

Development of Glass-Ionomer Cements as Dental Restorative Materials

Kefi Iqbal¹, Iqbal Ahmad² and Mohammad Aminuddin²

ABSTRACT:

Physico-chemical adhesion with tooth substance has necessitated the production of polyacrylic acid based cements such as glass-ionomer cements (GICs) as dental restorative material. These materials undergo specific adhesion with hydroxyapatite and have been proved to possess properties that are satisfactory for a variety of clinical applications. In order to improve toughness, speed of setting and resistance to dehydration, hybrid materials are incorporated in the formulations to achieve desired ambient polymerization.

FTIR, IR and Raman spectroscopic techniques have been used for observing the physico-chemical changes involved in the setting process. Different glass ionomer cement formulations used for this purpose have been presented.

INTRODUCTION

Glass ionomer cements¹ (GIC) belong to polyacrylic acid based cements and are extensively used as dental restorative materials. These materials are shown to undergo specific adhesion with hydroxyapatite and have proved to possess properties that are satisfactory for a variety of clinical applications. The development of amalgam, gold and porcelain restorative materials in the first quarter of the nineteenth century stimulated the development of dental cements as luting and lining materials and as more aesthetic materials. Zinc oxide-phosphoric acid cement² superseded the oxychloride and oxysulphate cements because of its lower irritation to the pulp and greater durability. The modern day zinc phosphate cement³ and the zinc oxide eugenol cement became very popular, especially the later was found to have a remarkable obtundent effect. A more aesthetic filling material, the silicate cement, was developed in England in 1873. This material received popularity only after an improved version was developed in 1904⁴. Later in 1908 a material was developed that contained fluoride. Thus by the end of first quarter of the last century⁵ three basic types of cements: (1) zinc phosphate^{6,7} (2) Zinc oxide eugenol⁸ and (3) silicate cement^{6,7} were established for the bonding of the inlays, crown, posts, bridges and orthodontic bands or on in the tooth and cavity linings.

The ionomer cements may be classified as follows:

- (1) Polyalkenoate cement
- (2) glass ionomer cement

- (3) alumino-silicate polyacrylic acid (ASPA) cement^{9,10}. All these are available as:
 - i) Powder/liquid in bottles
 - ii) Powder/distilled water (water settable cement)
 - iii) Pre-proportioned powder/liquid in capsules.¹¹

General composition of ionomer cements:

Powder

It consists of an ion-leachable calcium aluminofluoro silicate glass.

Modern cement powders (by weight) are composed of silicon dioxide (41.9%), aluminum oxide (28.6%), and calcium fluoride (15.7%). Also present may be aluminum phosphate (12%), aluminum fluoride (8%), and sodium fluoride (9%).¹²

Liquid

The liquid is an aqueous solution of polymers and copolymers of acrylic acid.

The setting of glass ionomer cement is complex and may vary with the composition. GICs can be described as moderately hard brittle materials, with a relatively high compressive strength, but with low fracture toughness, flexural strength and wear resistance. The cements' physical properties remain unaltered due to the release of fluoride. Fluoride release is greatest immediately after placement and diminishes over time¹³. A large release occurs over the first 24 to 48

hours which is then followed by a rapid decline.¹⁴

Compressive strength of GIC that is restorative cement containing glass particles up to 50 microns in diameter has been observed to increase over a one year period¹⁵. Glass ionomers expand under moist and contract under dry conditions.

LITERATURE REVIEW

Glass-Poly (alkenoate) dental cements commonly known as glass ionomer cements (GICs) are set by an acid-base reaction between polymeric acid typically a polyacrylic acid (PAA) and an acid degradable glass. Control over the reaction rate is often achieved by the addition of tartaric acid¹⁶. In more recent developed resin-modified glass-ionomer cements there is also a light-catalyzed free radical polymerization reaction of a hydrophilic methacrylate-based monomer^{8,17}. The extent of setting in GICs has largely been investigated by studies of cement properties such as surface hardness, compression and flexural strength, sample solubility and rheology¹⁸. The chemistry of simple glass ionomer cements without resin has recently been reviewed by Nicholson (1998)²³. Various techniques including pH studies¹⁹, ¹³CNMR²⁰ and ICp²¹ spectroscopic studies have shown that setting of the cement involves a first step, neutralization of the

polyacid by the basic glass. Infra-red^{22,23} has been particularly useful in characterizing the acid-base reaction. More recently the IR technique has been applied to show replacement of water in GICs by less polar molecules, inhibiting the acid base reaction.¹⁸ FTIR²⁴ and Raman spectroscopy²⁵ have been useful for reaction quantification and characterization of GICS glass. Setting reactions in glass ionomer cements have also been monitored by techniques such as rheology¹⁸ and differential scanning calorimetry²⁶. Physical properties of glass ionomer cements have considerable influence on clinical performance²⁷. There is an evidence of chemical bonding at bio-material hard interfaces²⁸. The investigation shows that an ultra thin layer of the polyalkenoic acid can be prepared on a hydroxyapatite based substrate by careful removal of non-bonded molecules. The percentages of functional groups of the polyalkenoic acid that bonded to calcium of hydroxyapatite have also been quantified. The properties of glass polyalkenoate cements based on the generic glass composition (6+X) SiO₂, (4-X) Al₂O₃, 1.5 P₂O₅, 4 CaOCaF₂ with varying aluminum to silicon ratio have been investigated²⁹. Setting and working time of the cement pastes, compressive strength, unnotched fracture strength, young's modulus, fracture toughness and toughness have been evaluated for the cements. Some typical glass ionomer powder formulations and their composition is given in Table1.

Table 1: Composition of glass powder formulations

| Formulation | Composition (%) | | | | | | | | Ref. |
|-------------|---------------------------|---|---------------------------|---------------------------|--|---------------------------------------|---|-------------|------|
| 1 | SiO ₂ 20-60 | Al ₂ O ₃ 10-50 | CaO 1- 40 | F 1- 40 | Na ₂ O 0-10 | P ₂ O ₅ 0-10 | | | 30 |
| 2 | SiO ₂ 18.22 | Al ₂ O ₃ 10.60 | CaF ₂ 12.50 | AlF ₃ 11.00 | Na ₂ AlF ₆ 5.88 | P ₂ O ₅ 2.60 | La ₂ O ₃ 38.20 | MgO 1.00 | 31 |
| 3 | SiO ₂ 41.9 | Al ₂ O ₃ 28.6 | CaF ₂ 15.7 | AlF ₃ 8 | NaF 9 | AlPO ₄ 12 | | | 12 |
| 4 | SiO ₂ 29.0 | Al ₂ O ₃ 16.6 | CaF ₂ 34.3 | AlF ₃ 5.3 | Na ₂ AlF ₆ 5 | AlPO ₄ 9.8 | | | 20 |
| 5 | SiO ₂ 29.0 | Al ₂ O ₃ 16.5 | CaF ₂ 34.3 | AlF ₃ 7.3 | | AlPO ₄ 9.9 | | | 44 |

The studies of long term flexural strength,³² comparative strength of commercial GICs with and without metal addition, mechanical properties and microstructure of GICs³³ and structure property relationships in GICs³⁴ have led to the knowledge of the fracture surfaces, strength of the cement and fluorine bonding to the calcium ions. GICs containing niobium might be used in the composition to achieve a best possible result in dental applications.³⁵

Other investigations include reactivity of fluoride containing calcium aluminosilicate glass,^{36,37} in vitro fluoride release from a light-cured glass-ionomer liner/bases,³⁸ effect of monovalent ions in GICs on their interaction with sodium fluoride solution³⁹ and the stoichiometry of the leaching process of fluoride containing aluminosilicate glass ionomer⁴⁰ to help establish the exact relationship between the composition of the glass and the properties.⁴¹

Expansion of the concept of incorporation of polymerization and polyelectrolyte salt formation mechanism within one molecule or a combination of molecules has led to a spectrum of materials⁴² which range from classical acid-base GIC to modified polymerceramic (glass) composites with little polyelectrolyte character. The objectives sought in the later materials are to improve the strength, toughness and resistance to dissolution whilst retaining the fundamental attributes of adhesion, fluoride release and biocompatibility associated with the GIC system. These cements, a component of conventional ionomer glasses like AL⁺³ has been linked with poor bone mineralisation and neurotoxicity.⁴³

DISCUSSION

The present literature review on GIC as dental restorative material indicates that the development of GIC powders over the time has led to the availability of such materials to meet the physico-chemical and biological requirements in clinical applications. The compositional variations in glass powder formulations may influence the quality of GIC in terms of its restorative properties. The development of these formulations is based on the study of physical, chemical and biological factors to achieve the desired standard. The chemical aspects of GIC formulations can be best studied by the application of various spectroscopic techniques as conducted by various workers mentioned in the literature review. It is necessary to meet to desirable physical and mechanical properties of GIC to achieve the best possible clinical performance.

CONCLUSION

Glass ionomer cements belong to polyacrylic acid - based cements and are extensively used as dental restorative materials. Various formulations of these cements are available in the literature which includes different ingredients and variable compositions. The physico-chemical characteristics of these formulations have been studied by FTIR, IR and Raman spectroscopic techniques to ascertain the chemical setting properties and leaching process. The aesthetic aspects are also an important consideration in the choice of these materials. All these factors are important and dependent on the composition of glass ionomer cements, therefore, we need to evaluate the different formulation of these cements to achieve the best possible results in their clinical application.

REFERENCES

1. Wilson, A.D., Kent, B.E. A new translucent cement for dentistry. The glass ionomercement. *Br.Dent.*, J., 1972; 132: 133-135.
2. Culbertson, B.M. Glass ionomer dental restoratives, *Prog. Polym. Sci.*, 2001; 26: 577-604.
3. Smith, D.C. Development of glass ionomer cement systems, *Biomaterials*, 1998, 191: 467-478.
4. Steenbock, P. Glass Ionomer Cement, German Patent 1903; 174, 557.
5. Shoenbeck, F. Process for the production of tooth material, United States Patent 1908; 897160.
6. Going, R.E., Mitchen, J.C. Cement for permanent luting., *J. Am. Dent. Assoc.*, 1975; 91; 1: 107-117.
7. Smith, D.C. Dental Cements. *Dent. Clin. North Am.*, 1971; 15:3-31.
8. Milosevic, A. Calcium hydroxide in restorative dentistry, *J. Dent.*, 1991; 19: 313.
9. Millet, D.T., Mc Cabe, J.F. Orthodontic bonding with glass ionomer cement. A review. *Eur. J. Orth.*, 1996; 18: 385-399.
10. White, S.N., Yu, Z., Kipnis, V. Film thickness of new adhesive luting agents. *J. Prosthet. Dent.*, 1992; 6:476-481.
11. Mc Cabe, J.F., Resin modified glass ionomers. *Biomaterials*, 1998; 19: 521-528.
12. Philips, A. K. J. Science of Dental Materials, 2003; 11 th ed., Elsevier Science, London.
13. Forsten, L. Short- and long-term fluoride release from glass ionomer and other fluoride-containing filling materials in vitro. *Scand. J. Dent. Res.*, 1990; 98: 179-185.
14. DeSchepper, E.J., Berry, E.A., Cailleteau, J.G., Tate W.H. A comparative study of fluoride release from glass-ionomer cements. *Quintessence Int.*, 1991; 22: 215-220.

15. Saito, S., Tosaki, S., Hirato, K. Characteristics of glass-ionomer cement, In., Davidson, C.L., Mjor L.A. (eds). *Advances in glass-ionomer cements*, Quintessence Publishing Co., Chicago, 1999, 15-50.
16. Mc Lean, I.W. Cement cements. *J. Am. Dent. Assoc.*, 1990; 120: 43-47.
17. Wilson, A.D., Austice, H.M., Pearson, G.J. Glass ionomer cements: the current status, *Asian J. Aesthet. Dent.*, 1997; 5: 21-27.
18. Austice, H.M., Nicholson, J. W. Studies in the setting of polyelectrolyte materials, *J. Mater. Sci. Mater. Med.*, 1994; 5: 292-294.
19. Wasson, E.A., Nicholason, J.W. Change in pH during setting of polyelectrolyte dental materials, *J.Dent.*, 1992; 21: 120-124.
20. Prosser, H.J., Richards, C.P., Wilson, A.D. NMR spectroscopy of dental cements. The role of tartaric acid in glass ionomer cement, *J. Biomed. Mater. Res.*, 1982; 16: 431-445.
21. Wasson, E.A., Nicholason, W.A. A study of relationship between setting chemistry and properties of modified glass polyalkenoate cements, *Br. Polym. J.*, 1990; 23: 179-183.
22. Crisp, S., Pringur, M.A., Wardleworth, D., Wilson, A.D. I. Reactions in Glass ionomer-cements, II An infrared spectroscopic study, *J. Dent. Res.*, 1974; 53: 1414-1419.
23. Nicholson, J.W. Chemistry of glass ionomer cements, *Biomaterials*, 1998; 48:5494.
24. Banwell, C.N., Mc Cash, E.M. *Fundamentals of Molecular Spectroscopy*, 4th ed., 1994, Maidenhead Mc Graw-Hill, New York.
25. Young, A.M., Sherpa, A., Pearson, G.J., Schottlander, B., Waters, D.N. Use of Raman spectroscopy in the characterization of the acid-base cement. *Biomaterials*, 2000; 21: 1971-1979.
26. Khalil, S.K.H., Atkins, E.D.T. Investigation of glass ionomer cements using differential scanning calorimetry, *J.Mater.Sci.*, 1998; 1: 529-533.
27. Pearson, G. J. Physical properties of glass-ionomer cements influencing clinical performance, *Clin. Mat.*, 1991; 7: 325-331.
28. Yoshida, Y., Van Meerbeek, B., Nakayama, Y., Snauwaert, J., Hellemans, L., Lambrechts, P., Vanherle, G., Wakasa, K. Evidence of chemical bonding at biomaterial-hard tissue interfaces. *J. Dent. Res.*, 2000; 79: 709-714.
29. Griffin, S.G., Hill, R.G. Influence of glass composition on the properties of glass polyalkenoate cements. Influence of aluminum to silicon ratio. *Biomaterials*, 1999; 20: 1579-1586.
30. Powdered dental material and process for the preparation thereof. United States Patent 1985; 4527979.
31. Glass ionomer cement powder. United States Patent 1987; 4808228.
32. Azillah, M.A., Austice, H.M., Pearson, G.J. Long term flexural strength of three direct aesthetic restorative materials, *J. Dent.*, 1998; 26: 177-182.
33. Xie, D., Brantely, W.A., Culbertson, B.M., Wang, G. Mechanical properties and microstructure of GICs, *Dent. Mater.*, 2000; 16: 129-138.
34. Wood, David., Hill, R. Structure property relationship in ionomer glasses, *Clin. Mat.*, 1991; 7: 301-312.
35. Bertolini, J., Zaghet, M. A., Rossano, G., Gislaine, C. P. Determination of the properties of an experimental glass polyalkenoate cement prepared from niobium silicate powder containing fluoride, *Dent. Mater.*, 2008; 24: 124-128.
36. De Maeyer, E.A.P., Verbeeck, R.M.H., Vercruysse, C.W.J. Reactivity of fluoride containing calcium aluminosilicate glass used in dental GICs. *J. Dent. Res.*, 1998; 77: 2005-2011.
37. Moshaverinia, A., Ansari, A., Moshaverinia, M. Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements, *Acta Biomaterialia*, 2008; 4: 432-440.
38. Camillrie, J., Montesin, F. E., Juszczak, A.S., Papaioannou, S., Curtis, R.V., Mc Donald, F., Pitt Ford, T. R. The constitution, physical properties and biocompatibility of modified accelerated cement, *Dent. Mater.*, 2008; 24: 341350.
39. Hadley, P.C., Billington, R.W., Pearson, G.J., Williams, J.A.C. Effect of monovalent ions in GICs on their interaction with sodium fluoride solution, *Biomaterials*, 2000; 21: 97-102.
40. Behr, M., Rosentritt, M., Lohr, H. Changes of cement properties caused by mixing errors: The therapeutic range of different cement types, *Dent. Mater.*, 2008; 24: 1187-1193.
41. Burgess, J.O., Norling, B., Summitt, J., Hunt, P.R. Resin ionomer restorative materials - the new generation. In *Glass ionomers: the next generation. Proceedings of the 2nd International Symposium on Glass ionomers*, Philadelphia, 1994; 75-86.
42. Nicholson, J.W. Polyacid-modified composite resins ("compomers") and their use in clinical dentistry, *Dent. Mater.*, 2007; 23: 615-622.
43. Gillingham, K.H., Reaney, I. M. In vitro biocompatibility of a novel $FeZrO_3$ based glass ionomer cement, *J. Dent.*, 2006; 34: 533-538.
44. Shama Bhat, V., Nandish, B.T. *Science of Dental Materials Clinical Applications*, 6th ed., 2003, SBS, New Delhi, India.