluoride release (Greig, 2012; An atlas of glass-ionomer cement , 2002) Zinc oxide and barium glasses can be added to the powder to increase radiopacity (Greig, 2012). The liquid component of the original glass ionomer cements is an aqueous polyacrylic acid at a concentration of 45% by mass (Tyas, 2004). The polyacid either is part of the liquid as an aqueous solution or is incorporated into the cement powder as a dried powder. In the latter case, the liquid is simply water which the dried polyacid dissolves upon mixing (Saito, 1999). The new liquid formulation is 40-50% solution of 2:1 polyacrylic acid – itaconic, maleic, or tricarboxylic acids. These acids reduce the viscosity of the liquid and inhibit gelation caused by intermolecular hydrogen bonding and increase reactivity of the liquid.(10.,2) The reactivity depends on the ingredients of the acid as well as on its molecular weight and concentration . By adding maleic or itaconic acid there is increase in the number of carboxylic groups relative to the total molecular weight and thus the reactivity is increased (Saito, 1999).

A higher polyacrylic acid concentration will lower the pH, increase the rate and extent of reaction, and lower water contents. This factor, in addition to the increased ionic cross links, result in a lower content of unbound water. It is likely that this will also serve to increase Young's modulus, since unbound water will act as plasticizers. At very high concentrations of acids, the reaction may be suppressed by the lack of water for hydrating the complexes formed or by insufficient metal cations being available for a complete neutralization (Crisp, 1979). Additives such as L-(+)-tartaric acid is effective since it prolongs working time and provokes a snap set. In presence of L-(+)-tartaric acid , metal ions are still extracted from the glass , but on release , they apparently react preferentially with the tartaric acid to form the glass, and thus delays the formation of the polysalt matrix (Crisp, 1979) L-(+)-Tartaric acid not only react rapidly to yield calcium tartrate, but also enhance the rate at which aluminum polyacrylate is formed within the cement (Nicholson, 1988). In addition, it has a beneficial effect on the early strength and hardness (An atlas of glass-ionomer cement, 2002; Crisp, 1979) Anhydrous (water – settable) glass ionomer was made to overcome the problem of high molecular weight of glass ionomer liquids which reduce their shelf life. Polyacid is freeze dried and added to the glass fillers. This powder is mixed with 30% solution of tartaric acid or tartaric acid is freeze dried and added to glass powder which is then mixed with distilled water. These anhydrous glass ionomers have an unlimited shelf life. The acid powder dissolves to reconstitute the liquid acid and this process is followed by the acid base reaction, when the powder is mixed with water. Semihydrous materials are based on using both hydrous and anhydrous forms of polyacid in the same product. This combination provides intermediate liquid viscosities for luting that speeds the initial slow set associated with the anhydrous materials. The shelf life is somewhere between the hydrous and anhydrous forms (Anusavice, 2003; Albers et al., 2002)

Reaction of conventional glass ionomer cements: Conventional glass ionomer cements set through an acid base reaction. This reaction takes place in three phases. The first phase: setting starts initially by neutralization of acid groups on polymeric acids, like polyacrylic acid, with powdered solid groups (calcium fluoroaluminosilicate glasses). These glasses are alkaline because they are proton acceptors, even though they are not soluble in water. The hydrogen ions formed from the ionization of polyacrylic acid, attack the glass particles converting their peripheries into silica based hydrogels with the release of calcium and fluoride ions, in addition to silicic acid from the glass surface (Nicholson, 1998). The attack of acid on the glass particles is not uniform and occurs rapidly when the components are mixed and preferentially at the calcium rich sites. (Wilson, 1989) In the second phase, ions migrate out of the hydrogel and into the aqueous cement phase where they precipitate out as the pH increases. The resulting calcium and aluminum polycarboxylates ionically cross-link the polymer chain to form the basic cement matrix. Because calcium ions are released in greater quantities from glass than do aluminum ions, the calcium polycarboxylate forms first. Calcium ions have a divalent rather than trivalent charge which enables them to migrate faster into the aqueous cement and do not form stable fluoride complexes as do aluminum ions. As a result, they are more readily available to perform the cross linking. The aluminum polycarboxylate is stronger and more stable than calcium polycarboxylate. Therefore, the properties of the cement improve over time as aluminum polycarboxylate forms in greater quantity (Jones, 1998). This calcium polycarboxylate gel is sensitive to moisture and changes after several hours into a stable, water insoluble calcium- aluminum polycarboxylic gel through the additional deposition of aluminum ions and at that time the materials reaches the polysalt gel phase which is the third phase (Zimehl, 2000). As the cement matures over the first twenty four hours and beyond, progressive cross linking occurs with hydrated aluminum ions. This leads to decreased sensitivity to moisture and increase in the percentage of bound water as well as glass transition temperature of the set cement (Brein, 2002). The set cements consists of unreacted particles surrounded by silica gel, held together by an amorphous matrix of hydrated aluminum and calcium polyacrylate salt. (Prosser, 1984). Release of fluoride occurs through this acid base mechanism (Mount, ?). Oxalic acid has accelerating effect on both the working and setting times, due to its pH lowering action. This would enhance the release of ions from the surface of the glass and increase the rate of cross linking of the matrix. This effect would be further enhanced by the addition of a more acidic buffer (Prentice, 2006). Water plays a key role for proper maturation of glass ionomer cement. Both water contamination and dehydration during the initial setting stages can compromise the physical properties of the restoration (Czarnecka, 2002). During the first stages of the setting process, water from the cement liquid is fully incorporated into the cement structure. (Barry, 1979). During cement setting, the cement paste has to be protected from additional water in order to prevent dissolution of metal cations. If water comes in contact with cement surface, Al^{+3} and Ca^{+2} will be washed out, leading to loss of translucency and easily disintegration of the cement in the oral fluids. Once the cement has set into a solid state, water can occupy various locations, for example coordination sites around metal cations or hydration regions around the polyanion chain (Wasson, 1993). At this stage, loss of water can lead to cracking and crazing of the cement surface, resulting in a chalky surface appearance (Nicholson, 2009). As the cement ages the proportion of loosely bound water decreases relatively to the proportion of tightly bound water (Crisp, 1979; Naasan , 1998). To prevent the cement from those disadvantages, it is recommended to strictly exclude water during the weak setting stage, which is reported to last for 1 hour until even 2 weeks after placement (Prosser, 1986). Petroleum jelly, cocoa butter and waterproof varnishes, have been recommended as suitable surface coating agents (Hotta, 1991; Rodrigues Garcia, 1995). With time, those coatings are lost by oral masticative wear, but during this time, the cements become more resistant to variations in water balance due to their post hardening (Naasan, 1998). Among the coating strategies , light polymerized bonding agents are able to limit water movement across the setting cement surface (Rodrigues et al., 1995). Recently, a new restorative system application consisting of posterior restorative glass ionomer cement combined with a novel nanofilled coating material is available. This self-adhesive nanofilled resin coating provides a high hydrophilicity combined with an extremely low viscosity that accounts for a perfect seal of glass ionomer cement surface and improves the esthetic properties of the system (Tanaka, 2007).

Properties of conventional glass ionomer cement: Conventional GICs have the main advantages of chemical adhesion to the tooth surface through ionic bonding. In addition cavity sealing, pulpal protection, prevention of leakage at themargins as well as the decrease of secondary caries occurrence are amongst the important advantages of GICs (Wilson, 1988). These properties allow cavity forms to be more conservative and to some extent, reinforces the remaining tooth by integrating restorative material with the tooth structure (Cho, 1999). Conventional GICs are tooth coloured and available in different shades. They have containuous fluoride release, which could lead to prevention of further breakdown of tooth structure (Wilson, 1988). The chemical bond of GI to enamel and dentine takes place by the reaction of phosphate ions in the dental tissue with carboxylate groups from polyacrylic acid. (Wilson, 1983). When freshly mixed conventional glass ionomer cement is placed on enamel or dentine, dissolution of any smear layer occurs but demineralization is minimal since the tooth hydroxyapatite buffers the acid, and polyalkenoic acid is quite weak.(38) Phosphate ions (-vely charged) and calcium ions (+vely charged) are displaced from the hydroxyapatite, and are absorbed into the unset cement. This results in an intermediate layer between the pure glass ionomer cement and the pure hydroxyapatite; the so called ion-exchange layer. (GJ M, 2002) Conventional GICs show good biocompatibility because they have; rapid PH neutralization (Cook, 1982) and low setting exotherm (Crisp, 1978) They are known to release Na, Al, Si, P and F under neutral conditions, and to also release Ca under acidic conditions (Czarnecka, 2002; Brookman, 1986). Fluoride release is considered one of the important clinical advantages of glass ionomer cements. Release occurs by two mechanisms, a relatively rapid early dissolution process "wash-out" from the surface layers, in addition to a slower long-term process that relies on diffusion of the fluoride ions through the bulk of the cement. If fluoride release occurs by a wash out mechanism, it results in leaching of other ions from the material like calcium, associated with gradual disintegration of the material.

It was suggested that there were at least three simultaneously occurring processes that ought to be considered; surface erosion, dissolution from cracks and dissolution by solid state diffusion from the bulk (Nicholson, 2014). Fluoride release have an initial "burst" effect to stop caries and induce remineralization, in addition to the long-term release. However, the inherent fluoride is depleted fairly quickly within the first few months. The greatest fluoride release takes place in the first 24-48 hours followed by a low prolonged elution. The rate of release of fluoride (after the initial burst) from glass ionomer is diffusion-controlled, not related to their chemistry and significantly higher at PH 4 by a factor of 3 to 4 times greater than at neutral condition (Tiwari et al., 2013). Bell et al. (1999); (Bell, 1999) reported that maximum fluoride release occurs within the first day following the setting of the material and falls to a plateau after several weeks. It is assumed that glass ionomer cements have a caries-inhibitory effect which is due to their long-term and sustained fluoride release. Also, fluoride from glass ionomer cement is responsible for bacterial inhibition (especially against streptococcus mutans), in conjunction to other components such as zinc, aluminum and strontium.

The coefficient of thermal expansion of conventional glass ionomer cements is close to that of dental hard tissues, which produce good marginal adaptation of glass ionomer restorations (Burgess, 1994). Also, glass ionomer cements are good thermal insulators over a wide range of powder-liquid ratio not as the other polyelectrolyte cements such as polycarboxylate and silicate cements in which the thermal diffusivity increase with increasing powder- liquid ratio (Burgess, 1994). Concerning the limitations of conventional GICs, it can be mentioned that they relatively lack strength and have low resistance to abrasion and wear. Conventional glass ionomer cements are very brittle material and prone to bulk fracture as they.

Clinical applications of conventional glass ionomer cements
GICs have been used in a variety of clinical applications at an expanding rate since their introduction to dentistry. It is used for restoring carious lesions in low stress areas, as a luting

cement in crown and bridge work, lining cement under metallic restorations, a base for composite restorations and as a long term sealant over an active carious lesion. (48) Recently, glass ionomer cements have also been used as coatings on obturation points.(36) GICs are the material of choice for root caries restorations because of their excellent ion exchange, adhesion to dentine, caries inhibition and simplified placement protocol as compared with dental resin composite.(47)

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