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**Research Paper**

# Recent Advancements in Glass Ionomer Cements

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***Abstract-***
*There have been significant advancements in the formulation of Glass Ionomer Cements, including the incorporation of metal ions or resin elements, which have enhanced their physical characteristics and expanded their utility as an effective dental restorative material. Light-cured polymer-reinforced materials show considerable advantages, while maintaining the benefits of fluoride release property and adhesion. Further studies are needed to enhance their properties, such as durability and aesthetics, while preserving their key features, including fluoride release and adhesion. This review of literature provides an insight to various developments in Glass ionomer cements.*

***Key words-*** *Glass ionomer cement, advancements, direct aesthetic restorative materials*

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## I. Introduction-

The trend in dentistry today is to use more non-metallic based bioactive restorations rather than metal ones. The primary drivers of motivation are functionality and biocompatibility. An ideal restorative material should possess identical properties and should adhere tenaciously to the surrounding enamel and dentin. The glass ionomer cements are one of the products developed in this direction. Innumerable changes and inclusions were made in its properties and composition to overcome its inherent drawbacks such as lack of strength, early moisture sensitivity and inadequate aesthetics.[1]

Most recent versions of GICs typically consist of powders that contain some of the polymeric acids in dried form, resulting in the formation of a low-viscosity acid solution. The freshly mixed cement prepared under these conditions contains high amounts of acid that promote the rapid setting of the material. The process also imparts good strength. These types of materials are labelled as "high-viscosity" GICs, a term commonly applied to materials characterized by high powder/liquid ratios of at least 3.6:1. [2]

In 2015, a novel GIC material known as the Equia Forte (GC Inc., Kyoto, Japan) was introduced for application (in high-load-bearing areas) in posterior teeth. It is a glass hybrid restorative material containing a multifunctional monomer & is reinforced with ultrafine, highly reactive glass particles.[3,4]

The time frame for the development of glass ionomer materials is presented chronologically in the table (Table A.) below[5]-

| **Date** | **Glass ionomer developments** |
|---|---|
| ***1972*** | *The invention of conventional GICs* |
| ***1977*** | *Metal (silver)-reinforced GICs* |
| ***1980*** | *RMGICs self-polymerized* |
| ***1990*** | *RMGICs photo-polymerized* |
| ***1991*** | *RMGICs (photo+self)-polymerized* |
| ***2003*** | *Glass Carbomer* |
| ***2007*** | *Nano-modified RMGICs* |
| ***2008*** | *Nano-modified conventional GICs* |
| ***2008*** | *High-viscosity conventional GICs* |
| ***2015*** | *Hybrid restorative GICs* |

Table A. - Developments in Glass Ionomer Cements

## ❖ Recent Modifications of Glass Ionomer Cements-

### 1. Metal-modified glass ionomer cements-

Metallic fillers have been recently added to glass ionomer cements to improve their strength, fracture resistance, toughness, and wear resistance property.[6]

### a) Silver alloy modified GICs-

- Two distinct 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 of a spherical silver amalgam alloy powder with Type II glass ionomer powder.[7,8]
- In the second method, the mixture of spherical silver alloy powder and Type II GIC is sintered at high temperatures, resulting in the fusion of glass powder with silver particles. The obtained product is ground to a fine powder and is referred to as “cermet”. [7,8]

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

- These cements surpass conventional glass ionomer cement in terms of compressive strength and fatigue limit values. The erosion resistance of these materials has improved noticeably as 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. [7]

### b) Fe2O3 based GICs-

- 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.[9]
- Hurrell Gillingham et al. (2006) [9] 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 are 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. [7]

### c) Zinc-based GICs-

- Boyd et al. (2005)[10] combined a calcium-zinc-silicate glass powder with the PAA( Polyalkenoic acid) . The flexural strength of these newly developed formulations was comparable to that of conventional GICs. They did, however, have a lower compressive strength than the conventional GICs, which can be attributed to the powder's $Zn^{2+}$ions, which form ionic bonds with the carboxylate ($COO^-$) groups of PAA.[11]

- Hopeite ($Zn^{+3}(PO_4)_2.4H_2O$) is a non-cohesive, crystalline structure formed in cements with high zinc & low calcium content. [12]

- 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 $ZnO_4$& reduce their reactivity in cements with the high calcium content.[10]

### d) Stainless-steel incorporated GIC-

- Stainless steel incorporated GIC was introduced by Kerby et al.[13]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 it with distilled water & 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 & setting times, and low solubility. On the other hand, stainless steel particles impart a greyish colour, which makes the material appear unesthetic. [6]

## 2. Resin Modified Glass Ionomer Cements (RMGICs)-

- RMGICs were introduced in the field of dentistry in the late 1980s. These are hybrid materials with combined properties of conventional GICs and composite resins. The components present in the powder are almost the same as the components present in conventional GICs. The liquid methacrylate monomers and a photo-initiator system are also present in the system.[14]
- The monomer is typically 2-hydroxyethyl methacrylate (HEMA), and the photo initiator is usually camphorquinone (CQ).[15]
- Two different chemical reactions occur during the process of setting of RMGICs. The acid-base reaction is initiated immediately after the process of powder/liquid mixing. The polymerization of the methacrylate monomers is stimulated using a dental light-curing unit such as light-emitting diode (LED) devices. The properties of the material can potentially degrade due to the simultaneous progress of the two antagonistic reactions.[16]
- The method of mixing and the light curing should be conducted following the instructions provided by the manufacturer to avoid deleterious effects on the structure of the cement.[16]
- Post the photopolymerization process, the material is then exposed to conditions of a fast initial hardening process to form the polymer network. However, the acid-base reaction continues after light-curing and is completed within 10-12 minutes of mixing. Unlike conventional GICs, moisture-protecting substances need not be used immediately after application, and this can be attributed to the formation of the polymer network. They also showgreater resistance to compression, diametrical tensile strength, degree of bending, and modulus of elasticity than the conventional GICs. [17]

- They present lower water sorption ability, a lesser degree of solubility, and higher translucency than conventional GICs. These improve the aesthetic performance of the materials. The process of polymerization shrinkage during setting limits the application of RMGICs. The extent of fluoride release recorded for the RMGICs is lower than that recorded for the conventional GICs. This can be attributed to the low solubility (attributable to the less hydrophilic nature) of the material and the release of unreacted monomers to the surrounding tissues. Fluoride is released in two phases in conventional GICs. A large amount of fluoride is released during the first phase (burst effect). This is followed by the steady release of a small amount of fluoride ions during the second phase. The second phase is longer than the first phase. [18,19]
- Small amounts of $Na^+$, $Al^{+3}$, $PO_4^{-3}$, and $Ca^{+2}$ ions are also released during the process. They exhibit buffer properties and increase the pH of the oral fluids in an acidic environment.[20,21]

- In terms of biocompatibility, RMGICs lag behind conventional GICs because they release the monomer HEMA, especially during the first 24 h. It penetrates dentinal tubules and is considered potentially cytotoxic to pulpal cells .[22,23,24]

- It has been previously reported that low cytotoxicity (determined by conducting MTT assays) values were recorded for all the tested materials (conventional GICs, RMGICs and resin composites) and low extraction times were involved, indicating minimal cytotoxicity of the materials (less than 30% inhibition). One RMGIC presented significantly higher cytotoxicity compared to the other materials.[24]

- RMGICs should be light-cured for at least the manufacturers' recommended time at thicknesses no greater than the maximum recommended value to minimize the HEMA release.Efforts have been continuously made to improve RMGICs with nanoparticles and bioceramic particles to combat the persisting issues.

### 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 i.e.ionomer and composite, respectively. The carious-affected teeth are restored using these aesthetic materials.[12]
- Critical properties such as 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-aluminium - 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.[12,25,26]

- 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.[27]

- The microhardness, flexural & compressive strengths of the compomers were higher compared to GIC but lower than Composite. Surface roughness between the two materials was not noticeably different.[26]

- According to Bansal D and Mahajan M (2017)[28]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.[29]

- Compomers are known to be biocompatible in nature. They are considered aesthetically pleasing than GICs as they allow for the shade selection. Due to release of fluoride and excellent buffering capacity it decreases the incidence of secondary caries, therefore shows anti-cariogenic effect. However, the fluoride releasing capacity of compomer is known to be much less than the self-curing GIC. Compomers show poor colour instability and poor wear resistance. They also lack adhesion to the tooth surface like composites.

### 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. [30]
- 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 "Fluoro-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. [30,31]
- The indications of Giomers are almost similar to that of the conventional GICs. The indications include restoration of cervical erosion and root caries,restoration of primary teeth, laminates and core build-up and repair of fracture of porcelain and composites.
- Giomer has the fluoride release and fluoride recharge properties of glass ionomer cement, has excellent aesthetics, is easy to polish, has strength, has physical properties, and resin composite handling. [30,31]
- Pre-reacted glass ionomer technology is classified in two categories such as full pre-reacted glass (F-PRG) and surface pre-reacted 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, aluminium, 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.[30,31,32,33]

### 5. Nano particles reinforced GIC-

- Nanotechnology is particularly 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 primary focus of nanotechnology. GICs modified by incorporating nanostructures exhibited fewer air voids and internal microcracks. In addition, apparently modified materials are easier to handle than unmodified cements, which resulted in greater strengths in compression.[34]

- The nanofillers widely used in GICs include nanohydroxyapatite,silica, titanium, zirconium, Barium-sulphate nanoparticles, etc.

- Nicholson et al. (1993) [35] first investigated the impact of hydroxyapatite addition to GIC and their findings have ever since guided subsequent research in this area. The addition of nanohydroxyapatite (nHA) to GIC improved the mechanical properties, fluoride release, and resistance to bacterial invasion. [36,37]

- Lucas et al. (2003)[37] added hydroxyapatite particles to the standard GIC because they have excellent biological properties, a similar crystal structure, and a composition similar to the hydroxyapatite found in natural teeth. In their study, GIC with particle sizes ranging from 0.3 to 200 microns was mixed with the hydroxyapatite particles. They found that addition of hydroxyapatite 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)[38] discovered that the mechanical properties of restorative GIC containing zirconia powder and nHA were superior to those of hydroxyapatite alone. This improvement 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.[39]

- The addition of 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, as well as the shear bond strength. 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, setting time and various physical properties.[40]

### 6. Packable Glass Ionomers-

- Also termed as "high-strength glass ionomer cements”. These were developed for use as part of the atraumatic restorative therapy(ART) in third-world countries. The use of curing light is not required for these potent caries-controlling restorations.
- The setting reaction is comparable to that of conventional cement. They require large P:L ratios and exhibit superior flexural & compressive strengths. In comparison to conventional glass ionomers, they also have less solubility, increased wear resistance, superior surface hardness, & greater "Packability”. [12,41]

### 7. Low Viscosity Glass Ionomer Cements-

- These substances are also referred to 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 used as endodontic sealers, fissure protection materials during the teeth eruption period, and for sealing the hypersensitive cervical area of the tooth.[12]

### 8. Amino Acid Modified Glass Ionomer Cements-

- The fracture toughness of GICs can be improved by adding N-acryloyl-or N-methacryloylamino acids to acrylic acid copolymers, for example. N-methacryloyl glutamicacid.[12]

### 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.[12] The commercially available material 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.[12,42]

- 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.[12,42]

**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.[6]
- Gu et al. (2005) 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.[43]

**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 dosedependent 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. [44]

**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)developed niobium silicate glasses and evaluated the keyproperties 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 toacid attack. A decrease in the microhardness and diametral tensile strength was observed with these modified GICs.[47]

**13. Silicon 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 silanizedSiC 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. [50]

## II. 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 glassionomer 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.

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