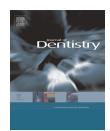
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Review

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Conventional glass-ionomer materials: A review of the developments in glass powder, polyacid liquid and the strategies of reinforcement

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ABSTRACT

Introduction: The development of glass-ionomers (GIs) from the earliest experimental GI formulations to the modern day commercially available GIs was reviewed. The aim of the review was to identify the developments in the glass powder and polyacid liquid constituents of GIs since their inception in the late 1960s.

Data: The glass powder has undergone major changes from the earliest GI powder formulation (G200) in an effort to enhance the reactivity with the polyacid liquid. The GI liquids have also been optimised by the manufacturers in terms of polyacid composition, molecular weight and concentration to improve the handling characteristics. Despite these developments in the glass powder and polyacid liquid constituents, GIs cannot 'truly' be advocated for the restoration of posterior dentition due to the poor mechanical properties when compared with dental amalgam and resin-based composites (RBCs).

Sources: Various attempts to improve the mechanical properties of GIs through substitution of reinforcing fillers to the GI powder or modification of the GI liquid were identified in the dental literature. Despite the claimed improvements in mechanical properties of the modified GIs, a wide variation in mixing and testing conditions was identified which prevented a valid assessment of the reported reinforcement strategies. When investigating a GI reinforcement strategy it is crucial that the mixing and testing conditions are standardised to allow a valid comparison between studies.

Conclusion: Nevertheless, major improvements in GI formulations through a reinforcement strategy have yet to be made to enable clinical usage of GIs for the restoration of posterior Q2 dentition.

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1. Historical development of glass-ionomers

15 Q3 Glass-ionomers (GIs) were developed and patented¹ in the late 1960s by Alan Wilson and co-workers at the Laboratory of the 16 Government Chemist (LGC) in London to replace dental 17 silicate cements. Dental silicate cements - then the primary 18 19 material of choice for the restoration of anterior dentition -20 were inherently brittle, susceptible to acid erosion, failed to 21 adhesively bond to sound tooth structure and raised concerns owing to increased pulpal sensitivity.² A major impediment to 22 23 the developmental progress of dental silicate cements was the 24 lack of understanding of the setting chemistry.³ The discovery 25 by Wilson and Batchelor^{4,5} that the dental silicate cement matrix was partially composed of aluminium and calcium 26 phosphates led to the suggestion to replace phosphoric acid 27 28 with a less aggressive organic chelating acid.

29 For this purpose, experimental cements were prepared by 30 Wilson and co-workers by mixing series of pyruvic, tartaric, 31 tannic, fluoroboric, glycerophosphoric and tetraphosphoric 32 acids, at concentrations of 35–50% in solution and polyacrylic 33 acid at a concentration of 25% in solution with the aluminosilicate glass powder.⁶ The resultant cements (formed from 34 35 pyruvic, tartaric, tannic, fluoroboric, glycerophosphoric and 36 tetraphosphoric acids in the concentrations investigated) 37 demonstrated adequate handling and working characteristics but slow setting characteristics and poor hydrolytic stability 38 39 which precluded clinical usage. However, the cement formed with the 25% polyacrylic acid solution⁶ highlighted a reduced 40 41 susceptibility to hydrolytic disintegration but had 'little or no 42 working time'.³

Wilson and Kent⁷ discovered that the reactivity of the glass 43 44 was controlled by the alumina:silica ratio, whereby hydrolytically stable cements could be formed by employing novel glass 45 formulations. The early cements formed from modified 46 47 alumina:silica ratio glass formulations also had poor working 48 and setting characteristics⁸ and it was not until the 200th glass 49 composition (G-200) - which was high in fluoride and calcium -50 that a usable dental cement was formed.³ The cement was 51 reported⁷ as a GI or aluminosilicate polyacrylate (ASPA) cement. Despite the heightened anticipation for the clinical 52 53 success of GIs, the first practical cement (ASPA-I) failed to 54 impress John McLean, the clinical consultant who raised concerns regarding the poor setting characteristics and 55 limited working time.³ Delayed hardening of the earliest GIs 56 57 exposed them to the deleterious effects of moisture contamination during clinical placement⁹ and desiccation^{10,11} during 58 the early stages of the setting reaction. In an attempt to 59 60 improve the setting characteristics of GIs, Wilson et al.12 investigated the role of a third component, a chelating agent, 61 62 in the setting reaction using citric acid, salicyclic acid, acetylone, sequestric acid, polyglycol and tartaric acid. The 63 results for tartaric acid were promising¹² and proved to be 64 'effective beyond all expectations'.³ Tartaric acid lengthened 65 the working time,¹² shortened the setting time,^{13,14} increased 66 the compressive fracture strength (CFS)¹⁴ and increased the 67 resistance to acid dissolution.³ 68

A subsequent version of ASPA-I containing tartaric acid,
the G-200 glass and polyacrylic acid (ASPA-II) showed
favourable handling characteristics when used as a pit and

fissure sealant.¹⁵ Interestingly, the discovery of the role of tartaric acid in the setting reaction provided opportunities for the use of glasses other than G-200. However, changes to the liquid component of ASPA-II were required due to gelation of the polyacrylic acid hompolymer¹⁶ which prompted investigations into the use of a methanol containing modification (ASPA-III) and later a further variant containing a copolymer of acrylic and itaconic acids (ASPA-IV).^{17,18} Thereafter, the use of the acronym 'ASPA' as a generic term was abandoned and confined to coding experimental materials developed at the LGC.³ ASPA-IV was the first commercial GI material, launched by the Amalgamated Dental Company (Dentsply DeTrey, Konstanz, Germany) as a hand-mixed GI cement in 1975 under the trade name 'ASPA'.¹⁹ When five dental nurses and one dentist were asked to hand-mix the ASPA material in a clinical simulation study, Mount and Makinson²⁰ identified a wide range of powder:liquid mixing ratios below that specified by the manufacturer. On average, 85% (by weight) of the manufacturers recommended powder content was incorporated by the operators, although powder contents as low as 42% (by weight) were identified.²⁰ As a result of the difficulties in operators reproducing the manufacturers powder:liquid mixing ratio in a clinical simulation, Dentsply DeTrey launched an encapsulated version of ASPA in 1978²¹ which eliminated operator induced variability in proportioning the powder and liquid constituents.

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Today a wide variety of commercial hand-mixed and encapsulated GIs are available to the general dental practitioner for clinical use as luting agents, liners and bases for placement under amalgam restorations or the restoration of anterior and posterior dentition. GIs are routinely supplied in two presentational forms: as a separate glass powder and polyacid liquid⁷ or as a blend of glass powder and vacuumdried polyacid which is mixed with distilled water or a solution of tartaric acid termed 'anhydrous' GIs.^{22,23} The handling characteristics and mechanical properties of commercial GI products have been optimised by the manufacturers through developments in the glass powder and polyacid liquid constituents used in the GI formulations.

2. Developments in GI powder

GIs are composed of an ion leachable glass powder and a 112 polyacid liquid which are mixed together using a predeter-113 mined power:liquid mixing ratio to form a solid mass on 114 setting. The GI powder is prepared from an aluminosilicate 115 glass which serves as a source of ions for the cement forming 116 reaction.^{24,25} The glass composition controls the setting rate of 117 the cement forming reaction^{26,27} and the refractive index 118 match to the polysalt matrix dictates the translucency of the 119 set GI.²⁸ The glass component is prepared by sintering 120 mixtures of powdered silica (SiO₂), alumina (Al₂O₃), cryolite 121 (Na₃AlF₆), aluminium trifluoride (AlF₃), fluorite (CaF₂) and 122 aluminium phosphate (AlPO₄) at 1100–1500 °C depending 123 upon the chemical composition of the glass.²⁷ The glass melt 124 is shock quenched in water, the resultant course glass frit is 125 ground using a ball mill and sieved to form a powder with a 126 maximum particle size of 45 μm for GI restoratives and 15 μm 127 for GI luting cements.²⁷ 128

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