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Advances in glass ionomer cement: A review

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Abstract
Glass ionomer cements are the commonly used restorative material in young children. They adhere to slightly moist enamel and dentin without the need of any adhesive system, release fluoride and have anticariogenic properties. But their disadvantages include poor tensile and flexural strength which may result in a higher rate of early fractures and also occlusal wear compared to other filling materials. To overcome these poor mechanical properties of glass ionomers, several modifications have been introduced to the conventional glass ionomer cements. Hence the aim of this paper is to review the modifications undergone by glass ionomer cement to improve their physicochemical properties.

Keywords: advances in GIC, glass ionomer cements

Introduction
Dental caries is perhaps the most prevalent chronic disease. Once dental caries occurs, restoring carious lesion becomes mandatory [1].
The introduction of glass ionomer cement in the early 1970s by Wilson and Kent marked a new era in restorative dentistry. Glass ionomer cement are clinically attractive dental materials that possess certain unique properties that make them useful as restorative and luting materials. They adhere to slightly moist enamel and dentin without the need for any adhesive system, release fluoride and have anti-cariogenic properties for an extended period of time, thermal expansion similar to enamel better aesthetics, less sensitivity to dentin moisture and are biocompatible [2].
Limitations of glass-ionomers include brittleness, poor fracture toughness and sensitivity to moisture in the early stages of placement. To overcome these disadvantages several modifications were done in both the powder and liquid components of glass ionomer cement. Hence this review deals with the various modifications glass ionomers have undergone till date [3].

1. Water – hardening glass ionomer cements
In the conventional glass ionomers, when the polyacid is present in solution, an increase in either molecular weight or concentration will increase the viscosity of the liquid, thus making the cement paste more difficult to manipulate. Hence there is a limitation from the usage of poly acrylic acid in solution and it is used more in solid form for blending with glass ionomer powder. To overcome this, in water hardening glass ionomer cements, the liquid for cement formation is either plain water or an aqueous solution of tartaric acid.

2. Metal reinforced glass ionomer cement
Sced and Wilson found that metal fibers were best to increase the flexural strength. Simmons suggested mixing amalgam alloy powders in to cements and developed “Miracle mix”.

3. Cermet ionomer cements
To improve the resistance to abrasion, McLean and Gasser developed cermet ionomer cements. It was found that by sintering the metal and glass powders together, strong bonding of the metal to the glass was achieved.

4. Resin modified glass ionomer cement
Resin modified glass ionomer cement was designed to overcome the problem of moisture sensitivity and lack of command cure of conventional glass ionomers. It produces favorable physical properties similar to those of resin composites while maintaining the basic features of the conventional glass ionomer cement.

5. Highly viscous conventional glass ionomer Cement
To simplify the insertion of the material similar to that used for amalgam, high viscous glass ionomers were developed. They were designed as an alternative to amalgam for posterior preventive restorations. Examples of highly viscous glass ionomer cements are Fuji IX and Ketac Molar [4].

6. Strontium oxide added GIC
Strontium is a cement forming ion and it slows down the setting reaction at both 21°&37°centigrade; hence imparting more radiopacity as compared to calcium aluminate added glass ionomer [5].

7. Calcium Aluminate GIC/Ceramir
Calcium aluminate component in the cement contribute to increased strength and retention over time, biocompatibility, better sealing of tooth-material interface, bioactive because of apatite formation, stable, shows sustained long-term properties, lack of solubility/ degradation [6].

8. Amalgomer

This (ceramic reinforced glass ionomer cement) is introduced into restorative dentistry to match the strength and durability of dental amalgam. It contains a high level of fluoride with good aesthetics and it requires only minimal cavity preparation. It bonds to tooth structure and has excellent biocompatibility [7].

9. Giomers

This fluoride-releasing, light-cured restorative material is touted as true hybridization of glass ionomer and composite restorative materials. Other advantages of giomers are its good esthetics, ease of handling and improved physical properties of the set material [8].

10. Hainomers

These are newer bioactive materials developed by adding hydroxyapatite within glass ionomer powder. They are mainly being used as bone cements in oral maxillofacial surgery and can be used as retrograde filling material. They bond directly to bone and affect its growth and development [9].

11. Fluorinated Graphene

Sun et al in his study concluded that the addition of fluorinated graphene to conventional GIC enhanced their mechanical, biological and antibacterial properties. Also, the incorporation of fluorinated graphene to GIC had no negative affect on the color, solubility, and fluoride ion release property of the material [10].

12. Stainless steel glass ionomer

Kerby et al, in his study suggested that the stainless-steel cements provided the most desirable physical properties including high compressive and tensile strength, favorable working and setting times and low acid solubility. But the main disadvantage is the grayish color which makes it not a suitable choice for anterior tooth restoration [11].

13. Reactive glass fibers: fiber reinforced glass ionomer cements

Lohbauer et al. reported that a reactive glass fiber has the ability to increase the fracture toughness of glass-ionomer cements.[12]

Yli-Urpo et al found that bioactive glass particles likely acted as fillers that do not adhere to the matrix of GIC leading to decreased compressive strength and modulus of elasticity. Hence, their usage ought to be restricted to applications where their bioactivity can be beneficial, such as root surface fillings and liners [13].

14. Incorporation of hydroxyapatite (HA) and HA/ZrO_2in GICs

Lucas et al found that HA-ionomers are promising dental filling materials and the incorporation of HA particles into the powder of glass-ionomer cements increased
the mechanical properties of the set cement [14].

15. GICs containing YbF3 and BaSO4

Prentice et al found that nanoparticles of YbF_3 and $BaSO_4$ when added to conventional glass-ionomer cement powder significantly reduced 24 h compressive and surface hardness of glass-ionomers. Also YbF_3 accelerated the glass-ionomer curing reaction, as did low concentrations of $BaSO_4$, but higher amounts of $BaSO_4$ had opposite effects [15].

16. Yttria stabilized ZRO2-GICs

Gu et al. added nano-sized yttrium stabilized ZrO_2 (ysz) (8 mol%) powder and 7 m%
Y_2O_3 stabilized ZrO2 powders to the glass ionomer cement powder composition and the results showed that ysz containing GICs are promising restorative materials only if the appropriate particle size distribution is used [16].

17. Niobium silicate GICs

Bertolini et al. used the following composition as the powder for glass-ionomer cements: 4.5 SiO_2: $3Al_2O_3$: x Nb_2O_3: 2CaO (0.1 < x < 2.0 and the results showed that the new glass composition has a similar structure to the commercial glass-ionomers with SiO_4 and AlO_4 tetrahedral structures with the bridging oxygen as an acid attack site. Still, it was found, that the micro hardness and DTS of the experimental glass-ionomer were decreased [17].

18. Zinc based GICs

Boyd et al. found that zinc based GIC had approximately one quarter the strength of their aluminum silicate glass counterparts after 30 days of maturation (57 MPa after 30 days). But, the flexural strength of these cements was comparable to the flexural strength of conventional GICs [18].

19. Boric acid added GICs

Prentice et al, added boric acid into the glass powder and found a significant reduction in the compressive strength of the GIC [19].

20. SrO added GICs

Deb et al in his study found that an increase in the amount of SrO led to increase in both working and setting times, indicating that SrO retarded the rate of reaction. Also, the compressive strength of SrO modified cement was increased significantly by (0–5% m/ m) SrO addition [20].

21. Fe_2O_3 added GICs

Hurrell-Gillingham et al develop an Fe_2O_3based glass-ionomer cement with no release of Al $^{3+}$for use as a bone cement. They found that it was possible to develop cements from all of the Fe_2O_3-based ionomer glasses and Fe2O3-based cements showed good in vitro biocompatibility [21].

22. Incorporation of casein phosphopeptide-amorphous calcium phosphate (CPP-ACP) in the GICs

Mazzaoui et al. found that incorporation of nanoparticles of CPP-ACP into the cross-linked matrix of GIC caused a 23% increase in compressive strength and 33% increase in micro tensile bond strength [22].

23. Titanium tetrafluoride added GICs

Pamir et al. in their study indicated that when TiF_4 was incorporated to GIC, fluoride release was reduced with the exception of 1% TiF_4. Also, compressive strengths of 0.5 and 1% TiF_4-added GICs were higher, but not significantly, than the control group (commercial GIC) [23].

24. Glass ionomers containing spherical silica filler (SSF)

Tjandrawinata et al. in their study found that the addition of SSF increased the compressive strength value by 1.1 times, while the increase of modulus of elasticity was 1.10 to 1.35 times increased [24].

25. SiC added GICs

SiC added GIC showed improved transverse strength, enhanced fatigue resistance and long-term bond to enamel, while not inhibiting fluoride release and forming a thicker intermediate layer. Disadvantage is the risk of SiC particles migrating to vital organs since they do not bond to the matrix of GIC and therefore they can be potentially hazardous to human health.[25]

26. Cellulose Microfibers/Cellulose Nano-Crystals added GICs

Silva et al concluded that the addition of only small concentrations of cellulose nano crystals to GIC led to significant improvements in all the mechanical properties [26].

27. Cellulose Nano-Crystals and Titanium Oxide added GICs

In as recent study conducted it was found that the physical properties of the modified GIC reinforced with 2 wt. % TiO_2 nano-particles and 1 wt. % of cellulose nano crystals showed significant improvement; similarly, compressive strength was increased by 18.9% and the shear bond strength increased to 151% when tested on enamel of extracted teeth [27].

28. Forsterite added GICs

It was reported that the addition of 1 wt. % forsterite to conventional GIC leads to an increase in compressive, flexural, and diametral tensile strength of the modified material. However, the fluoride ion release property of the modified material was slightly less than the conventional GIC [28, 29].

29. Montmorillonite Clay added GICs

Dowling et al in their study successfully combined two types of nano-clay, an Ca-MMT and an organic ADA-MMT clay to conventional GIC at 0.5 to 2.5 wt. %. It was reported that the compressive strength of the cement increased with the addition of ADA-MMT. But the addition of Ca-MMT resulted in the reduction in compressive strength of the modified material as compared to conventional GIC [30].

30. Oxalic acid added GICs

It is expected that by adding this acid to glass-ionomer liquids, the degree of cross-linking increases and polysalt bridge formation. Hence the mechanical properties of the set cement improved due to the presence of the two carboxylate groups [31].

31. Phosphoric acid added GICs.

It was observed that the phosphate ions in phosphoric acid, can act as a network former and increase the degree of the cross linking in GIC systems. The incorporation of phosphoric acid up to 2% by weight, considerably increases the compressive strength of the cement, but the compressive strength decreases as the concentration of phosphoric acid increases [19].

32. Polyphosphonate cements

This cement is the result of reaction between specially formulated calcium aluminosilicate glass and poly vinyl phosphonic acid (PVPA), the composition of the glass is slightly different from conventional glass-ionomers. Higher amounts of Al in glass leads to formation of stiffer glasses, this reduction may have a negative effect on the stiffness of the final cement. Thus, the aluminum level in glass composition should be in balance between the reactivity and mechanical properties [32, 33, 34].

33. Amino acid containing polyelectrolyte

Since carboxylic acid groups are closely attached to the backbone of the polyelectrolyte; as the cement vitrifies, it prevents the conversion of all carboxylic acid groups to ion bonding carboxylate groups during setting reaction, hence reducing the formation of the salt-bridges. Therefore, the introduction of monomers with various spacer lengths of the carboxylic acid groups to the polymeric backbone seems to be a solution to improve the properties of the cement by enhancing salt bridge formation [35].

34. N-Vinylpyrrolidone containing polyelectrolyte

Studies showed that the cement formed from a copolymer of N-Vinylpyrrolidone and acrylic acid with commercial Fuji II glass-ionomer powder at the recommended powder to liquid ratio improved the flexural strength (10%) and diametral tensile strength (25%) compared to conventional GIC [36, 37].

35. N-Vinyl caprolactam (NVC)-containing polyelectrolyte.

Experimental results demonstrated that the addition of NVC into GIC polymers significantly increase the mechanical strength compared to the unmodified cement [38].

36. Application of super critical CO_2 in GIC copolymerization

Studies showed that, both the mechanical and working properties of glass-ionomer cement samples formulated using polymers prepared in supercritical solutions were comparable or higher than those of samples formulated using polymers prepared in water [39, 40].

37. Hyperbranched and star-shaped polyacrylic acids

Zhao and Xie in their study concluded that the resin-modified glass-ionomer cement system composed of newly synthesized hyperbranched poly acrylic acid is a clinically attractive dental restorative with potential application for high-wear and high-stress-bearing site restorations [41].

38. Amphiphilic molecules in polyelectrolyte

Even though limited reports on the modification of polyelectrolytes with amphiphilic comonomers exist in literature, there might be a possible improvement in general properties of GIC such as shrinkage, handling and mechanical properties by using modified surfactants [42].

39. Polyelectrolytes with antibacterial properties

Studies reveal all the poly quaternary ammonium salt containing cements showed a significant antibacterial activity, accompanying an initial reduction in compressive strength [43].

40. Chlorhexidine added GICs

According to Yap *et al*, [44] addition of 0.5% chlorhexidine improves the antimicrobial properties of the glass ionomer cement. [45] However, addition of chlorhexidine digluconate at different concentrations can interfere with physical and mechanical properties of the GIC [46].

41. Silk fiber reinforced GICs

Mina etal, in their study found that silk fiber reinforcement significantly increased the compressive strength, flexural strength, and diametral tensile strength of the conventional glass-ionomer restorative material [47].

42. Chitosan modified GICs

A study conducted by Karthik etal has found that the microshear bond strength of 10v/v% Chitosan modified glass ionomer cement is significantly greater than conventional glass ionomer cement [48].

43. Basalt fiber reinforced GICs

A study conducted concluded that introducing basalt fibers could significantly increase the mechanical properties of GIC. However, because of the weak interaction between basalt fibers and GIC matrix, mechanical properties, water sorption and solubility of basalt reinforced GICs were negatively influenced by aging in water [49].

44. Incorporation of all-ceramic additive to GICs

A study conducted in 2020 concluded that the addition of 10% concentration of the two all-ceramic powders successfully increased the strength of glass ionomer cements used [50].

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