Glass ionomer polyalkenoate cements and related materials: past, present and future

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Key points

Reviews the historical development of glass ionomer cements (GICs).	Explores the advantages and disadvantages of GICs.	Suggests potential ways GICs can be improved, notably for minimally invasive procedures such as autraumatic restorative therapy.

Abstract

The aim of this article is to review the development of glass ionomer cements (GICs) over the last 40 years and look critically at both their clinical advantages and disadvantages. Primarily, it will explore the future development of both GICs and related ion-releasing materials in relation to improved mechanical properties, capability to prevent secondary caries and promoting remineralisation of hard carious dentine left after minimal cavity preparation procedures, including atraumatic restorative treatment. This article will also introduce new materials with a focus on degradable fluorine-containing glass fillers, including alkasite glasses and fluorine-containing bioactive glasses, that have the capability to raise the pH and promote remineralisation with the potential for fluorapatite formation.

Glass ionomer cements

Glass ionomer cements (GICs) were invented by Wilson and Kent[1,2] at the government chemist in the early 1970s. Wilson and Kent replaced the orthophosphoric acid in the silicate cements with poly(acrylic acid), which paralleled the replacement of orthophosphoric acid in zinc phosphate cements, carried out earlier by D. C. Smith, that created the zinc polycarboxylate cements.[3,4] GICs are formed by mixing a calcium fluoro-alumino-silicate glass powder with an aqueous poly(acrylic acid) solution. The acid degrades the glass hydrolysing the aluminosilicate (Al-O-Si) bonds of the glass network and releasing aluminium and calcium cations that are chelated by the carboxylate groups and ionically crosslink the polycarboxylic acid, resulting in a fast-setting ceramic-like cement.

The original cements were called alumino-silicate polyacrylic acid (ASPA) cement.

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However, the first commercialised cements were not successful and were later rebranded as 'glass ionomer cements'.

GICs have been widely used in dentistry as a restorative material for almost 50 years due to their general ease of use clinically and their beneficial properties, which includes: fluoride release, chemical adhesion to tooth, a thermal expansion coefficient close to dentine and good biocompatibility with dental pulp. In addition, since there is no polymerisation involved in the setting reaction, there is no polymerisation shrinkage and no marginal gap formation, which is associated with current resin-based composites.

Despite the aforementioned advantages of GIC, it suffers from a number of drawbacks. These include:

1. Sensitivity to saliva/water during the early stages of setting (<1 hour). Water ingress into the surface results in a softer and often crazed surface. This dramatically influences the mechanical properties, reducing their strength. Protecting the surface by coating with petroleum jelly, cocoa butter or a light-cured varnish can all help in reducing this problem. Shahid and co-workers[5] have developed a light-cured coating based on microscopic plates of glass that align parallel to the surface that is more protective than particle-filled coatings. Further, GICs can undergo acid erosion in strongly acidic

beverages where the surface is partially dissolved and the crosslinking cations are removed, resulting in a softer surface that is more prone to wear in the mouth

2. Lack of a command set. This can be overcome by the use of radiant heat curing or ultrasonic curing to accelerate the acid base reaction.[5] These curing techniques also reduce the sensitivity to water and generally improve the mechanical properties

3. Lack of sufficient flexural strength and fracture toughness.

GICs vary substantially depending on the manufacturers. Some GICs have excellent translucency and aesthetics while some GICs do not. It is also important to note that since the setting reaction continues with time, the translucency and aesthetics will change with time.

GICs have been widely advocated for minimally invasive dentistry, such as atraumatic restorative treatment (ART).[6,7] ART was originally developed for preventative care in underserved areas of the world that lack resources, such as electricity or rotating and cutting equipment. ART uses only hand instruments to remove carious tissue and is commonly used in paediatric dentistry, particularly as it is associated with a reduction in pain, discomfort and avoids the need for local anaesthetic.

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Originally, GICs were hand mixed, but modern GICs have since evolved to capsulated and vibratory mixed. Capsulating greatly simplifies the process for the operator and ensures the correct powder-to-liquid ratio is used. In contrast, hand mixing often results in lower polyacid concentrations and a higher water content in the cement, resulting in far inferior strengths than specified by the manufacturers.

Since their conception, GICs have undergone systematic and progressive improvements over time: the original glass used in ASPA was only partially melted and contained crystalline inclusions that scattered light, resulting in poor translucency and aesthetics. Calcium has been replaced by strontium or by other high atomic number elements in the glass to make radio-opaque cements. There have also been improvements in the type of polyacids used, progressively moving to higher concentrations and/or higher molecular weights, which are commonly referred to as 'high viscosity GICs'. The overall properties of GICs, particularly the flexural strength and fracture toughness, are very dependent upon the polycarboxylic acid concentration and molecular weight.[8,9,10] However, this, in turn, leads to much higher viscosities and cements that are much more difficult to mix.

The 3M Company attempted to address this problem by having short poly(acrylic) acid chains with unsaturated carbon-carbon double bonds that were polymerised to make long chains. However, getting a free radical polymerisation to occur in an aqueous media was a challenge and a substantial amount of hydroxyethylmethacrylate (HEMA) had to be added in order to achieve this.[11,12] This resulted in what became known as 'resin-modified GICs'. While hybrid material gave the clinician control over command curing, it also resulted in several issues, including: polymerisation shrinkage, a potentially cytotoxic response from the release of residual HEMA and a general reduction of fluoride ion release.

The first attempt to develop stronger GICs for Class I and II cavities involved mixing the glass powder with silver metal particles (these were known as 'CerMets'), but since GIC failure is commonly associated with crack propagation through the polysalt matrix, there was minimal improvement in the overall restoration strength. Later, in 1991, Ellis et al.[13] developed GICs based on poly(vinylphosphonic acid) (PVPA), where vinylphosphonic acid is a much stronger acid
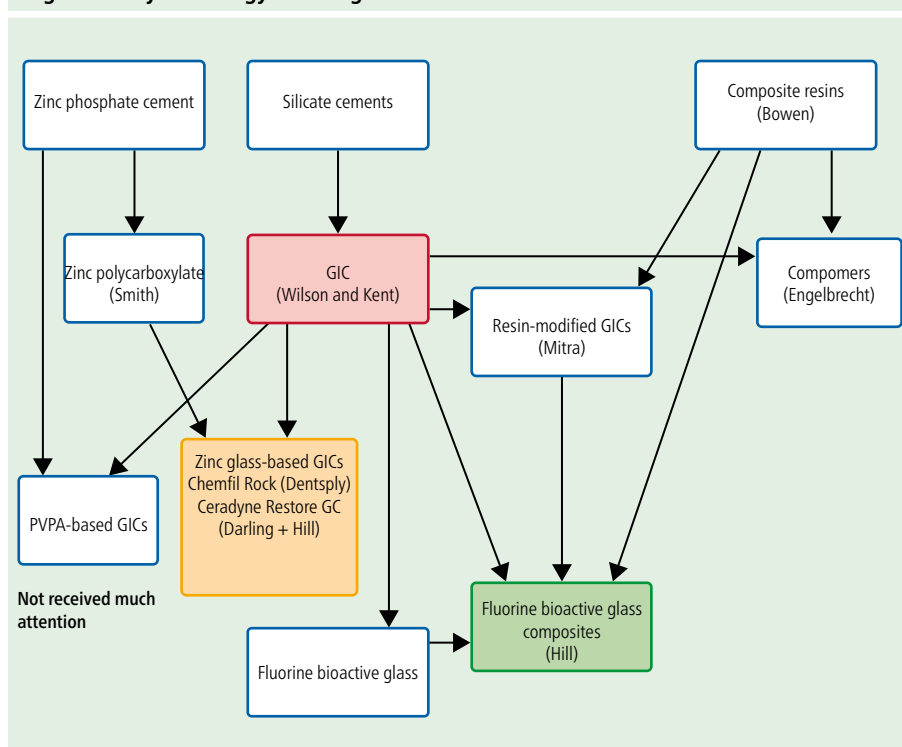
than poly(carboxylic acid), used in current GICs and is closer to the orthophosphoric acid used in the original silicate cements. One of the major problems faced with these cements was that it was not possible to produce high molecular weight PVPA because of the low reactivity of the monomer. However, there have been progressive improvements in molecular weight and there are a number of GICs based on PVPA-acylic acid copolymers. These cements show much better resistance to acid erosion.

In 1993, Darling et al.[14] developed zinc-based glasses for GICs. In these new glasses, zinc oxygen silicon (Zn-O-Si) bonds are acid hydrolysed, releasing zinc (Zn^{2+}) cations to ionically crosslink the polycarboxylate chains in an analogous fashion to the acid hydrolysis of Al-O-Si bonds in conventional ionomer glasses. Initially, these new cements were used as a root canal sealant, but in the last ten years, a new restorative filling material[15,16] and a GIC based on this type of glass have been developed for treating root caries in the older people,[17,18,19] which is a growing problem within the ageing population. These zinc-based glasses can be regarded as an amalgamation of the zinc oxide-based zinc polycarboxylates developed by D. C. Smith and the GICs developed by Wilson and Kent (see Figure 1). In the case of the material for treating root caries, the zinc released from these cements has an anti-caries

function, while in the restorative material, the slightly weaker ionic crosslinking at the crack tip associated with Zn^{2+} cations result in more plasticity at the crack tip and this, combined with the use of a high molecular weight polycarboxylic acid, results in a high fracture toughness and strength cement suitable for Class I and II cavities. Unfortunately, the material is much more opaque and much less aesthetic than most conventional GICs.

The role of fluorine in GICs and the mechanism of fluoride release

Fluorine is added to the glasses in GICs to lower melting temperatures and reduce refractive index of the glass in order to get a refractive index match to the polysalt matrix and a translucent cement.[20,21] Incorporating fluorine into the glass also results in the release of fluoride ions. There is a generalised perception that 'the more fluoride released from GICs the better'; however, the mechanism of fluoride release is equally important, in addition to the release of other ions present within the restoration.

The dominant mechanism of fluoride release involves the ion exchange of fluoride ions for hydroxyl ions from the dissociation of water in the external media.[22] This results in an increase in the hydrogen ion ($[H^+]$) of the external media and a reduction in pH. If the amount of external water is small and the

Fig. 1 History technology flow diagram

fluoride release large, the pH will fall. If the pH is <4, the hydroxyapatite tooth mineral will dissolve and reprecipitate as calcium fluoride (CaF^2). If the pH is 4–4.5, then reprecipitation as fluorapatite will occur. Formation of fluorapatite is attractive because it is less acid soluble than hydroxyapatite and its formation provides additional protection against caries.

Figure 2 shows the mineral profile through a calcium-based GIC-dentine interface; after seven days, there is a mineral gain in the dentine at the surface, but a corresponding mineral loss from deeper within the dentine. The explanation for this is the hydroxyapatite of the dentine is dissolving as a result of the pH decrease discussed earlier and then reprecipitating as fluorapatite. It is important to note that there is no net remineralisation.

New GICs for ART

While GICs release a lot of fluoride and this has an anti caries role, this alone is insufficient to remineralise hard carious dentine, (demineralised dentine where the protein is intact) sometimes referred to as 'affected dentine' left behind after an ART procedure. Here, we want to replace the lost apatite ($Ca_5[PO_4]^3OH$) in the dentine and to do this we need an additional source of orthophosphate ions (calcium [Ca^{2+}] or strontium [Sr^{2+}] ions), which are not released in significant amounts by GIC. For this reason, there has been a lot of interest incorporating bioactive glasses into GICs to achieve this objective. However, conventional bioactive glasses have a high sodium content and these glasses react during the acid-base cement reaction releasing Na^+ cations that interfere with the cement setting reaction, negatively impacting the material's physical properties and extending the setting time. Therefore, bioactive glasses containing little or no sodium have been introduced as the solution.[24]

Restorative materials related to GICs based on fluorine-containing glasses

Most of the research effort with existing composites in the last 20 years has been to try and reduce polymerisation shrinkage and eliminate marginal gap formation, which increases the risk of secondary caries, also known as caries associated with restorations. To help minimise shrinkage, composites need to be built up incrementally and dental dam is also advised to reduce moisture

contamination. These are time-consuming clinical procedures, where such stringent criteria can be demanding to achieve in a general practice setting. Amalgam restorations corrode and release bactericidal ions (silver-copper [Ag,Cu], zinc [Zn] and tin [Sn]) which is thought to protect amalgam from secondary caries. Therefore, in an attempt to overcome marginal deficiency complications, glasses have been incorporated into resin composites which degrade over time, releasing fluoride and/or bactericidal ions, aiding in protection from secondary caries.

Many manufactures have also incorporated fluoride-containing ionomer glasses, used in conventional GICs, into resin based composites. This strategy is fundamentally flawed in the opinion of the author for the following reasons. Ionomer glasses degrade under acidic conditions at pH 4–4.5 as a result of the acid hydrolysis of Al-O-Si bonds of the glass network. They do not degrade at a neutral pH; consequently, composites containing such glasses are fairly stable in the mouth and will release very few fluoride ions.

The bioactive glasses originally invented by Larry Hench,[25] in contrast, degrade by a mechanism involving ion exchange and will degrade at neutral pH but will degrade even faster at lower pH, where there are more H^+ ions for ion exchange with Ca^{2+} and Na^+ in the glass. Since the first step in the degradation process is ion exchange and the consumption of H^+ ions, the local pH is increased. This is particularly attractive, since cariogenic bacteria thrive at low pH. Raising the pH in a marginal gap adjacent to a restoration should inhibit secondary caries. This is the strategy behind the 'alkasite' technology developed by Ivoclar.[26] While they do not term the glass used as 'bioactive glass', it is structurally and chemically similar to fluorine-containing bioactive glasses. Table 1 compares an alkasite glass composition with fluorine-containing bioactive glass compositions. The only difference is the alkasite glass does not contain a source of orthophosphate. Composites based on alkasite glasses release calcium and fluoride ions and raise the pH.[27] They can form either calcium fluoride on their surface

Fig. 2 Mineral density plotted against distance for a calcium-based GIC[23]
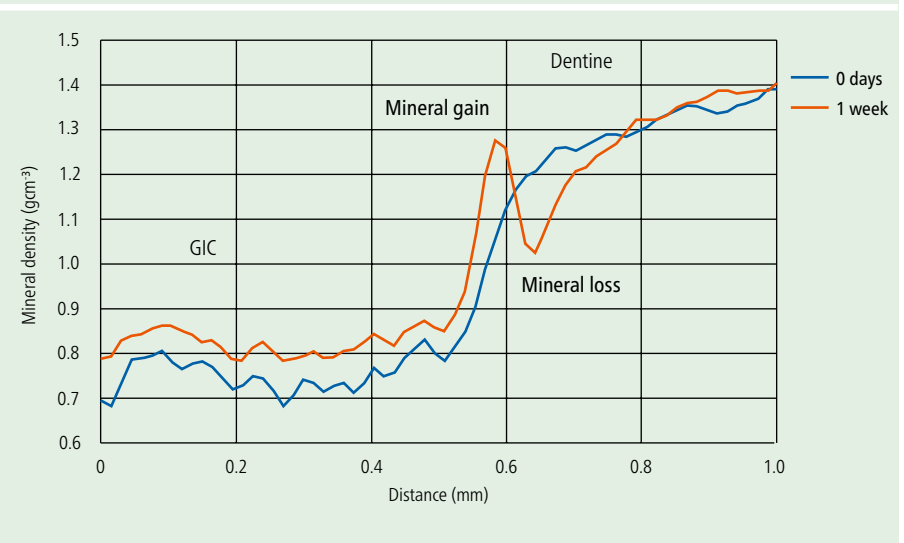

Table 1 Chemical composition of a typical alkalisite and fluorine-containing bioactive glasses (FBG). Also included is the original bioglass from Hench

Material	SiO2	P2O5	CaO	SrO	MgO	Na2O	CaF2	NC	RFI
Bioglass45S5	46.1	2.5	26.9			24.4		2.100	1.557
FBG1	36.41	6.04	32.02	15	1	5	4.53	2.083	1.589
FBG2	35.25	5.75	43			6	10	2.199	1.571
FBG3	36.1	5	38.1			10.9	9.9	2.116	1.565
Alkalisite	48.0		31.0			8.0	10.0	2.380	1.510

Key:
NC = network connectivity; RFI = refractive index

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or fluorapatite, depending on the availability of phosphate in the external media.[27] Composites containing alkasite glass are available in the Far East and have been shown clinically to have a low incidence of secondary caries.[28] The fluorine present in both alkasite glasses and the bioactive glasses is used to reduce the refractive index in order to get a match to the resin to facilitate light curing and to give a translucent aesthetic composite.

It is important to note that both the alkasite glass and the fluorine-containing bioactive glasses (FBG) when incorporated into resins must have a low sodium content. High sodium contents in the glass result in dissolution, rather than degradation. Complete dissolution of the glass in resin matrices is undesirable, since it results in holes or voids which will have an adverse effect on the strength of the composite. Despite this, most studies in the literature have incorporated high sodium content glasses based on 45S5 glass. While the alkasite composites represent a major step forward and are commercially available, using a bioactive glass that also contains phosphate is probably a better option in the longer term. This is because such glasses can not only raise the pH in marginal gaps to release calcium and fluoride but also provide orthophosphate ions for remineralisation of dentine. When used in an ART procedure, these new FBGs can form fluorapatite on their surface[28,29,30,31,32] and within marginal gaps can remineralise hard carious dentine.[33]

Figure 3 shows a scanning electron microscope image of a FBG resin composite, after three months' immersion in artificial saliva at pH 7. A dense layer of fluorapatite forms on the surface. Note the partially-reacted glass particles in the surface and the absence of any holes associated with complete dissolution of the glass particles.

When FBG resin composites are used to fill cavities in teeth prepared using ART, the formation of apatite and the remineralisation of carious lesions can be followed in the laboratory using x-ray microtomography[34] that is capable of both imaging the tooth in three dimensions, but also determining absolute mineral contents. Figure 4a shows a difference image taken from such a study, where the scan taken immediately after filling has been subtracted from the scan after two weeks. Areas in the image that are lighter represent an increase in mineral content, while areas that are dark represent a loss in mineral. It can be seen that the composite at the base of the filling has lost mineral and the carious dentine has gained mineral. In addition, pores in the composite from hand mixing and the marginal gap have gained mineral. Apatite is being formed in any empty space including pores and marginal gaps, as well as within the hard carious dentine.

Figure 4b shows the linear attenuation coefficient, a measure of the mineral content along the line in Figure 4a from the composite to the hard carious dentine that illustrates the apatite formation.
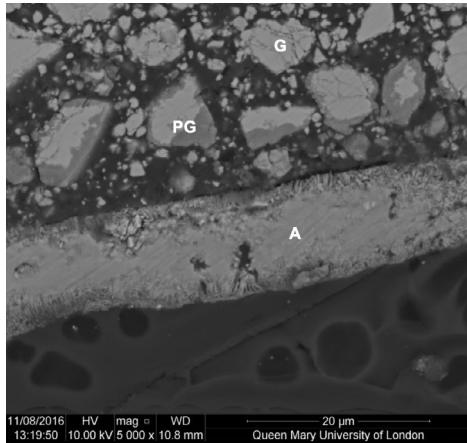

Fig. 3 Back scattered scanning electron micrograph of a cross-section of a FBG resin composite after immersion in artificial saliva at pH 7 for three months. (Note: A = apatite layer; PG = partially-reacted glass particle; G = unreacted glass particle)
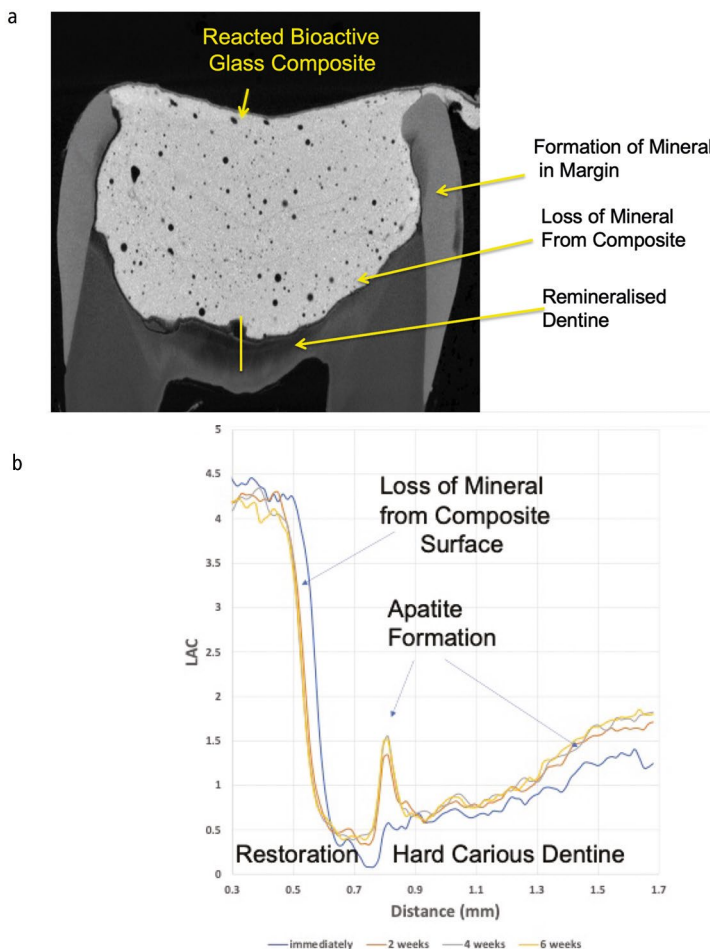

Fig. 4 a) X-ray microtomography difference image of a slice through a FBG composite after two weeks immersion. b) Linear attenuation coefficient as a function of distance across the FBG composite-dentine interface along the yellow line in panel a

It can be seen that there is an increase in the mineral content in the carious lesion with time but there is little further improvement after two weeks. It is thought that a layer of fluorapatite forms at the interface between the restoration and the dentine that acts as a barrier to the movement of Ca^{2+} and phosphate ions into the lesion that inhibits further remineralisation.

One of the drawbacks to including degradable glass fillers in resin-based composites is that particles at the surface will degrade and particularly on occlusal surfaces, this is likely to result in excessive wear *in vivo*. This problem may be potentially overcome by using a sandwich type restorative strategy and laminating over the top with a hard wear resistant coating that mimics the function of enamel.

Conclusions

GICs with their fluoride release, lack of shrinkage upon setting and ability to chemically adhere to enamel and dentine are attractive restorative materials for clinical use, particularly for ART type procedures. Further improvements are required to improve their remineralising capability.

Ethics declaration
The author is an inventor on the two granted fluoride bioactive glass patents WO 2011/000866 and WO 2011/161422 and owns shares in BioMin Technologies Ltd.

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