Review article | International Journal of Dental Materials 2022;4(4) | ISSN:2582-2209

An overview of advances in glass ionomer cements

Udaya Sri Naga Gayatri Saridena[1,*], Gnana Siva Sai Jayalaksmi Sanka[1], Rama Krishna Alla[2], Ramaraju AV[3], Suresh Sajjan MC[3], Satyanaryana Raju Mantena[3]

[1]Undergraduate Student, Vishnu Dental College, Bhimavaram, West Godavari, Andhra Pradesh, India.
[2]Associate Professor, Department of Dental Materials, Vishnu Dental College, Bhimavaram, Andhra Pradesh, India.
[3]Professor, Department of Prosthodontics and Implantology, Vishnu Dental College, Bhimavaram, Andhra Pradesh, India.

Article History

Received *7th November 2022*

Accepted *12th December 2022*

Available online *31st December 2022*

*Correspondence

Udaya Sri Naga Gayatri Saridena

Undergraduate Student,
Vishnu Dental College, Bhimavaram,
Andhra Pradesh, India

E-mail: saridena.gayatri@vdc.edu.in

DOI: http://dx.doi.org/10.37983/IJDM.2022.4403

Abstract

Glass-ionomer dental cements (GICs) are aesthetic direct restorative materials with anticariogenic activity. Glass-ionomers are composed of alumino-silicate glass powder and poly acrylic acid liquid. The significant characteristics of GICs among restorative materials are their ability to bond to moist tooth structure without any pre-treatment and to provide a prolonged period of fluoride release, which prevents subsequent tooth decay (caries). These characteristics, along with the materials' acceptable aesthetics and biocompatibility, make them popular and desirable for use in medical and dental applications. However, GICs exhibit poor mechanical qualities and moisture sensitivity. To improve their mechanical and physical qualities, the GIC powders have undergone extensive formulation and modification. This paper provides an overview of various fillers used to enhance the mechanical and physical properties of GICs.

Keywords: Dental Glass Ionomer Cement, Compomer, Resin modified GIC, Giomer, Nanoparticles

1. Introduction

Wilson and Kent developed glass ionomer cement in 1969. The reaction of acid polyacrylate and basic glass particles produced this cement. The generic name for glass ionomer cement was derived from its primary ingredients, alumino-flouro-silicate glass and polyacrylic acid (PAA). Glass ionomer cement was produced to capitalize on the advantages of both silicate cement and polycarboxylate cement [1,2]. GIC has evolved into a diverse dental product that is used in a variety of dental procedures as a Restorative material, luting agent, cavity liner and base, pit and fissure sealant, Endodontic sealant, and atraumatic restorative material over the last few years. GIC is the material of choice for many dental procedures, including the Sandwich technique, root caries, non-stress bearing build-up, and long-term provisional restorations [2].

The advantages of GICs include their biocompatibility, chemical adhesion with the natural tooth, aesthetic nature, fluoride-releasing, and coefficient of thermal expansion similar to the natural tooth, which aids in the remineralization of caries-affected dentin [1-3]. However, GICs are not ideal in every aspect, with shortcomings such as low compressive strength, susceptibility to moisture, and limited or less wear resistance. To address the previously mentioned deficiencies of GICs and meet the patients' demands, they have been undergoing tremendous modifications in the composition, which led to the development of numerous GICs [4]. Various GICs developed are listed in the Table 1. This paper reviews the various Glass Ionomer cements developed.

2. Modified Glass Ionomer Cements

2.1 Metal Modified glass ionomer cements

Metallic fillers have been added to glass ionomer cements to improve their strength, fracture resistance, toughness, and wear resistance.

2.1.1 Silver alloy modified GICs

Two different approaches have been proposed with the addition of silver alloy powder. The materials obtained with the first method are known as "Silver alloy admix," which involves mixing a spherical silver amalgam alloy powder with type II glass ionomer powder [2,4]. In the second method, the mixture of spherical silver alloy powder and type II GIC is sintered at high temperatures, resulting in the fusing of the glass powder with silver particles. The obtained product is ground to a fine powder and frequently referred to as "cermet." [2,4]

Biological properties are comparable to those of traditional glass ionomers. The pH is approximately 6-7. Because the admixed cement emits more fluoride ions than type II glass ionomer cement, it is more anticariogenic. Cermet has a lower fluoride ion release than type II glass ionomer cement [2].

These cements surpass conventional glass ionomer cement in compressive strength and fatigue limit values. The erosion resistance of these materials has improved noticeably compared to the majority of other glass ionomer cements, which is probably due to the rapid setting of these materials. The flexural strength of these cements is comparable to that of the traditional GIC. However, the addition of silver alloy powder resulted in poor aesthetics [2].

2.1.2 Fe_2O_3 based Glass Ionomer cements

Table 1. List of Glass Ionomer Cements developed

1. Metal modified GIC	10. Incorparation of hydroxy apatite (HA) and HA/ZrO_2 in GIC
2. Resin modified GIC	11. GIC containing YbF_3 and $BaSO_4$
3. Packable GIC	12. Yttria stabilised ZrO_2 GIC
4. Low viscosity GIC	13. Niobium silicate GIC
5. Compomers	14. Boric acid modified GIC
6. Giomers	15. ZrO_2 added GIC
7. Ceramic reinforced GIC	16. Fe_2O_3 containing GIC
8. Amino acid modified GIC	17. Zinc containing GIC
9. Stain less steel GIC	18. SIC in GIC

Conventional GIC produces Al+3 ions, which are neurotoxic and have a negative impact on bone mineralization. To mitigate these effects, Fe_2O_3 is used instead of Al_2O_3. The Fe_2O_3 releases Fe^{3+} ions, which the body can manage and have fewer toxic effects [5].

Hurrell Gillingham *et al.* (2006) [5] substituted the Al_2O_3 with Fe_2O_3 in the conventional GIC and demonstrated good in vitro biocompatibility. The following is the chemical composition of these modified cements:
$4.5SiO_2.3Fe_2O_3.XP_2O_5.3CaO.2CaF_2$
Where X is in the range of 0-1.5.

They found that the handling properties of Fe_2O_3 modified cements ate similar to conventional GIC. Also, a relative improvement in the in vitro biocompatibility were noted for all GICs fabricated from Fe_2O_3-containing glasses [5].

2.1.3 Zinc-based Glass Ionomer cements

Boyd *et al.* (2005) [6] combined a calcium-zinc-silicate glass powder with the PAA. The flexural strength of these newly developed formulations was comparable to that of conventional GICs. They did, however, have a lower compressive strength than conventional GICs, which can be attributed to the powder's Zn^{2+} ions, which form ionic bonds with the carboxylate (COO^-) groups of PAA.

Hopeite ($Zn_3(PO_4)_2.4H_2O$) is a non-cohesive, crystalline structure formed in cements with high zinc and low calcium [2]. In addition, in the glass structure, Silica tetrahedra are replaced by ZnO_4 tetrahedra. The remaining Zn ions make the glass more vulnerable to attack. Calcium ions stabilise ZnO_4 and reduce their reactivity in cements with the high calcium content [6].

2.1.4 Stainless-steel incorporated GIC

Stainless steel incorporated GIC was introduced by Kerby *et al.* [7]. This cement was formulated by mixing stainless steel particles with an average size of 9mm with conventional GIC. First, the stainless-steel powder was acid treated and followed by washing with distilled water and anhydrous methyl alcohol. This washing helps in obtaining clean and grease-free surfaces with high surface ionization. These cements exhibited a progressive increase in mechanical properties from 1hr to 24 hrs. The addition of stainless-steel particles into GIC demonstrated superior compressive and tensile strengths, favourable working and setting times, and low solubility. On the other hand, stainless steel particles impart a greyish colour, which makes the material unesthetic.

2.2 Resin Modified Glass Ionomer Cement

The resin-modified glass ionomer cements (RMGIC) were developed to address two fundamental limitations: moisture sensitivity and poor early strength due to a slow acid-base reaction. Different types of RMGICs are available depending on the setting mechanism method. They include chemical-, light-, dual-, and tri-cure glass ionomer cements [2].

RMGICs have higher tensile strengths than traditional glass ionomer cement because of increased plastic deformation. RMGIC has a compressive strength of approximately 105 MPa. However, they have a weaker shear bond strength than conventional glass ionomer cements [2].

RMGICs primarily serve as bases and liners and exhibit stronger bonds with composite materials. During the setting reaction, they contract more, changing the marginal adaptation. These glass ionomer cements are water-sensitive, and liner variants especially are prone to dehydration and water absorption [1,2,8].

Forsten L [9] reported an increase in the fluoride release for a longer time, up to 9 months, with the RMGICs compared to auto-cure GIC. They also discovered that the cement mix's consistency and pH have a significant impact on the fluoride release. They demonstrated that the thin consistency mixes with low pH resulted in releasing more fluoride ions.

2.3 Compomers

Compomers, also referred to as polyacid-modified composites, were first used in dentistry in the early 1990s. As suggested by its name, the word "compomer" refers to the two "parent" materials, ionomer and composite, respectively. The carious-affected teeth are restored using these aesthetic materials [2]. Critical properties like fluoride release, bonding with the tooth, and aesthetics are derived from its parent materials, GIC and composites.

Compomers are typically made up of resins and glass powder. The glass powder is a calcium-aluminum-fluorosilicate glass that has been embedded in a polymeric matrix. Dimethacrylate macromonomers are the main constituents of the resin matrix. The majority of the resins are composed of bifunctional monomers and modified methacrylates (UDMA, BisGMA, etc.). These resins are very viscous, but their viscosity can be decreased by adding suitable diluent monomers and strengthened by using silane-coated fillers [2,10,11].

Compomers also can release fluoride, though perhaps more slowly and ineffectively than self-curing GIC. This slow release may be because the matrix has fluoride ions enclosed within it, which slows the release of fluoride. Topical fluoride agents can help composite materials regain their ability to release fluoride [12]. The fracture toughness of compomers is less than that of the composites [10]. The microhardness, flexural and compressive strengths of the compomers were higher compared to GIC but lower than Composite. Surface roughness between the two materials was not noticeably different [11]. According to Bansal D and Mahajan M (2017) [13], adding 3% hydroxyapatite and 4% bio-active glass to the compound improved the enamel's demineralization resistance properties by raising the microhardness of marginal enamel. When compomer exposed to fresh lactic acid at weekly intervals for a period of six weeks, they were found to consistently change the pH of lactic acid storage solutions in the direction of neutrality [14]

Compomers are biocompatible in nature. They are aesthetically pleasing than GICs as they allows for the shade selection Due to release of fluoride and buffering capacity it decreases the incidence of secondary caries, therefore has anti-cariogenic effect [2,11]. However, fluoride releasing capacity of compomer is much less than self-curing GIC [10]. Compomers have poor colour instability and poor wear resistance. They lack adhesion to the tooth surface like composites.

2.4 Giomers

Giomer is a new family of fluoride releasing direct aesthetic restoratives. Giomer is a true hybridized restorative material of glass ionomer and resin composites [15]. Giomers are characterized by the presence of pre-reacted glass (PRG) fillers in the composites. Hybridization of GIC and composite involves the pre-reaction of "Flouro-aluminosilicate glass" powder with polyacrylic acid and forms a wet siliceous hydrogel. This hydrogel is then freeze, dried and ground to form the PRG fillers. These fillers are then incorporated into resin matrix [15, 16].

The indications of Giomers are almost same to those of the conventional GICs. The indications include restoration of cervical erosion and root caries, laminates and core build up, restoration of primary teeth, and repair of fracture of porcelain and composites [15-18].

Giomer has the fluoride release and fluoride recharge properties of glass ionomer cement, has excellent esthetics, is easy to polish, has strength, has physical properties, and resin composite handling [15,16].

Prereacted glass ionomer technology is classified in two categories such as full prereacted glass (F-PRG) and surface prereacted glass (S-PRG). In FPRG, all filler particles contain polyacrylic acid, and the fillers release a large amount of fluoride because the particle core reacts completely. In S-PRG, only the surface of glass filler containing polyacrylic acid, the glass core remains and releases sodium, borate, aluminum, silicate, strontium ions in addition to fluoride ions. Giomer S-PRG technology is a true hybridized restorative material of glass ionomer and resin composites, which has fluoride release and fluoride recharge properties [15-18].

2.5 Nano particles reinforced GIC

Nanotechnology is especially anticipated to contribute to advancements in dentistry and innovations in oral health-related diagnostic and therapeutic methods, along with advancements in materials science and biotechnology. The physical, chemical and biological characteristics of structures and their individual constituents are the focus of nanotechnology. Nanotechnology is centred on the concept of controlling individual atoms and molecules to produce functional structures. This technology will enable numerous advancements in the field of oral health sciences [19].

Numerous nanofillers have been experiments with the GICs to modify their characteristics and clinical performance. The nonofillers used in GICs including nanohydroxyapaptite [20-24], silica [25-28], titanium [29-32], zirconium [33], Barium Sulfate nanoparticles [34], etc.

Nicholson *et al.* (1993) [35] first investigated the impact of hydroxyapatite addition to GIC in 1993 and their findings have since guided subsequent research in this area. The mechanical properties, fluoride release, and resistance to bacterial invasion were all improved by the addition of nanohydroxyapaptite (nHA) [36-38].

Lucas *et al.* (2003) [38] added hydroxyapatite particles to the standard GIC because they have excellent biological properties, a similar crystal structure, and a composition to the hydroxyapatite found in natural teeth. In their study, GIC with particle sizes ranging from 0.3 to 200 microns was mixed with hydroxyapatite particles. They found that adding HA particles to traditional GIC did not prevent the release of fluoride ions, and that there was a significant improvement in the mechanical properties of the set matrix as well as long-term bond strength with dentine.

Gu *et al.* (2005) [39] discovered that the mechanical properties of restorative GIC containing zirconia powder and nHA were superior to those of hydroxyapatite alone. This increase in properties can be attributed to high strength, high modulus, hardness and insoluble nature of zirconia.

According to Gjorgievska E *et al.*, adding Al_2O_3, ZrO_2, and TiO_2 nanoparticles to GICs is advantageous because it reduces the microscopic voids in the set cement. Increased compressive strength was also achieved with these materials when ZrO_2 and TiO_2 nanoparticles were used. Al, Zr, or Ti ions were not detected in nanoparticles at detectable levels, making them appropriate for clinical use [31].

The addition nano particles like titanium oxide increased the material's mean compressive fracture strength. The use of silica nano particles enhances the microhardness, compressive and flexural strength, and shear bond strength [25]. When zirconia nano particles are introduced, the material is strengthened while becoming less brittle. Barium sulphate was observed to have an impact on the GIC's working conditions and setting times and Physical properties [40].

2.6 Packable Glass Ionomers

The term "high-strength glass ionomer cements" is another name for packable GICs. These were developed for use as part of the atraumatic restorative therapy in third-world countries (ART). A curing light is not required for these potent caries-controlling restorations [2].

The setting reaction is comparable to that of conventional cement. They require large P:L ratios and exhibit superior flexural and compressive strengths. In comparison to conventional glass ionomers, they also have less solubility, increased wear resistance, superior surface hardness, and greater "Packability" [2, 41].

2.7 Low Viscosity Glass Ionomer Cements

These substances are also known as flowable glass ionomer cements. Unlike Packable GICs, these cements require lower

P:L ratios as it is necessary to increase their flow. They are employed as endodontic sealers, fissure protection materials during the teeth eruption period, and sealing the hypersensitive cervical area [2].

2.8 Amino Acid Modified Glass Ionomer Cements

Glass ionomer cement's fracture toughness can be increased by adding N-acryloyl- or N-methacryloylamino acids to acrylic acid copolymers, for example. N- methacryloyl glutamic acid [2].

2.9 Ceramic Reinforced Posterior Glass Ionomer Cements

These are designed to be as durable and strong as amalgam. It is available in two colours: a general tooth tint and white. Additionally, it can be administered in powder-liquid or water-settable form [2]. The commercial material available is Amalgomer.

The powder component comprises of Fluoro-aluminosilicate glass, polyacrylic acid powder, tartaric acid powder and ceramic reinforcing powder. The liquid component comprises of polyacrylic acid and distilled water. Literature reported that these cements exhibit superior compressive strength compared to the conventional cement and it increases as the restoration matures. The one-month compressive strength of these cements is almost similar to that of the dental amalgam [2,42].

These cements are indicated in Class I and Class II Cavities, repair of amalgam restored tooth, as a base under composite restorations, as core build-up under crowns, on the root surfaces for locating over-dentures and long-term temporary replacement for cusp(s) and repair to crown margin [2,42].

2.10 Yittria-stabilized Zirconia (YSZ) added GICs:

YSZ is a ceramic filler with good dimensional stability, chemical stability, mechanical strength, and toughness. In addition, they are tooth-coloured and can pack densely with the set matrix of GIC due to their wide distribution of particle sizes.

Gu *et al.* (2005) [43] showed that YSZ ceramic fillers added to GIC had better mechanical properties than Miracle Mix, including compressive strength, diametral tensile strength, and hardness. Additionally, they stated that the micro-sized YSZ/glass powders displayed a uniform particle distribution and a packing density of GIC, which led to better mechanical properties than the nano-sized powders.

2.11 Boric acid containing GIC

Prentice *et al.* (2006) [44] added various concentrations of boric acid (H_3BO_4) into the conventional glass ionomer cement powder to study the impact of boric acid on the compressive strength of GIC. They demonstrated a dose-dependent reduction in compressive strength. The compressive strength decreases as boric acid addition increases in concentration. The acidic behaviour of the boric acid could be responsible for this decrease. Due to its low acidity (pKa 9.2), boric acid is likely to dissolve in ionomer solutions while remaining completely protonated and inert at the acidic pH values of GIC. Intake of water by borates reduces the water's availability for ion transfer and flow ability, lowering the polyalkenoate's final degree of cross-linking variations in set cement and leading to a decrease in the compressive strength of the hydrated set matrix.

2.12 Niobium (Nb_2O_5) Silicate GIC

Numerous researchers reported that the addition of Nb_2O_5 in silicate systems with a favourable effect on several physical and chemical properties [45,46]. Bertolini *et al.* (2005) [47] developed niobium silicate glasses and evaluated the key properties of modified GICs. The composition of the modified GIC is $4.5SiO_2$:$3Al_2O_3$: xNb_2O_3: 2CaO ($0.1<x<2.0$). These newly formed cements require lower manufacturing temperatures (400-700), and their composition is similar to that of traditional GICs. These modified cements demonstrated a significant increase in the setting time due to the formation of Si-O-Nb bonds, which are more resistant to acid attack. A decrease in the microhardness and diametral tensile strength was observed with these modified GICs.

2.13 Silicone Carbide whiskers added GIC

Silicon carbide (SiC) whiskers are fiber-like materials with a wide range of industrial applications. SiC possesses superior tensile strength, weight advantage over metals and exhibits stability at higher temperatures [48]. Literature reported the addition of silanized SiC whiskers to the GIC enhanced bonding between the polymeric matrix of GIC and SiC whiskers. The addition of SiC whiskers improved the transverse strength and fatigue resistance of GIC. Additionally, a sustained bonding with enamel without preventing the GIC's release of fluoride was observed [49]. SiC whiskers, on the other hand, have dimensions that are comparable to those of asbestos, raising concerns about possible health effects for workers exposed to work environments [48]. According to research, SiC particles migrate to critical body organs and do not adhere to the GIC matrix, potentially harming the person's health [49].

3. Conclusion

Glass-ionomer cements, in particular, have drawn attention because of their unique properties and have undergone significant improvements compared to other dental materials. Recent studies and trials have improved formulations, enhanced mechanical properties, and decreased water sensitivity for conventional glass ionomers. Numerous studies have demonstrated that conventional glass-ionomer cements can be reinforced in ways that enhance their mechanical properties. However, the recent modifications in the GICs have not shown the mechanical strength that is required to withstand the masticatory forces, especially in the posterior region of the mouth. Many reinforcing fillers failed to show adequate bonding with the GIC polymer matrix leading to the failure of the restorations during their service. Therefore, the research is on the way to improving the characteristics of the GICs.

Conflicts of interest: Authors declared no conflicts of interest.

Financial support: None

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How to cite this article: Saridena USNG, Sanka GSSJ, Alla RK, Ramaraju AV, Sajjan MCS, Mantena SR. An overview of advances in Glass Ionomer Cements. Int J Dent Mater. 2022;4(4): 89-94. DOI:*http://dx.doi.org/10.37983/IJDM.2022.4403*