Glass Ionomer Cement – The Different Generations

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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. In recent years there have been considerable changes in the formulations, properties and handling properties of the glass ionomer cements for different clinical applications. It is certain that no material is perfect, but with the current level of intensive research on glass ionomers, the deficiencies that exist seem to be eliminated or at least reduced, resulting in an ever – improving range of materials of this type.

Keywords : Glass ionomer, Biocompatibility, Co-polymer.

Introduction:
In dentistry adhesion of restorative materials to tooth substance is an important objective. It is believed that a restorative should resemble the tooth in all respects. It should possess identical properties and would adhere tenaciously to the surrounding enamel and dentin. The glass ionomer cements are one of the products developed in this direction. The invention of the glass ionomer cement resulted from previous fundamental studies on dental silicate cements and studies where the phosphoric acid in dental silicate cements was replaced by organic chelating acids. It was assisted by work on the zinc polycarboxylate cement in which Smith showed that dental cements exhibiting the property of adhesion could be prepared from poly (acrylic acid). Glass ionomer cement has therefore been described as a hybrid of dental silicate cements and zinc polycarboxylates.

Glass ionomer cements, are materials made of calcium, strontium aluminosilicate glass powder (base) combined with a water-soluble polymer (acid). When the components are mixed together, they undergo a setting reaction involving neutralization of the acid groups by the powdered solid glass base. Because both components are materials of wide chemical diversity, the range of glass – ionomer cements is very wide indeed and the material has considerable potential for further development.
Identification and classification of glass ionomers

The term glass ionomer cement should be applied only to a material that involves a significant acid – base reaction as a part of its setting reaction and show a continuing fluoride release. Within the scope of the above definition there are a number of applications for these cements and accordingly they are classified.

Type I : Luting crowns, bridges and orthodontic brackets
Type II a : Aesthetic restorative cements
Type II b : Reinforced restorative cements
Type III : Lining cements, Base.

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. Glass ionomer cements have certain characteristics that are attractive to the dentist. They bond adhesively to enamel and dentin, release fluoride ions over a prolonged period of time, are biocompatible and have approximately the same coefficient of thermal expansion as that of tooth structure. In spite of these advantages, conventional glass ionomers suffer from the disadvantages such as short working times and rather long setting times, brittleness, low fracture toughness, poor resistance to wear, susceptible to moisture contamination or dehydration during the early stages of the setting reaction. It is well – known that the mechanical and physico- chemical properties and the working and setting characteristics of a glass ionomer cement critically depend on several factors, such as the composition of aluminosilicate glass and the poly acrylic acid liquid used in the formulation, the particle size of the glass powder, the relative proportions of the constituents in the cement mix (glass/poly acrylic acid/ tartaric acid/water) and the mixing process. The manufacturer controls most of these factors; the clinician can control the mixing process. Attempts have been made to improve the performance (drawbacks) of glass ionomer cement by the addition of inorganic or organic components to glass powders or poly acrylates.

First generation of glass ionomer cement:

The material originated from the general dissatisfaction with the clinical performance of the dental silicate cement. Wilson et al made extensive studies on the dental silicate cement and concluded that this cement could not be further improved. They examined cements prepared by mixing dental silicate glass powder with aqueous solutions of various organic acids, including polyacrylic acid as liquid cement – former. The resultant cement pastes were almost unworkable, set slowly and sluggishly, and hydrolytically unstable. The initial problem with these cements was the less reactivity of the glass towards the polymer. Investigations carried out on variants of these glasses showed that their reactivity depended on the ratio of alumina to silica in the fusion mixture used for their preparation. This ratio, which is the ratio of basic oxide to an acidic oxide, determines the basicity of the glass and because the reaction between glass and liquid is an acid base one, an increase in the basicity of the glass will increase the rate of the setting reaction. This was the key observation in the development new cement system. Accordingly, Wilson and Kent in 1972 produced a first glass that was high in fluoride (G – 200) and that gave usable cement. This cement was originally called as ASPA, an acronym of Alumino – Silicate Polyacrylic acid. However the first glass ionomer, ASPA I (De trey Division, Dentsply International) set sluggishly, susceptible to moisture while
setting and was having very low translucency, resulting in limited use by the clinician.

Fast – setting cements:
The solution to the setting problem was discovered by Wilson and Crisp in 1972 and published in 1976. They found that optically active d- tartaric acid modified the cement forming reaction, thus improving manipulation, extending working time, and sharpening the setting rate. Therefore it is recognized as reaction controlling additive. When added in moderate amounts, tartaric acid enables a wider range of glass that can be used for glass ionomers. The introduction of tartaric acid allowed the use of lower fluoride-containing glasses, which are clear or slightly opaque. This refinement of ASPA I was termed as ASPA II and constituted the first practical glass ionomer cement.

The first practical glass ionomer cement ASPA II used poly acrylic acid as a cement–forming liquid. However, solutions of poly acrylic acid tend over a period of time to gel when their concentration in water approaches 50% by mass. This is attributed to slow increase in intermolecular hydrogen bonds (Crisp et al 1975). Poly acrylic acid chains are flexible and are constantly changing their configurations; when segments of a pair of chains approach each other, an intermolecular hydrogen bond can be formed. This is a slow but continuing process.

One approach adopted by Wilson and Crisp (1974) was to add methyl alcohol to poly acrylic acid solutions as an agent that inhibits the ordering of structures in solution. This glass ionomer cement was known as ASPA III. Although the gelation of polyacrylic acid was prevented, McLean found that the cement stained in the mouth.

Crisp and Wilson (1977) reasoned that copolymers of acrylic acids would be less regular than simple poly acrylic acid and so less liable to form intermolecular hydrogen bonds. They synthesized a copolymer of acrylic and itaconic acid, which proved indefinitely stable in a 50% aqueous solution. This copolymer was used in ASPA IV. This was the first commercial marketable cement.

Second-generation glass ionomer cement:

Water – hardening glass ionomer cements:
The conventional glass ionomer cement is usually supplied as a powder and a Polyacid liquid. Unfortunately when the Polyacid is present in solution, an increase in either molecular weight or concentration will increase the viscosity of the liquid, making the cement paste progressively more difficult to manipulate. Hence there is a trend away from using poly acrylic acid in solution and toward using it in solid form for blending with glass ionomer powder. The liquid for cement formation is then either plain water or an aqueous solution of tartaric acid. These cements are called as water mixed or water hardened cements. The main advantages of using this system are the development of low viscosity in the early mixing stages, improved shelf life because there is then no possibility of gelation occurring and improvement in the strength since the molecular weight and poly acid concentration can be increased with this system. Products of this type include, Chem–fil, Ketac–Cem etc.

Reinforced glass – ionomer cements:
The conventional glass ionomer cement has been used successfully for the esthetic filling of cavities subjected to low stresses, for example, the restoration of class V erosion lesions, class III restorations and for the filling
or sealing of pits and fissures. However the low tensile strength of existing formulations (7 – 14 MPa) makes the cement unsuitable for use in high stress sites such as class II restorations, particularly where there is lack of support from the cavity wall (for example, with MOD restorations). The cement must be improved in strength if it is to find a wider range of applications. Attempts have been made to improve the strength of the glass ionomer cement by modifying the chemical composition of the original glass powder.

1. Disperse – phase glasses
Glasses may be modified by phase separation. Wilson et al (1980) observed that clear glasses yielded weaker cements than glasses containing droplets of a disperse phase. So, novel glasses were prepared with deliberately large amount dispersed – phases of strengthening crystallites in order to improve the strength (Prosser et al 1986). Suitable disperse phases were found to be corundum (Al₂O₃), rutile (TiO₂), baddeleyite (ZrO₂) and tielite (Al₂TiO₅).

2. Fibre reinforced glasses
The incorporation of alumina fibres and other fibres such as glass fibre, silica fibre, carbon fibre etc to the existing glass powder at suitable filler / glass ratio was tried mainly to improve the flexural strength of the cement. Unfortunately these composite materials are very difficult to mix if sufficient quantity of fibre is used to produce a significant increase in strength. In addition, resistance to abrasion decreases due to lack of bonding between fibre and matrix.

3. Metal reinforced glass ionomer cement
The addition of metal powders or fibres to glass – ionomer cements can improve strength; Seed and Wilson found that metal fibres were best for increasing flexural strength. Simmons suggested mixing amalgam alloy powders in to the cements and developed this system clinically under the name “Miracle mix”. He used this alloy / glass - ionomer mix for core building and for the treatment of mouths with high caries incidence. However, their aesthetics are poor and they do not take burnish. Simple mixtures of metal powders failed at the metal / polyacrylate matrix interface and this was the weak link. Simple additions of either metal powders or fibers did not however, improve resistance to abrasion and may reduce it when compared with regular glass – ionomer cement.

4. Cermet – ionomer cements
The solution to the problem of improving resistance to abrasion was the development of cermet – ionomer cements by McLean and Gasser. By sintering the metal and glass powders together, strong bonding of the metal to the glass was achieved. Ion leachable calcium aluminium 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. After a number of clinical experiments, gold and silver were found to be the most suitable materials. Cermet – ionomer cements have greatly improved resistance to abrasion when compared with glass – ionomer cements and their flexural strength is also higher. However, their strength is still insufficient to replace amalgam alloys and their use should be confined to low stress – bearing cavity preparations.

Resin modified glass ionomers cement:
Despite all these improvements, the two problems of conventional glass ionomer cements still remained: moisture sensitivity
and lack of command cure. To overcome these problems, attempts have been made to combine glass ionomer chemistry with the well-known chemistry of composite resins. In the late 1980s and early 1990s a couple of so-called light cured glass ionomers were released on the market. So, resin modification of glass – ionomer cement was designed to produce favorable physical properties similar to those of resin composites while maintaining the basic features of the conventional glass ionomer cement.

In these newer materials the fundamental acid/base curing reaction is supplemented by a second curing process, which is initiated by light or chemical. These products are considered to be dual – cure cements if only one polymerization mechanism is used; if both mechanisms are used, they are considered to be tri – cure cements. These new materials are called as resin modified glass ionomer cements or hybrid ionomers. These materials are defined as hybrid materials that retain a significant acid – base reaction as part of their overall curing process. In their simplest form, these are GICs with the addition of a small quantity of a resin such as hydroxyethyl methacrylate (HEMA) or Bis – GMA in the liquid. More complex materials have been developed by modifications of the Polyacid with side chains that can be polymerized by a light – curing mechanism. They remain GICs by their ability to set without light activation, although this reaction takes place more slowly than for the traditional cements. The actual formulation varies between manufacturers but the amount of resin in the final set restoration may be in the region of 4.5% to 6% and is probably more in the lining materials. The first such materials to be developed and marketed were lining cements, restorative versions being introduced later. The first commercial RM GICs available were liners, Vitrebond (3M Dental Pdts, St Paul, Mn, USA) being the first introduced. Resin modified glass ionomer cements appear to have properties intermediate to conventional glass ionomer materials and resin composites. In general they have the advantages of both such as greater working time, command set on application of visible light, good adaptation and adhesion, acceptable fluoride release, aesthetics similar to those of composites, and superior strength characteristics. However, resin modified glass ionomer cements suffered from certain drawbacks such as setting shrinkage, limited depth of cure especially with more opaque lining cements. The development of compomers (Polyacid modified composite) has largely force this group of materials in to the market.

Highly viscous conventional glass ionomer cement:

With the development of resin modified glass ionomer cements, it might be tempting to conclude that the original conventional glass – ionomer cements (self cure) are obsolete. However, this is far from the case. These materials, too, are undergoing exciting developments of their own. Once such product is highly viscous glass – ionomers. These glass ionomers are particularly useful for atraumatic restorative treatment technique (ART). This is a procedure based on excavating carious dentin in teeth using hand instruments only and restoring the tooth with adhesive filling materials (tooth restoration without rotating instruments in third world nations). Glass ionomer, because of its adhesiveness and release of fluoride, is the natural choice to fill that gap. In this technique glass ionomer cement is pressed in to the excavated tooth cavities and pits and fissures in contrast to the...
flow technique used with resin–based sealant. To simplify the insertion of the material in a manner similar to that used for amalgam, a highly 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.

These cements set only by a conventional neutralization reaction but have properties that exceed those of the resin modified systems. Setting is rapid, early moisture sensitivity is considerably reduced and solubility in oral fluids is very low. According to manufacturers, the relatively higher viscosity is the result of the addition of polyacrylic acid to the powder and finer grain–size distribution. Soon after the popularity of glass ionomers for restoration of posterior teeth (ART), the same glass ionomer technology was developed for anterior restorative for ART. One such product is Fuji VIII. It is a resin reinforced glass ionomer restorative for anterior teeth where higher flexural strength and better translucency is required.

Easily mixable glass ionomer cements:

Conventional glass ionomer cements are supplied as powder and a liquid system. The dispensing and mixing of the powder and liquid are critical and may introduce a considerable variability in the mechanical and physicochemical properties of the set cement. In order to allow for simpler and easier manipulation and hence a reduced variability of the properties, other modified versions of dispensing system of glass ionomer cements were introduced.

1. Capsules

The glass ionomer cement in the form capsule system is a modern application method, which simplifies and allows procedures to be performed with greater ease and efficiency. These capsules contain pre–measured glass ionomer powder and liquid, which ensures correct ratio, consistency of mix and a predictable result. These capsules have angled nozzle that act as a syringe for accurate placement of the material in to a cavity or a crown for cementation.

2. Paste–Paste dispensing system

This is the latest development in the glass ionomer cement technology. This dispensing system was designed with the objectives of providing optimum ratio, easy mixing, easy placement, total reliability, using a specially designed cartridge and an easy to use material dispenser. In order to provide the material in a paste–paste consistency, an ultra fine glass powder was designed specifically. The low particle size provides the mixed cement with a thixotropic creamy consistency.

3. Modified powder–liquid system

The rational of this development was to enhance the manual mixing procedure with a product with improved handling features and high reproducibility of dosing. To be able to accomplish this task specialized processing procedure for powder was followed (specialized granulates). This system has improved wetting of the powder by the liquid rendering the mixing process much easier and faster.

Glass ionomer stabilization and protection material:

There is a need for a material to control the active carious lesions where a temporary restoration is required to seal the cavity during the period of disease stabilization and to protect the susceptible tooth surfaces during “at – risk” for intermediate/high risk patients.
To accomplish these objectives, specially designed glass ionomers were developed. One commercially available product under this category is Fuji VII. It has a pink chroma for easy identification of margins and as a visual reminder of its temporary nature. It has a high fluoride release and thus offers greater protection to surrounding tooth surfaces.

**Amino acid modified glass ionomer cements:**

One of the factors affecting the strength of glass ionomers is the chemical composition of the polymer matrix. Most of the conventional glass ionomers contain homopolymers or copolymers of unsaturated mono-, di-, and tri-carboxylic acids. With these formulations, the major problem lies in that the acrylic acid homo- or copolymers have –COOH groups which are directly attached to the backbone and are closely oriented to each other, resulting in a rigid polymeric structures. It is presumed that strength or fracture resistance of the ionomer material is weakened due to this steric hindrance, which brings about a significantly reduced –COO ‘Al+++ interaction in the set cement. So acrylic acid copolymers were modified with N-acryloyl- or N-methacryl-oylamino acids, such as N-methacryloyl – glutamic acid, providing a possible path to improved conventional glass ionomers. These newly formulated polyacids have flexible side chains tethering the carboxylic acid groups at various distances from the main chain polymer backbone, allowing for more freedom and less steric hindrance when the carboxylic acid groups are undergoing chemical reactions. This type of modification has improved the fracture toughness of the glass ionomer cement. The copolymers with pendant amino acid residues have also been developed for preparing visible light cure formulations.

The monomer N-Vinylpyrrolidinone (NVP) has been explored for modification of poly (acrylic acid – co – itaconic acid), providing a path to new polyelectrolytes for formulating glass ionomers. Formulations containing NVP residues have also developed for VLC applications.

**Conclusion:**

Since the development of glass ionomer cements nearly three decades ago, these materials have found increasing applications in clinical dentistry. Clinical experience has defined the practical advantages and disadvantages of glass ionomer cement system. This has resulted in improved formulations and more controlled techniques. Of course it is difficult to produce an ideal material, but with the current level of intensive research on glass ionomers, the deficiencies that exist can be eliminated, or at least reduced, resulting in an ever – improving range of materials of this type.

**References:**

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