The History and Background to Glass-Ionomer Dental Cements

1

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Abstract

This chapter provides a historical perspective and an insight into how the glass-ionomer cement was invented following a long series of studies on dental cements, beginning with the now obsolete dental silicate cement. It reviews the experiments on the predecessor materials and also the early studies of the glass-ionomer dental cement. Glass-ionomer cements emerged from research on the former dental silicate cement and the zinc polycarboxylate cement. Dental silicates were poorly understood materials in the early 1960s when studies were started at the Laboratory of the Government Chemist in the UK. These studies showed for the first time that dental silicates were acid–base materials that set to form a matrix of metal phosphates containing unreacted glass filler. From this, the role of the glass was understood for the first time and, in particular, the importance of its alumina/silica ratio in controlling basicity. Following this discovery, the means of producing a practical glass-polyacrylate dental cement was clear and was achieved by altering the alumina/silica ratio of the glass to increase its basicity and balance the reduced acidity of the poly(acrylic acid). The original glass capable of forming a practical cement, known as G200, was high in fluoride and hence fairly opaque compared with modern ionomer glasses. Consideration of the role of fluoride led to the concept of chelating additives to control the setting reaction which led to the discovery of the effect of tartaric acid. This allowed glass-ionomer cements of good translucency for clinical use to be developed. These inventions led on to the pioneering work described in this chapter in which the setting reactions were elucidated, the role of water established, the release of fluoride studied and the factors affecting strength determined. This knowledge informed early ideas of how these materials might be used in dentistry, and the chapter concludes with a review of these early clinical applications.

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1.1 Introduction

A substantial part of modern dentistry is concerned with the restoration of function and increasingly the appearance of the teeth following damage by caries, non-carious tooth surface loss or occasionally through trauma.

The topic of dental materials is a critical aspect of restorative dentistry (Wilson 1978). It is a complicated subject, as it is not only concerned with mechanical and chemical function, i.e. strength and toxicity/biocompatibility. It also includes considerations of aesthetics, as increasingly good matches for the appearance of the natural tooth are required as patients are concerned about the cosmetic aspects of tooth repair at least as much as function (Mount and Hume 2005).

For much of the history of restorative dentistry, functional repair was considered paramount, and aesthetic considerations simply did not feature in the process of selection of materials. Repairs were made using either silver amalgam or gold foil (Skinner and Phillips 1960). The former was more economical, and silver amalgam has remained until now a widely used material within restorative dentistry throughout the world, particularly in certain geographical locations (Kovarick 2009).

However, for well over a hundred years, dental cements have been available to the profession which, if not fully matching the appearance of the natural tooth, were at least white and less obtrusive than either gold foil or silver amalgam. The first of these cements was the zinc oxychloride cement invented by Sorel in 1855 (Sorel 1855). It was prepared by reaction of zinc oxide powder with aqueous solutions of zinc chloride. The concentration of zinc chloride was quite high, typically of the order of 40–50 % by mass, so that reaction with zinc oxide powder was rapid and quickly led to the formation of a solid ceramic-like mass of reasonable strength and insolubility in oral fluids. This cement was pioneered in dentistry in 1858, but proved unsuccessful (Wilson 1978). It was difficult to manipulate and subject to erosion within the mouth; hence, its overall clinical performance was poor.

Next came the zinc phosphate cement, which was invented around 1878 (Pierce 1879). It was not particularly successful as first formulated, but was refined by Fleck in 1902 (Fleck 1902), as a result of which it was much easier to use and capable of satisfactory service in clinical dentistry. The refinements introduced by Fleck were necessary in order to reduce the excessively vigorous setting reaction between the components, zinc oxide and aqueous phosphoric acid. The modifications involved changes to both components to slow down the setting reaction and to reduce the exotherm. The zinc oxide powder was deactivated by heat treatment in the range 1100–1200 °C. This causes a degree of sintering between the particles of the powder and also a slight loss of the oxygen to form a nonstoichiometric compound $Zn_{(1+x)}O$, where x is up to 70 ppm (Dollimore and Spooner 1971). The resulting solid is pale yellow in colour and reacts much more slowly with the phosphoric acid solution than untreated zinc oxide, so that a satisfactory paste can be mixed and placed prior to setting.

The phosphoric acid solution was also deactivated to prevent the reaction with zinc oxide occurring too quickly. This was achieved by incorporation of controlled amounts of aluminium and zinc salts. They have the effect of pre-reacting with a small portion of the acid to form salts of the type which make up the matrix of the set cement and hence can be readily incorporated as the cement solidifies. The overall effect of these additives is to reduce reactivity and contribute to the ease of mixing of the final cement formulation.

The resulting cement has excellent properties and is still widely used in clinical dentistry, notably for luting crowns (Hill and Lott 2011). The cement is easy to mix, forms a smooth off-white paste and hardens at an appropriate rate to give a strong solid with good dimensional stability.

The third cement in this group is the now obsolete dental silicate cement. Of the three cements, it attained the highest degree of clinical importance and was also critical to the development of the glass-ionomer cement. Although successful, it was a material with deficiencies in clinical service, and it was because of these deficiencies that the Laboratory of the Government Chemist in the UK was called upon to investigate these materials

(Wilson 1996a). A small group was established under the leadership of Dr. Alan Wilson, whose pioneering work in understanding the setting and structure of the dental silicate cement paved the way for the invention of the far superior glass-ionomer cement (Wilson and Kent 1971).

The early history of the dental silicate cement is obscure (Wilson 1978) though there is evidence that it may date back as far as the zinc phosphate cement. However, it was not until 1908 that a successful version appeared (Schoenbeck 1980). This cement, like the others already described, is a two-component material. The powder was a glass based on calcium aluminosilicate with added fluoride flux, and the liquid was a concentrated solution of phosphoric acid. Like the zinc phosphate cement, the dental silicate cement was improved considerably by the inclusion of salts in the aqueous phosphoric acid component, as this reduced the vigour of the setting reaction and allowed workable pastes to be mixed and placed. The paste that was formed was off-white and set rapidly to form a solid, strong material with a degree of translucency. This translucency gave an appearance that was superior to that of the zinc phosphate cement, and this made the cement suitable for the aesthetic repair of the anterior teeth (Wilson 1978). Another advantage of the dental silicate cement was that the strength was high, of the order of 250–300 MPa in compression at 24 h. This was also a superior property of these cements compared with the zinc phosphate cement.

Development of a proper understanding of the setting and structure of dental silicate cements was slow. Due to its importance in the genesis of the glass-ionomer cement, this topic is considered in detail in the next section of this chapter.

1.2 Dental Silicate Cement

Until the 1960s, dental silicate cement was the most widely used filling material for the anterior teeth. In fact, until the first simple acrylic-based composite materials appeared in the mid-1950s, it was the only aesthetic (tooth-coloured) dental material available to dental clinicians (Kakaboura and Vougiouklakis 2001; Wilson and Nicholson 1993). In the mid-1960s, 40 brands were available (Wilson 1969), but with the advent of the first bis-GMA composite resins in 1962, and then the glass-ionomer in 1971, its use has dwindled and it is now almost completely obsolete.

The name dental silicate is incorrect and was applied early in its history in the erroneous belief that the setting involved the formation of a silicate structure (Voelker 1916). It was the early work of Wilson and his co-workers in the 1960s that established that the cement is, in fact, phosphate-bonded (Wilson and Nicholson 1993).

The earliest successful dental silicate cement was developed by Steenbock in the early years of the twentieth century (Steenbock 1904). This cement used glasses based on blends of calcium alumina-silicates and beryllium silicates (Steenbock 1904), compositions which almost certainly gave cements of poor translucency (Wilson and Nicholson 1993). An early development was the inclusion of fluoride, initially as a flux to lower the melting temperature of the glass-forming mixture. The presence of fluoride not only lowered the melting temperature of the glass; it also improved both the strength and the translucency of the set cement (Wilson and Nicholson 1993). By 1938, all dental silicate glasses were fluoride-containing and also were no longer formulated with beryllium silicates (Paffenbarger et al. 1938). In other words, they were calcium fluoro-aluminosilicates of the same general type as modern glasses for glass-ionomer cements (Wilson and Nicholson 1993).

Although dental silicate cements were strong and aesthetic, and also offered the therapeutic benefit of sustained fluoride release, they had several drawbacks. These were noted by early workers in the field (Wilson and Nicholson 1993) and included porosity, a tendency to stain, a susceptibility to acid attack in the mouth, dimensional instability and the absence of adhesion to the tooth. In certain patients, the acid attack could be so severe that the restoration eroded significantly and even disappeared completely in extreme cases (Wilson and Nicholson 1993)

These problems were tolerated for many years, but in the early 1960s, it was no longer considered acceptable within the UK. At this time, the UK Department of Scientific and Industrial Research (DSIR) set up a committee to stimulate and co-ordinate research in universities and government research establishments on the subject of dental materials and equipment (Wilson 1996a). It was through this committee that the Laboratory of the Government Chemist became involved. This organisation is now a private company, operating as LGC and based in Teddington but was originally established as a public sector laboratory in 1842, based in central London (Hammond and Egan 1992). It has a wide-ranging brief to apply chemical analysis in the service of government, mainly where issues of revenue are at stake. Improving the reliability of dental silicate cements fell within this remit because of the cost of this failure to the tax payer-funded National Health Service in the UK. The original commission to the Laboratory of the Government Chemist from the DSIR was to examine the structure and properties of silicate cements with the aim of determining whether or not they had any potential for improvement (Wilson 1996a).

1.2.1 Composition of Dental Silicates

As we have seen, dental silicate glasses were based on the SiO_2–Al_2O_3–CaF_2 system, with a relatively high aluminium to silicon (Al/Si) ratio. This composition is necessary in order to make the glass basic, a requirement for reaction with aqueous phosphoric acid in the setting process. The Al/Si ratio controls the basicity of the glass and hence the ability of the glass to react with acid solutions (Wilson 1996b). The Al/Si ratio is lower in dental silicate glasses than that in glasses for glass-ionomer cements because of the different strengths of the acids involved in the setting reaction. The acid in glass-ionomers is a weak organic acid based on a water-soluble polymer such as poly(acrylic acid), whereas the acid in dental silicates is strong. However, the discovery of the rate-modifying effects of (+)-tartaric acid in glass-ionomer cements has somewhat obscured these differences. A wider range of glasses, including those with Al/Si ratios approaching those in dental silicate glasses, are capable of forming glass-ionomer cements when (+)-tartaric acid is present in the acid liquid (Wilson 1996a).

Table 1.1 Composition of typical dental silicate liquid

Species	Mass (%)
H_3PO_4	48.8
Al	1.6
Zn	6.1
H_2O	43.3

Based on data from Wilson and Nicholson (1993)

The liquids in dental silicate cements were concentrated solutions of orthophosphoric acid H_3PO_4, generally with additions of aluminium and zinc (Wilson et al. 1968), as shown in Table 1.1. The optimum acid concentration was 48–55 % by mass (Wilson et al. 1970a), although higher concentrations were used in certain brands. Important properties of dental silicate cements relate to the concentration of the phosphoric acid in the liquid component, including strength and resistance to acid attack (Wilson et al. 1970a, 1979).

The sensitivity of these properties to acid concentration led to practical difficulties in the deployment of dental silicate cements. The optimum concentration of phosphoric acid is stable only in an atmosphere of 70 % relative humidity. In more humid atmospheres, the solution takes up water, reducing the acid concentration and leading to inferior cements (Paffenbarger et al. 1938; Wilson et al. 1970a; Worner and Docking 1958). Similarly, in less humid atmospheres, the acid liquid loses water and increases the concentration of the acid. Cements made from such solutions are also inferior. This sensitivity to the prevailing humidity was a further disadvantage of these cements as practical dental materials.

1.2.2 The Setting Reaction of Dental Silicate Cements

A critical step in the development of the glass-ionomer cement was the understanding of the setting reaction of the dental silicate cement, which was achieved by Wilson et al. from 1968. The earliest view had been that the cement was formed by gelation of silicic acid in the solid state (Ray 1934). This was shown to be incorrect in a study of the effect of acid storage environments on dental silicates, from which Wilson and Batchelor concluded that the matrix could not be silica gel (Wilson and Batchelor 1968). They suggested initially that the matrix might be a silico-phosphate material instead, but it was then found that infrared spectroscopy could not detect the presence of any P–O–Si bonds (Wilson and Mesley 1968). The nature of the setting reaction was finally established in 1970 in a paper by Wilson et al. (1970b) which, while primarily concerned with the role of water in these cements, showed that the main products of setting were amorphous aluminium phosphates. Some siliceous material was formed, but it remained as a coating around the partly reacted glass filler particles. The set cement was thus shown to consist of partly reacted glass particles embedded in a matrix of calcium phosphate.

Careful examination of the results obtained led Wilson to conclude that the setting of the dental silicate cement took place as follows. As the powder and liquid are mixed, the reaction begins with the attack on the basic glass particles by hydrogen ions from the phosphoric acid solution (Wilson and Mesley 1968; Wilson and Batchelor 1967a). This causes migration of aluminium, calcium and sodium ions into the matrix (Wilson and Kent 1968) and leaves behind what is essentially silicic acid. Fluoride ions are also released into the matrix at this stage (Wilson and Kent 1968), possibly as complexes of the type AlF^{2+} and AlF_2^+, both of which are known from other studies (Connick and Poulsen 1957; O'Reilly 1960; Akitt 1989).

As the metal ions migrate into the matrix phase, the ionised acid forms metal salts based on the anionic species $H_2PO_4^-$ (Kent and Wilson 1969). As this happens, the pH of the matrix rises towards neutral and the reaction gradually ceases. The products formed are substantially insoluble and also rigid, and their formation thus causes the cement to set to a hard non-deformable body. Wilson et al. referred to this process as "precipitation", a term that is not wholly satisfactory as precipitation strictly refers to the formation of an insoluble solid that separates from the solution in which it is formed. Dental silicate cements, like other materials of this type, show no phase separation. Instead, all of the water originally present in the acid solution becomes incorporated into the final cement. In fact, one of the defining features of cements is that they consist of pastes which set hard in their entirety, without expelling water (Wilson and Nicholson 1993).

Despite this infelicity in terminology, the studies by Wilson et al. offered a brilliant explanation of the setting of dental silicate cements. Their results showed that hardening reached 65 % of its final value within 30 min and ceased after about 72 h (Wilson et al. 1972). The pH was shown to reach 5.2 after 48 h. However, electrical conductivity studies showed that some form of reaction continued slowly for at least 7 weeks (Wilson and Kent 1968), though hardness did not change. Strength had been known for some years to continue rising in these materials for at least 12 months after fabrication (Paffenbarger et al. 1938), and hence, the discovery of a slow long-term reaction in the solid state was not particularly surprising. The final matrix, as shown by electron probe microanalysis (Kent et al. 1970), is predominantly amorphous aluminium phosphate that also contains fluorite (CaF_2) and sodium acid phosphates.

As previously mentioned, silicic acid is also formed in the early stages of the setting process. This substance polymerises readily to form silica, SiO_2 (Kent et al. 1970; Tarutani 1989). This result is consistent with the known aqueous chemistry of silica (Iler 1979), in particular that low pH favours the occurrence of silicic acid, $Si(OH)_4$, but this changes rapidly in the pH range 5–6, and gelation to silica becomes favoured (Iler 1979).

Water also plays an important role in the setting and post-hardening reactions of these cements. Its initial function is as the medium for the reaction, but as the setting proceeds, it hydrates the products of reaction and becomes incorporated into the solidifying mass. Studies have shown that water exists in fully hardened cements in two states, namely, bound and unbound water. These have been named alternatively as non-evaporable and evaporable, respectively (Wilson et al. 1979). These two states differ in that bound water is retained by the cement when stored in a strongly desiccating atmosphere for 24 h, whereas the unbound water is lost under these conditions, causing a reduction in mass (Wilson et al. 1979). The precise location of the bound water is not clear, though the possibility of hydrating the components of the aluminium phosphate, particularly the Al^{3+} ions, is likely (Enderby and Nielson 1989).

In their studies of the set cement, Kent et al. 1970 (Tarutani 1989) used glass powders that had been sieved to remove the finest particles. Electron probe microanalysis showed that the matrix of the dental silicate cement contained Al, P, Na and F only, with the Si restricted to layers around the partly reacted glass filler particles. This was important in establishing how these materials set, but it is not a true picture of the elemental distribution in clinical dental silicates. In a later study, Brune and Smith (1982) showed that silicon was distributed throughout the matrix. It seems probable that this was caused by the reaction of very fine glass particles that were so small that they degraded completely as the reaction proceeded. Hence, this later observation does not invalidate the conclusions of Wilson et al. (1970b) that the setting of dental silicates does not consist of the formation of silicates but of phosphates.

1.2.3 Physical Properties of Dental Silicate Cements

Physical properties of dental silicates vary with the powder/liquid ratio and the best cements are mixed at high ratios, up to 4 g/cm^3 (Wilson et al. 1972). Mixing was done by gradually incorporating the powder, so as to minimise the effect of the reaction exotherm between the components of the cement (Brune and Smith 1982). Properties of the resulting cements are shown in Table 1.2.

The values of strength are all quoted at 24 h, but they all continue to rise for at least a year after fabrication (Paffenbarger et al. 1933). The overall strength of the dental silicate is generally considered to be higher than that of any other acid–base cement, though glass-ionomers with strengths exceeding 300 MPa in compression have been reported (Guggenberger et al. 1998).

Table 1.2 Properties of clinical dental silicate cements

Property	Value
Powder/liquid ratio	2.70–4.02
Working time (23 °C), min	3.6
Setting time (37 °C), min	3.25–7.0
Compressive strength (24 h), MPa	68.5–255
Flexural strength (24 h), MPa	24.5
Tensile strength (24 h), MPa	13.6
Solubility/disintegration strength (24 h), %	0.34–0.38
Opacity, $C_{0.7}$	0.42–0.71

Based on data from Wilson and Nicholson (1993)

1.2.4 Solubility and Ion Release

The properties of dissolution and ion release from dental silicate cements were widely investigated, as they were of such importance in the clinical performance of these materials. Erosion and dissolution limited the acceptability of dental silicates, but fluoride release was beneficial in view of the therapeutic effect of fluoride for teeth damaged by caries (ten Cate et al. 2008).

When fully set, dental silicate cements were resistant to attack in neutral solutions. The main species eluted were sodium, fluoride and silica, all in very small amounts (Wilson and Batchelor 1967a). However, before hardening was complete, the cements were vulnerable to attack even in neutral conditions because of the presence of a variety of water-soluble intermediates, including sodium salts, acid phosphates and fluorides.

The removal of such matrix-forming ionic species was found to cause significant changes to the cement surface. To prevent this, clinicians adopted the practice of covering the surface of a freshly placed dental silicate with a layer of varnish. Once a properly formulated dental silicate had hardened fully, it was safe from attack by neutral solutions. It should be noted, though, that poorly formulated cements, including those prepared from incorrect powder/liquid ratios, could contain relatively large amounts of soluble reaction products and consequently disintegrate when immersed in neutral solutions. Studies showed that the main species eluted into neutral solutions were soluble salts of sodium and phosphate and also fluoride (Wilson and Batchelor 1967a, b). As time passed, the rate of elution dropped rapidly, and acid phosphate species ($H_2PO_4^-$ and HPO_4^{2-}) ceased to be released.

By contrast, in acidic conditions, erosion of these cements was shown to be much more rapid (Wilson and Batchelor 1968). This susceptibility to acid attack was suspected as being the cause of the variable performance of these materials from the beginning (Voelker 1916), a view that was confirmed during the 1950s (Norman et al. 1957) and 1960s (Jorgensen 1963). The extent of erosion by acids was found to vary not just with pH but also with their complexing ability. Citric acid, in particular, was found to be especially erosive (Wilson and Batchelor 1968; Stralfors and Eriksson 1969), a concern given the extent to which citric acid drinks are consumed. Studies of erosion of dental silicate cements in service showed that they tended to develop a pattern of grooving at the margin of the restoration and the tooth (Tay et al. 1974, 1979) and, when left unchecked, led to eventual failure of the restoration.

Although dental silicate cements failed under acid attack, their resistance was compared favourably with all other dental cements except the glass-ionomer (Norman et al. 1959; Kuhn et al. 1984). This lack of acid resistance was not considered a particular problem; in fact, when properly prepared and placed, dental silicate cements gave very good results in patients (Robinson 1971). The problem was that the range of optimum performance was relatively narrow. Poor handling and preparation, allowing the acid concentration to change by exposure to the atmosphere at varying humidities and preparing the cement at less than the recommended powder/liquid ratio were all factors that would lead to a cement containing too much water-soluble material and result in clinical failure. It was this unreliability that gave the dental silicate cement its reputation as an unsatisfactory material and left the door open for the development of a much less sensitive material: the glass-ionomer cement.

1.3 Zinc Polycarboxylate Cements

The development of the zinc polycarboxylate cement was also an important step in the invention of the glass-ionomer cement. First reported by Smith in 1968 (Smith 1968), this cement was prepared from the reaction of zinc oxide with aqueous poly(acrylic acid). The setting process involved gelation of the poly(acrylic acid) solution with zinc ions released from the powder as a result of attack by the acid. Setting involved incorporation of all of the water in the original acid solution and the formation of a rigid mass from the initial viscous paste.

The zinc polycarboxylate cement was invented as a result of a rational exploration by Smith of factors that can cause adhesion to the tooth surface, and the work was carried out with the aim of producing a material that could act as a luting cement yet show true adhesion to the tooth (Smith 1968). It was the first inherently adhesive dental material and, as such, represented an important advance in restorative dentistry.

The zinc polycarboxylate cement remains a useful material for clinical dentistry, with applications as liners and bases, luting cements and periodontal packs (Wilson and Nicholson 1993). It can be used in all applications of zinc phosphate cements, with the possible exception of post crowns and cantilever bridges (Smith 1982). This does not mean that zinc phosphate has become obsolete or completely superseded in these applications. The choice of material varies between clinicians, and individual clinical technique may favour one material over the other. Consequently, zinc phosphate is still employed in the restorative dentist's armamentarium.

The critical aspect of the invention of the zinc polycarboxylate was the use of aqueous solutions of poly(acrylic acid) as the cement-forming liquid. Concentrations were relatively high, typically 30–43 % by mass (Wilson and Nicholson 1993), which means that the liquid had a reasonably high viscosity. Although poly(acrylic acid) is the principal acid polymer used in these cements, other polymers were quickly proposed, including copolymers of itaconic or maleic acid (Bertenshaw and Combe 1972).

The molar mass of the polymers used varies between about 22,000 and 49,000 (Bertenshaw and Combe 1976) and needs to be carefully controlled in order to obtain satisfactory cements. High molar mass polymers lead to cements of high strength; however, the consequently high viscosity of the polymer solution makes mixing the cement difficult. As a result, molar mass tends to represent a balance between these conflicting requirements and is chosen as a compromise between being low enough to allow satisfactory mixing and high enough for useful strength. Similar issues arise with the glass-ionomer cement, and molar mass of the constituent polymer for these materials also represents a compromise between the need for ease of mixing and high final strength.

The powders for zinc polycarboxylate cements are also complex and do not consist simply of pure zinc oxide (see Table 1.3). As is the case for zinc phosphate cements, the zinc oxide for zinc polycarboxylates has to be deactivated for use in practical cements. Pure powdered zinc oxide reacts too quickly with aqueous poly(acrylic acid) solution to form a smooth paste. Instead, it forms clumps of powder agglomerated by prematurely formed zinc polyacrylate, and this lumpy mixture cannot be mixed further to form a smooth usable paste.

Zinc oxide is deactivated partly by sintering, as mentioned previously for zinc phosphate, a process which results in a pale yellow powder that is very slightly oxygen-deficient (Dollimore and Spooner 1971). In addition, the zinc oxide is mixed with up to 10 % by mass of magnesium oxide powder. Powders may, in addition, contain silica, alumina or bismuth salts, the latter to impart radiopacity. Another key additive is stannous fluoride, which is added at 4–5 % by mass, and was originally added as a source of fluoride (Foster et al. 1974). In fact, stannous fluoride itself probably dissolves out of these cements, rather than free fluoride, as SnF_2 is soluble in water and exists in aqueous solution at very low levels of dissociation (Turner et al. 2013). In addition to providing a source of fluoride, stannous fluoride was found to increase the strength of zinc polycarboxylate cements (Foster et al. 1974), a phenomenon that has yet to be explained.

Table 1.3 Composition of zinc polycarboxylate cements

Component	% by mass
Zinc oxide powder: ZnO	85.2–96.8
MgO	4.73–10.06
Poly(acrylic acid), concentration in solution	32.4–42.9

Based on data from Bertenshaw and Combe (1972, 1976)

The majority of brands of zinc polycarboxylate cement consist of two components, an appropriately formulated deactivated zinc oxide powder and an aqueous solution of polymeric acid, typically poly(acrylic acid). Quite early on, it was found that this cement could be formulated as a dry powder consisting of the zinc oxide powder plus dried polymer, with reaction initiated by mixing this powder with the correct volume of pure water (Bertenshaw and Combe 1972). Setting of these water-activated cements proceeds satisfactorily, and there appear to be no important differences in setting, ultimate strength or clinical performance between these materials and cements formulated more conventionally from aqueous acid solutions.

The way in which zinc polycarboxylate cements are formulated has been shown to influence cement properties, including working and setting times, and strength when set. Factors affecting these include powder/liquid ratio, composition of the powder, molar mass and type of the polymeric acid and also its concentration in the cement-forming liquid (Smith 1971). Typical properties of these cements are shown in Table 1.4.

Setting and hardening of zinc polycarboxylates occur reasonably quickly. A typical formulation

Table 1.4 Properties of zinc polycarboxylate cements

Property	Value
Working time (23 °C)/min	2–5
Setting time (37 °C)/min	3–12
Compressive strength (24 h)/MPa	48–80
Tensile strength (24 h)/MPa	4.8–15.5
Adhesion to enamel (tensile, 24 h)/MPa	4.1–6.9
Adhesion to dentine (tensile, 24 h)/MPa	2.2–5.1

Based on data from Wilson and Nicholson (1993) reaches its maximum strength at 24 h, after which it shows little or no change over subsequent time periods (Watts et al. 1979; Osborne et al. 1978; Paddon and Wilson 1976). The cement shows some viscoelastic properties, and measured strength is influenced by the crosshead speed of the testing machine, particularly at low speeds (Wilson and Lewis 1980). This viscoelasticity remains as zinc polycarboxylate cements age, and distinct creep has been detected under static loading conditions in samples aged for 24 h (Wilson and Lewis 1980). Significant stress relaxation was also found in specimens aged for 4 weeks (Paddon and Wilson 1976).

Zinc polycarboxylates were the first adhesive dental restorative materials and have been shown to bond to untreated dentine and enamel (Mizrahi and Smith 1969). Bond strength to enamel is higher than to dentine, as shown in Table 1.4. In general, zinc polycarboxylate appears to be mild in clinical use, having minimal effects on the dental pulp (Plant 1970; Beagrie et al. 1972; Wilson 1968). They are also nonirritating when used in implants in soft tissue and bone (Wilson 1968).

1.4 Invention of the Glass-Ionomer Cement

It is important to understand the nature of the invention of the glass-ionomer cement. It did not consist of simply mixing the glass powder of the dental silicate cement with the poly(acrylic acid) solution of the zinc polycarboxylate and finding that an excellent cement was the result (Wilson 1996a). It is true that early attempts to improve the dental silicate cement did involve experiments with aqueous solutions of organic acids, though these acids were monomeric and the results, while interesting, were not successful in producing cements with significantly improved properties (Wilson 1968).

Poly(acrylic acid) was considered in those early experiments, but the results were so disappointing that they were not reported at the time (Wilson 1968). Instead, they were hinted at some years later (Wilson and McLean 1988) and not described in detail until Wilson published his personal account of the invention of glass-ionomers (Wilson 1996a). It turned out that these early glass-polyacrylate cements were disappointing in the extreme. They formed an intractable paste which underwent a sluggish reaction, as observed by an increase in the viscosity of the paste; hardening was very slow and the product was hydrolytically unstable. This cement was clearly of no use as a potential dental material (Wilson 1996a).

The invention of the glass-ionomer cement was, in fact, not a single act but rather a series of innovative steps. One key step was the finding that the alumina/silica ratio of the glass controlled the resulting basicity and hence the readiness with which a glass powder would react with an acid solution. This pointed the way towards the first successful glass for a glass-ionomer cement, one with sufficient basicity to react with aqueous poly(acrylic acid). Controlling the alumina/silica ratio allowed the glasses to set much more rapidly than the original glass-poly(acrylic acid) mixture, where the glass was of relatively low basicity. These improved mixtures not only set more rapidly; they were also hydrolytically stable when placed in water (Wilson and Kent 1971; Kent et al. 1973).

The first glass to give at least moderately satisfactory cements was designated G200 and contained alumina and silica in the appropriate ratio to give a high basicity; it was also high in fluoride. Its composition is given in Table 1.5. The resulting cement was known as ASPA 1, the term ASPA being an acronym for aluminosilicate poly(acrylic acid). ASPA was also the brand name of the very first commercial glass-ionomer cement, launched in 1975 (Wilson and McLean 1988).

Table 1.5 Composition of the glass G200

Component	% by mass
SiO_2	30.1
Al_2O_3	19.9
AlF_3	2.6
CaF_2	34.5
NaF	3.7
$AlPO_4$	10.0

Based on data from Wilson and McLean (1988)

The first glass-ionomer, based on G200, was far from the finished article, in that it set relatively slowly and retained a high degree of water sensitivity for a considerable time after setting, which was a distinct drawback. In addition, the glass itself was not particularly translucent, and therefore, the resulting cement had poor aesthetics.

The next inventive step along the path to creating a satisfactory glass-ionomer cement was the discovery of the effect of (+)-tartaric acid on the setting reaction. This discovery came about from a consideration of the nature of the G200 glass. It was exceptionally high in fluoride, a factor that seemed to be important as G200 was the only glass capable of forming a usable cement with poly(acrylic acid) solution (Wilson 1996a). Wilson and his team inferred that fluoride ions must play an important part in controlling the setting reaction, suggesting in particular that they interacted with aluminium ions released from the glass and prevented them from prematurely cross-linking the poly(acrylate) polymer chains. This, they postulated, was because of the high affinity of aluminium for fluoride ions and the formation of complex ions of the type AlF^{2+} and AlF_2^+, which had been proposed to occur during the setting of dental silicate cements (Wilson and Kent 1968).

Slowing the reaction of aluminium via chelation seemed to be a way forward. In the gravimetric analysis of rocks, the established method to prevent premature precipitation of aluminium as the phosphate was to include either citric acid or (+)-tartaric acid, both of which were known to form water-soluble complex ions with Al^{3+} (Lundall and Hoffman 1938). These two acids were therefore examined as potential additives in the glass-ionomer cement.

The results were striking, especially with (+)-tartaric acid. The resulting cements had longer working times and sharper setting, seemingly contradictory properties, both of which made the cement mixture easier to mix and to manipulate (Crisp et al. 1975; Wilson et al. 1976). The cements also had improved compressive strength and were more resistant to acid attack. Wilson considered this to be the most important discovery made in the whole process of inventing and developing the glass-ionomer cement (Wilson 1996a). The new formulation was named ASPA II, and it can be considered to be the first really practical glass-ionomer cement.

1.5 Pioneering Studies of Glass-Ionomer Cements

Following the preliminary reports announcing the development of the glass-ionomer cement (Wilson and Kent 1971; Kent et al. 1973), detailed scientific publications on these cements began to appear in 1974. As well as scientific studies, the first clinical report appeared that year (McLean and Wilson 1974). It covered fissure sealing and restoration with glass-ionomers and was the report of a 2-year clinical study undertaken with the original ASPA formulation of glass-ionomer.

The initial scientific studies were concerned with the setting reaction of these materials (Crisp and Wilson 1974a, b; Crisp et al. 1974). They broke the reaction down into two stages: the decomposition of the glass powder (Crisp and Wilson 1974a) and the reaction of the ions released to cross-link the polyacid, which was incorrectly termed “precipitation” (Crisp and Wilson 1974b). Gelation would have been a better term for this part of the setting process.

The remaining paper in this important series describes the application of infrared spectroscopy to the study of the setting reaction (Crisp et al. 1974) and was important in showing that the main products are calcium and aluminium polyacrylates. These two possible products can be distinguished on the basis of their infrared spectra. Calcium polyacrylate shows a carboxylate band at 1540 cm^{-1}, indicating a highly ionic structure, whereas aluminium polyacrylate shows an equivalent band at about 1600 cm^{-1}, indicating a degree of covalent character with distinct chelation of the central Al^{3+} ions by the surrounding carboxylate groups (Crisp et al. 1974). This paper also showed that the fully set cement contained some residual unreacted carboxylic acid groups, trapped within the cement as it hardened and unable to react for steric reasons (Crisp et al. 1974).

1.6 Early Research on Glass-Ionomers

1.6.1 The Composition and Structure of the Glasses

The first practical glasses for use in glass-ionomer cements were calcium aluminosilicates with added fluoride (Wilson and Kent 1971; Kent et al. 1979; Wilson et al. 1980). Their alumina/silica ratio was adjusted to make them sufficiently basic to set on reaction with aqueous poly(acrylic acid). Although numerous other glass systems have been investigated since these early studies, the glasses developed by Wilson and Kent remain the basis of all practical glass-ionomer cements used clinically. The one substantial change has been the development of strontium-containing ionomer glasses (Guida et al. 2003), where the element strontium is used in place of calcium in the formulation.

Fluoride is an essential component of the glasses (Wilson and McLean 1988). This element has several functions within the glass. It lowers the fusion temperature, it improves the working behaviour of the freshly mixed cement paste by preventing premature gelation and it improves the strength of the set cement. Fluoride-containing glasses are much less opaque than pure oxide ones, and this in turn means that cements prepared from them have improved translucency.

The essential property of glasses for use in glass-ionomer cements is that they are basic and can react with aqueous solutions of acid (Hill and Wilson 1988). This property arises from the ratio of alumina to silica in the glass. Right from the start of research into workable glasses for these cements, this need for basicity and how it could be achieved were well understood. The theoretical framework for this understanding was the random network model of glass as advanced by Zachariasen in 1932 (Zachariasen 1932).

This model considers the glass structure to be a random assembly of oxygen polyhedral, each comprising a small central cation surrounded by a number of negatively charged oxygen ions. A typical polyhedron is (SiO_4). These structures are linked at the corners via the oxygen ions to form an array of chains and interconnected units. The overall concept thus views a glass as consisting essentially of a polymer based on (SiO_4) tetrahedra joined at the corners and exhibiting varying degrees of cross-linking.

The reactivity of such glass structures towards aqueous acids can be increased by including cations such as calcium that can break up the continuous Si–O–Si structural units to form non-bridging oxygen. These ions are described as “network modifying”:

$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{CaO} \rightarrow -\mathrm{Si}-\mathrm{O}^{-}\mathrm{Ca}^{2+}\,{}^{-}\mathrm{O}-\mathrm{Si}-$$

The inclusion of aluminium has more complex effects than the inclusion of simpler chemical species such as calcium or sodium. Aluminium can act as a network modifier in an analogous way to calcium, but it can also be a network former. In the latter case, the presence of reasonable amounts of silica as tetrahedral building blocks of (SiO_4) forces the aluminium to adopt a similar tetrahedral geometry and to form species equivalent to (AlO_4). Although these tetrahedra are the same size as the (SiO_4) ones, they carry more formal charge. This is because the central cation is a 3+ ion, compared to the formal 4+ charge on the central silicon in (SiO_4). The presence of the (AlO_4) tetrahedra therefore has to be balanced by additional cations (e.g. Na^+, Ca^{2+}) in the structure close to the main oxide network (Lowenstein 1954).

These ideas show that the aluminosilicate glass structure of ionomer glasses can be regarded as consisting of linked (SiO_4) and (AlO_4) tetrahedral, with additional cations to balance the charge deficiency due to aluminium. It is the alumina units and their associated cations that serve as the point of reaction with aqueous acid solution, and reaction of the acid involves removal of the charge-balancing cations, followed by rupture of the aluminosilicate network (Wilson and McLean 1988). The Al/Si ratio cannot apparently be greater than 1:1; otherwise there are insufficient (SiO_4) tetrahedral to force the aluminium into fourfold co-ordination, and high basicity does not develop (Lowenstein 1954). Glasses for ionomer cements must have a minimum Al/Si ratio of 1:2, with practical glasses having ratios above this limit (Kent et al. 1979; Wilson et al. 1980). The upper limit in this ratio was found to be 0.75:1 by mass early in these studies (Wilson and McLean 1988), this limit being the point at which the mineral phase corundum (Al_2O_3) crystallises out within the glass structure. Glasses containing two distinct phases are inherently opaque, and resulting cements lack the aesthetics for clinical use.

The three essential components of the early glasses for ionomer cements were silica, alumina and fluorite, i.e. SiO_2, Al_2O_3 and CaF_2. In practice, additional components were added in order to improve properties such as the setting rate, translucency and final strength (Wilson and McLean 1988). Practical glasses typically belonged to complex systems such as:

$$SiO_2 - Al_2O_3 - CaF_2 - AlPO_4 - Na_3AlF_2$$

Table 1.6 Relationship between composition and cement properties for early ionomer glasses

Code	G241	G278	G279	G282
Composition				
SiO_2	120	120	120	120
Al_2O_3	102	102	102	102
CaO	112	101	84	11.2
CaF_2	0	15.6	39	140
Appearance below T_g	Clear	Clear	Clear	Opaque
Powder/liquid ratio/g cm^{-3}	2.5	2.5	2.0	2.5
Setting time (37 °C)/min	2.25	2.25	[a]	3.0
Compressive strength (24 h)/MPa	74	125	[a]	165

Based on data from Kent et al. (1979)

[a] Cement unworkable (set too quickly), hence no setting time recorded, and no specimens could be made for determination of compressive strength

The glasses were prepared by fusion of these components, typically in a ceramic crucible, with fusion temperatures varying between 1100 °C and 1500 °C, depending on the precise chemical composition of the fusion mixture (Wilson and McLean 1988; Hill and Wilson 1988). After melting and allowing the mixture to become thoroughly homogeneous at an elevated temperature, the melt was cooled rapidly by pouring it either onto a metal plate or directly into water. This resulted in the formation of a glass frit consisting of large pieces of glass. It was then ground to a fine powder, typically of 20–50 µm, depending on the clinical application of the cement (Wilson and McLean 1988).

The preparation results in glasses of varying structures. Some show a degree of phase separation that leads to an opaque appearance (Hill and Wilson 1988), whereas others have no visible phase separation and are clear in appearance. Phase-separated glasses were found to give rise to stronger cements than clear glasses (Wilson and Nicholson 1993; Kent et al. 1979), as shown by the results in Table 1.6.

The structure of G200, the first successful ionomer glass, was reported in 1979 (Barry et al. 1979). Although differing somewhat from modern ionomer glasses in that it is low in sodium and very high in fluoride, G200 was found to show some distinctive features that appear to be typical of glasses capable of forming satisfactory glass-ionomer cements. It was shown by scanning electron microscopy to contain phase-separated droplets of complex structure as well as substantial deposits of crystalline fluorite (Barry et al. 1979). The phase-separated droplets had an average diameter of 1.7 µm and represented about 20 % of the volume fraction of the glass. They had a different chemical composition from the rest of the glass and in particular were found to be richer in calcium than the surroundings. These phases were found to vary in basicity, meaning that acid attack occurred preferentially at the most basic of them, causing relatively high levels of calcium to be released from the glass compared with its overall calcium content. This has also been found for the more modern ionomer glass G338 (Wasson and Nicholson 1991). This is a glass that is widely used in clinical glass-ionomer cements and whose composition is given in Table 1.7.

The fact that glasses containing a droplet phase gave stronger cements led to some early work in which the amount of the disperse phase

Table 1.7 Composition of the glass G338

Component	% by mass
SiO_2	24.9
Al_2O_3	14.2
AlF_3	4.6
CaF_2	12.8
$NaAlF_6$	19.2
$AlPO_4$	24.2

Based on data from Wasson and Nicholson (1991)

Table 1.8 Effect of phase-separated crystallites on strength of cements

Glass	Crystalline phase	Flexural strength/MPa
G228	None	21
G309	Fluorite (CaF_2), corundum (Al_2O_3)	33
G381	Baddeleyite (ZrO_2)	28
G385	Rutile (TiO_2), tieilite (Al_2TiO_5)	30

Based on data from Prosser et al. (1986)

was deliberately increased in certain experimental glasses (Prosser et al. 1986). In this study, the mechanical property studied was flexural strength rather than compressive strength, but it was found that where identifiable disperse phases could be introduced, there was indeed a rise in strength. These results are shown in Table 1.8.

1.6.2 The Acidic Polymer Component

The original polymeric acid used in glass-ionomer cements was poly(acrylic acid) (Wilson and Kent 1971). It is still the most widely used acid, though a variety of other polymers have been studied since this acid was first reported. It was, of course, the polymer used in zinc polycarboxylates (Smith 1968) and, hence, was the natural choice when the glass-ionomers were being developed (Wilson 1996a).

Poly(acrylic acid) is an example of the class of substances called polyelectrolytes (Hara 1993). These are substances which combine the features of being both polymers and electrolytes. They derive the latter feature from the presence along the polymer chain of a substantial number of functional groups that are capable of carrying an electrical charge. In the case of most of the polyelectrolytes used to prepare glass-ionomer cements, these functional groups are carboxylic acids, $-CO_2H$. The physical chemistry of polyelectrolytes is complicated (Hara 1993) but can largely be neglected in considering the use of these substances for forming glass-ionomer cements. However, the presence of the polar functional groups able to carry charge does confer one very important property, namely, that polyelectrolytes are generally soluble in water (Hara 1993).

The polyelectrolytes used to prepare glass-ionomer cements are poly(alkenoic acid)s. This was recognised many years ago in the nomenclature agreed by the International Organization for Standardization (ISO) for these materials, where the formal name is glass polyalkenoate cement (Wilson and McLean 1988). In addition to the homopolymer of acrylic acid, copolymers were also studied in the early years of research on glass-ionomers (Crisp et al. 1980a; Schmidt et al. 1981), the main ones being acrylic/itaconic acid (Crisp et al. 1980a) and acrylic/maleic acid (Schmidt et al. 1981). The latter has become commercially important (Nicholson 2000), though the majority of commercial glass-ionomer cements are still formulated with poly(acrylic acid) homopolymer.

The solution of the polymeric acid is used at relatively high concentrations, typically in the range 40–50 % by mass (Wilson and McLean 1988). An early publication demonstrated the importance of the acid concentration in a study involving cements made from the glass G200 (Crisp et al. 1977). The cements in this study were also formulated to include tartaric acid, since the effect of this substance had been discovered by this stage. However, the ratio of tartaric acid to poly(acrylic acid) was maintained constant in all experiments, in order to avoid complicating the results. Unfortunately, the study involved cements formulated at varying powder/liquid ratios, as the aim was to keep the consistency of the freshly mixed cement pastes constant. This part of the study showed, not surprisingly, that as the polymer concentration

Table 1.9 Variation in properties of glass-ionomer cements with varying polymer concentrations

Concentration property	28.6 %	42.9 %	52.0 %
Compressive strength (24 h)/MPa	35	110	152
Diametral tensile strength (24 h)/MPa	4	9	12

Based on data from Crisp et al. (1977)

Table 1.10 Variation in properties of glass-ionomer cements with varying molar masses

Molar mass property	27,000	76,000	230,000
Working time (23 °C)/min	9.25	4.75	2.75
Setting time (37 °C)/min	6.50	5.00	3.25
Compressive strength (24 h)/MPa	17.0	31.0	113.0
Diametral tensile strength (24 h)/MPa	2.9	3.4	5.8

Based on data from Wilson et al. (1977a)

was reduced, more powder was needed to produce a cement of equivalent consistency. This did make results difficult to interpret. However, there were useful findings specifically that as polymer concentrations were lowered, the strengths of the resulting cements were reduced. Selected results from this study are shown in Table 1.9.

Another feature of the polymer which is important in controlling the properties of glass-ionomer cements is the molar mass (molecular weight) (Wilson et al. 1977a). This was first shown in a study which reported the properties of cements prepared from commercial poly(acrylic acid) samples of widely differing molar masses. The polymers were all used at a concentration in water of 25 % by mass, and cements were prepared from them at several different powder/liquid ratios. Some highlights from the data obtained are shown in Table 1.10, and these results show clearly that both the speed of the setting reaction and the eventual strength of the set cement vary with the molar mass of the polymer used.

These results also showed that, as with concentration, there was a balance to be struck between the speed of setting (and also ease of mixing which this implies) and compressive strength. High molar mass polymers give strong cements but set quicker than cements made from low molar mass polymers.

1.6.3 Tartaric Acid and Its Role

An early observation was that available fluoride present in the glass had considerable influence on the working time of glass-ionomer cements (Crisp et al. 1974). This was attributed to the ready formation of aluminium fluoride complexes, with the argument being that complexed aluminium fluoride complex ions were not immediately available for interacting with polyanion chains in the cement and cross-linking them. As a result, the working time was prolonged.

This led to the search for chelating agents that could be added to the cement and extend the working time by combining with ions leached from the glass, preventing them from interacting with the polyanion chains. In this way, premature gelation would be avoided and the working time extended. It was recognised that acidic chelating agents would be advantageous, as they could aid the removal of the cations from the glass and also suppress the ionisation and uncoiling of the polymer chains, thus further prolonging working time (Wilson et al. 1976).

The initial search for a successful chelating additive included a wide range of substances (see Table 1.11). These included hydroxyacids, such as tartaric acid and citric acid, hydroxybenzoic acids, diketones, ethanolamine and urea. The study involved the use of the oscillating rheometer to monitor setting profiles, from which the working time could be determined. Working times were also confirmed using a modified Gillmore needle, where resistance to indentation by a weighted needle is taken as the criterion of workability. Two methods were used because working time is not an exact property. Defining it by laboratory tests is not straightforward, though these early papers by Wilson et al. (1976) clarified a method that has since been widely used and which replaces much of the subjectivity that otherwise surrounds the concept. In fact, the two experimental methods used gave results that were in good agreement (Wilson et al. 1976).

As well as working time, the gel time was recorded (Wilson et al. 1976). This effectively corresponded to the setting time, but at a temperature of 23 °C. It was taken to be the time at

Table 1.11 Effect of chelating agents on the setting of ASPA glass-ionomer cement

Additive	P/L ratio (g/cm^3)	Working time (min)	Gel time (min)
None	3.5	1.8	9
None	4.0	2.4	8
5 % tartaric acid	3.5	2.0	6
5 % tartaric acid	4.0	1.9	5
5 % citric acid	4.0	1.9	6
2 % 2,6-dihydroxy benzoic acid	4.0	2.1	9
2 % acetylacetone	4.0	2.3	8
5 % urea	3.5	2.2	15
5 % ethanolamine	3.5	3.5	19

Based on data from Wilson et al. (1976)

which the cement was shown to be set on the oscillating rheometer, as characterised by the rheometer showing only small but constant amplitude.

Additives were found to have a variety of effects, but the best of them were tartaric acid and citric acid, with the former being superior overall. In both cases, they sharpened the setting rate, and this generally meant increasing the working time and reducing the gel time. The effects were greater with tartaric acid, and there was also some evidence that the resulting cements were less soluble in water than those containing citric acid (Wilson et al. 1976).

The effects of including tartaric acid in the cement formulation were studied in detail, mainly by infrared spectroscopy (Crisp and Wilson 1976). Samples were examined using the attenuated total reflectance (ATR) technique in which they were pressed against the face of a crystal and the spectrum recorded in reflectance mode. Also, ionic extracts were obtained from the cements at various time intervals and analysed. The results of the two approaches were combined in order to obtain a detailed account of the cement-forming reactions in the presence of tartaric acid. This study used G200 glass and a liquid comprising 47.5 % by mass poly(acrylic acid) and 5 % by mass tartaric acid. A powder/liquid ratio of 1.5 g/cm^3 was used, which is lower than that of practical cements. However, it reacted more slowly than a properly formulated cement, and this gave time to collect the spectra, which allowed the reaction to be studied in reasonable detail.

Table 1.12 Infrared absorption band (C=O asymmetric stretch) for species present in cements formulated with tartaric acid

Species	Band (cm^{-1})
Ca-tartrate	1595
Al-tartrate	1670
Ca-polyacrylate	1550
Al-polyacrylate	1559

Based on data from Nicholson et al. (1988)

The results of the ATR infrared part of the study were not particularly informative, partly because the absorption bands were broad and ill-defined. Attempts were made to monitor the reduction in the carboxylic acid bands, whose asymmetric stretch occurs at about 1700 cm^{-1}, and to monitor the increase in carboxylate salt bands, at 1540 cm^{-1} and 1600 cm^{-1} for calcium and aluminium, respectively. It was not until FTIR was first used in 1988 (Nicholson et al. 1988) that the differences between the positions of the bands due to the metal salts of poly(acrylic acid) and tartaric acid could be identified (Table 1.12). Consequently, the early studies by Crisp and Wilson (1976) were not able to confirm the early appearance of calcium and aluminium tartrates, nor the corresponding delay in the appearance of the respective polyacrylate salts. Nonetheless, they were able to confirm the essential similarity of the setting reaction with and without tartaric acid and that the presence of tartaric acid acts in part by increasing the rate at which ions are liberated from the glass powder in the first step of the process (Crisp and Wilson 1976).

Another early study applied ^{13}C NMR spectroscopy to the setting of glass-ionomer cements (Prosser et al. 1982). This showed quite clearly that the initial reaction is between the glass powder and the tartaric acid, forming complex tartrate cations. As neutralisation proceeds and pH reaches about 3, the poly(acrylic acid) starts to be neutralised by metal ions from the glass. The cement sets to a hard mass at pH 5.0–5.5 (Wilson and McLean 1988). Prosser et al. (1982) also noted that the presence of tartaric acid suppressed the ionisation of the poly(acrylic acid) with the result that its uncoiling was delayed. This reduced the viscosity of the cement paste and slowed the onset of gelation.

Glass-ionomer cements containing tartaric acid were found to be stronger than those without any additive (Wilson and McLean 1988; Wilson et al. 1976). This led to the suggestion that these cements contain specific bridging complexes that add strength to the set matrix (Wilson et al. 1976). However, this neglects the likely effect of the lower cement viscosity on mixing. A lower viscosity paste would be easier to manipulate, would wet the glass powder better and be less likely to entrap air during mixing, thus reducing the development of pores within the set material. All of these effects would improve the homogeneity of the mixed cement, reduce flaws and consequently enhance strength.

1.6.4 Maturation and the Role of Water

The main steps in the initial setting reaction were identified and described in the earliest papers on these materials (Crisp and Wilson 1974a, b; Crisp et al. 1974). However, it was also discovered early in the development of glass-ionomers that there were slow changes in the cements that continued for a considerable time, up to at least a year after preparation. For example, compressive strength increased during this time, with the strength being proportional to the logarithm of time (Crisp et al. 1976a).

The mechanical properties as a whole were shown to change with time. A newly hardened cement was shown to behave somewhat like a zinc polycarboxylate cement in that it had a degree of plastic character. Later, as the various slow maturation processes took place, it became much less plastic and increasingly rigid (Paddon and Wilson 1976). No other cements behave in this way. Zinc polycarboxylates, for example, retain their plastic character for considerable periods of time (Paddon and Wilson 1976), and indeed, there is no evidence that they ever lose it.

The changes in mechanical properties were found to correlate with increases in the proportion of bound water within the cement (Wilson et al. 1979, 1981). It was suggested that processes analogous to the hydration reactions in Portland cement took place in glass-ionomers, possibly due to increasing hydration of the metal carboxylate units within the cement (Wilson et al. 1979, 1981).

Due to its correlation with the physical changes on maturation, the role of water in glass-ionomers attracted considerable attention in the early research on these materials. Glass-ionomers are based on water-soluble polymers, yet there is no phase separation on setting, so it was apparent from the start that water played an important part in the structure and setting of these cements (Wilson and McLean 1988). As for dental silicates, water within the set cements was classified into “loosely bound” and “tightly bound”, this somewhat arbitrary division being based on whether or not the water can be removed by simple desiccation, by either storage in a desiccator over anhydrous silica gel or by heating at 105 °C for an hour (Wilson et al. 1979, 1981; Wilson and Crisp 1975; Elliot et al. 1975; Crisp et al. 1976b). It was shown that not only did glass-ionomers contain water in these two distinguishable states but also that their ratio changed on ageing. In particular, the proportion of bound water was shown to increase as maturation occurred. This change was accompanied by an increase in the compressive strength and a decrease in the plasticity (Wilson et al. 1979, 1981).

Water was found to be readily exchanged by freshly prepared cements, with water being gained under conditions of high humidity and lost at low humidity. Indeed, glass-ionomers were found to be stable to gain or loss of water only in an atmosphere of 80 % relative humidity (Hornsby 1980). As the cements aged and the proportion of bound water increased, the susceptibility to water loss in low humidity conditions was found to decrease (Hornsby 1980; Saito 1978). The period of time for which the earliest cements were at risk of losing water was found to vary with the brand and ranged between 1 and 30 days (Phillips and Bishop 1985).

Early contact with moisture was also shown to be damaging to freshly prepared glass-ionomer cements (Mount and Makinson 1982; Crisp et al. 1980b; Causton 1981; Earl and Ibbetson 1986). Such contact was shown to cause disruption to the surface, with swelling and loss of ions into the saliva. This led to roughened surfaces and reduced aesthetics (Phillips and Bishop 1985). Research around this time showed that these problems could be prevented by application of an appropriate varnish immediately after placement of the cement (Earl et al. 1985).

1.6.5 Fluoride Release

The ability of glass-ionomer cements to release fluoride is considered clinically beneficial, and it was first observed in the pioneering studies of Wilson and his co-workers (Crisp et al. 1976b). The initial report was concerned with the chemistry of erosion, and fluoride was seen to be part of that. It was soon studied as an independent phenomenon (Forsten 1977; Maldonado et al. 1978), even though the early work showed it to be accompanied by the release of other metal ions, such as sodium and calcium (Crisp et al. 1976b). Release was also shown to be sustained for considerable periods of time, initially for many months, and later for at least 5 years following fabrication of the cement (Forsten 1991).

Quite early on, the observation was made that fluoride release from glass-ionomers obeyed kinetic laws where release was proportional to the square root of time, a relationship that is consistent with release being a diffusion process, at least in part (Wilson et al. 1985; Tay and Braden 1988). The first equation proposed by Wilson et al. (1985) to describe the release process was:

$$\text{Total release} = C + At^{1/2} + Bt$$

Unfortunately, the best fit with the experimental data for this equation was found where the terms B and C were negative. This made assigning any physical meaning to the equation difficult.

The alternative form of the equation, based on just two terms, was proposed a little later by Tay and Braden in 1988 (Tay and Braden 1988). Their equation took the form

$$\text{Total release} = Bt + At^{1/2}$$

This study involved determining the release of fluoride for glass-ionomer cements for a period of two-and-a-half years. However, despite the duration of their experiments, Tay and Braden found that equilibrium was not reached by these materials, and because of this, they were not able to determine the diffusion coefficient for the release. However, they were able to confirm that fluoride release involved two processes, one short term and rapid and the other prolonged and gradual (Tay and Braden 1988). The latter followed a linear relationship with the square root of time and could thus be shown to be diffusion based. These two essential steps have been confirmed in later studies (De Witte et al. 2000), where the short-term process has been called “early wash-out” and shown to be directly proportional to time. The latter process has been confirmed as being diffusion based, on the basis of its directly proportional relationship with $t^{1/2}$.

1.6.6 Physical Properties

Glass-ionomer cements are materials that set rapidly when placed in the mouth, typically in 3–8 min. They are relatively brittle materials, an observation made for the earliest cements (Crisp et al. 1976a; Elliot et al. 1975; Prosser et al. 1984), and one that is still applicable to currently available formulations.

Typical values of physical properties of the early commercial cements are shown in Table 1.13. By the time these data were collected, both conventional and water-activated glass-ionomers were available to the profession. However, physical properties were not found to be influenced by which of these types a particular material belonged to. Other aspects of the composition were found to be much more influential, including the exact composition of the glass powder and the molar mass as well as the type of polymer and also its concentration in the overall cement formulation.

Table 1.13 Physical properties of early commercial glass-ionomer cements

Property	Range of values
Working time, 23 °C/min	1.3–3.8
Setting time, 37 °C/min	2.75–4.7
Compressive strength, 24 h/MPa	140–195
Diametral tensile strength, 24 h/MPa	9.0–19.3
Flexural strength, 24 h/MPa	8.9–30.0
Creep, 24 h/%	0.17–0.33
Water leachable material, 1 h/%	0.13–0.70
Opacity, $C_{0.7}$	0.44–0.85

Based on data from Prosser et al. (1984)

Early on in their evolution, brands of glass-ionomer were developed specifically as restorative cements and as luting cements (Wilson and McLean 1988). The latter were prepared initially from small-particle-sized glass powders in order to achieve the required consistency and flow characteristics (Wilson et al. 1977b). Such small glass particles were increasingly part of the glass blend in restorative grade materials, added to improve their overall physical properties (Wilson and McLean 1988).

Generally, glass-ionomers prepared for use as luting cements had lower strengths than those designed for use as restorative materials. The specification for them was published by the International Organization for Standardization (ISO) as early as 1986 (International Organization for Standardization 1986) and included the requirement of a minimum compressive strength of 65 MPa for luting grade glass-ionomers, compared with a minimum of 130 MPa for restorative grade cements. This is a consequence of the lower powder/liquid ratio used for luting cements (Wilson and McLean 1988). This lower powder/liquid ratio also slows down the setting and maturation reactions, so that the onset of resistance to moisture is delayed. Consequently, luting grade glass-ionomers were found to be more susceptible to early contamination by water than restorative grades (Wilson and McLean 1988).

Glass-ionomer cements are generally considered to have reasonable aesthetics (i.e. to match the appearance of the natural tooth). They are relatively inferior in this regard to composite resins, but superior to all cements available for use in clinical dentistry, including the former dental silicate cement. This derives mainly from the use of clear or opalescent glass powders in their formulation (Wilson and McLean 1988).

The earliest glass-ionomers were of poor translucency compared with materials that became available later, and because of this, they could not be made to match the appearance of the natural tooth (Crisp et al. 1979). However, quite early on, an experimental type of glass-ionomer cement called ASPA X was produced, and it had a translucency which was an excellent match for the tooth (Crisp et al. 1979).

One problem for the determination of appearance with these materials generally was its relationship to maturation. The slow hydration and other reactions that bring about increases in strength and reductions in plasticity also improve appearance, so that full translucency was not reached in the early commercial cements until at least 24 h had elapsed from placement (Wilson and McLean 1988).

A feature that adversely affected the aesthetics of glass-ionomers from the earliest days was that the darker shades were less translucent than the lighter shades (Asmussen 1983). Hence, they look less like natural tooth than the corresponding material in lighter shades. Also, if the freshly placed cement was allowed to come into contact with moisture, the surface was damaged, and this adversely affects the translucency. Overall, these problems meant that glass-ionomers need careful handling in order to optimise their appearance in vivo, and this contributed to their reputation as demanding materials to use.

1.6.7 Adhesion

The ability of glass-ionomers to form adhesive bonds to the surface of the natural tooth was recognised at the earliest point in their development. Indeed, by analogy with the zinc polycarboxylate, the use of poly(acrylic acid) in glass-ionomers was expected to make them naturally adhesive (McLean and Wilson 1974). Right from the start, the advantage of adhesion of these materials was apparent in allowing the repair of cervical erosion lesions in adult teeth and in sealing pits and fissures in children's teeth (McLean and Wilson 1977a, b).

Early studies were carried out to determine the tensile bond strengths on untreated enamel and dentine (Hotz et al. 1977; Prodger and Symonds 1977; Levine et al. 1977; Powis et al. 1982; Aboush and Jenkins 1986). Results varied with the brand used, but all types showed acceptable bond strengths to both substrates (Powis et al. 1982; Aboush and Jenkins 1986). Values on enamel varied from 2.6 to 9.6 MPa and on dentine from 1.1 to 4.1 MPa. Although these ranges overlap to an extent, all studies found higher bond strengths to enamel than to dentine (Wilson and McLean 1988). It was also found that adhesion developed rapidly, with about 80 % of the eventual bond strength being achieved by 15 min (Aboush and Jenkins 1986). Thereafter, it continued to increase for several days after attachment (Powis et al. 1982).

The mechanism of this adhesion was studied in early papers on this topic. Initially, when freshly mixed cement paste is applied to the tooth, wetting has to take place and the adhesion that develops rapidly was attributed to the formation of hydrogen bonds originating from the free carboxyl groups in the cement (Wilson 1974). It was suggested that these hydrogen bonds were later replaced by ionic bonds involving cations obtained from either the cement or the tooth mineral (Wilson 1974). Such a view is consistent with the subsequent findings of the slow formation of an ion-exchange layer between the tooth and the cement (Ngo et al. 1997; Hien-Chi et al. 2006). The concept of the formation of relatively strong bonds involving in part carboxylate groups from the poly(acrylic acid) component was also suggested by early results using infrared spectroscopy to study the bonded surface (Beech 1973).

The role of collagen in the tooth structure on the adhesion of glass-ionomers was unclear from these early studies, and indeed, there still seems to be doubt about how important it is. The finding that tensile bond strengths were greater to enamel than to dentine suggested that the most important bonds are formed with the mineral phase of the tooth. Based on this finding and the results of infrared spectroscopy, Beech stated that bonding involved the hydroxyapatite phase of the tooth only and that collagen had no role at all (Beech 1973). This was challenged by Wilson (1974), who argued that as collagen contains both amino and carboxylic acid groups, the possibility of strong interaction with both poly(acrylic acid) and polyacrylate is high, so that some degree of adhesion would be envisaged. However, he later conceded that, on balance, the evidence pointed towards the conclusion that glass-ionomers probably do not form any adhesive bonds to collagen (Wilson and McLean 1988).

In practical situations, bonding can be improved by surface conditioning. For glass-ionomers, originally this meant treating the tooth surface with a solution of 50 % aqueous citric acid (McLean and Wilson 1977a, b). This technique was found generally to increase the bond strength, though in certain cases, it had no measurable effect (Wilson and McLean 1988). However, citric acid is somewhat aggressive towards the tooth surface and was found to attack both the dentine and the enamel, and not only the smear layer as desired. The resulting loss of mineralizing ions caused substantial damage to the structural integrity of the substrate (Powis et al. 1982) and led to the recommendation that citric acid treatment should be limited to 5 s (Brannstrom 1981). Modern surface conditioning follows the procedure established by Powis et al. (1982) of using dilute solutions of poly(acrylic acid) to remove the smear layer only. They originally employed a 25 % solution, but later studies suggested that slightly higher concentrations, i.e. between 30 and 35 %, were preferred as these gave higher bond strengths (Long et al. 1986).

Adhesion by glass-ionomers is not only desirable because it aids retention of the cement within the tooth but also because it considerably reduces the problem of marginal leakage. Such leakage is a clinical problem, as gaps at the margin of restorations through which it occurs can result in the entry of harmful microorganisms, which then give rise to secondary caries beneath the restorations. In early studies of this problem, using a variety of in vitro methods, the expectation that adhesion would reduce the occurrence of leakage was confirmed (Maldonado et al. 1978; Hembree and Andrews 1978; Kidd 1978). A few years later, it was shown that glass-ionomer cements were able to provide a seal against the diffusion of radiolabelled sucrose, and this was effective for at least a year (Powis 1986). This result was superior to all other restorative materials tested, including composite resins placed with the aid of enamel etching.

1.6.8 Early Studies on Clinical Applications

The expected clinical applications of glass-ionomer cements were first explored in a series of papers published in 1977 (McLean and Wilson 1977a, b, c), though there had been one early paper on this topic in 1974 (McLean and Wilson 1974). It was obvious at this time that these materials had a future as restorations with preventive properties, based on their features of adhesion and fluoride release. They were also seen to have scope for being used successfully as liners and bases (McLean and Wilson 1977a) and also for luting (McLean and Wilson 1974).

Glass-ionomer cements were considered well suited for use in gingival Class V lesions (McLean and Wilson 1977b). The property of adhesion was key to this, as it allowed minimal cavity preparation and the aesthetics of the cement when set made it acceptable for use in such locations. The earliest clinical results published were of a 3-year study in Class V restorations, where a failure rate of only 9 % was reported (McLean and Wilson 1977a). Other early studies generally confirmed these good results (Mount and Makinson 1982; Charbeneau and Bozell 1979; Lawrence 1979), though there was one that found a 43 % failure rate (Smales 1981). These poor results were from a study involving a variety of operators working in a dental hospital and were attributed to lack of experience with these materials (Smales 1981). It was the first indication that they were sensitive to handling in the clinical situation.

Other early clinical applications included Class III interproximal lesions (McLean and Wilson 1977a). A detailed study involving 332 restorations gave extremely promising results (Knibbs et al. 1986), with only a 5 % loss in 3 years, mainly due to abrasion. Only three specimens failed due to poor adhesion, which was a remarkable finding, and it was also observed that there was no recurrent caries observed with any of the restorations (Knibbs et al. 1986).

Fissure sealing was also suggested as an application for glass-ionomers quite early on in their development (McLean and Wilson 1974, 1977a), with the expectation that the good adhesion would provide an excellent seal and that the fluoride release would confer caries resistance. Later studies seem to have confirmed these ideas, though retention has been problematic, despite the generally good adhesion.

Early studies suggested that glass-ionomers were particularly suitable for restoring deciduous teeth (McLean and Wilson 1977a), and soon after, clinical reports appeared confirming this view (Saito 1978; Plant et al. 1977; Vliestra et al. 1978). Luting grade glass-ionomers were also shown to be effective in clinical studies from this time (Reisbick 1981; McComb 1982). In a variety of applications, glass-ionomers were shown to provide protection against secondary caries (Kidd 1978; Hicks et al. 1986), so that there was early evidence that they were able to protect from caries at the interface of the restoration with the tooth. They were also shown to reduce the occurrence of lesions in the adjacent enamel (Kidd 1978). This is an aspect of glass-ionomers in which there has been significant progress in the intervening years, with improved materials and innovative techniques playing their part. These more recent developments lie outside the scope of the present chapter, but it was apparent from the beginning that glass-ionomers were materials with potential for development and for deployment in novel ways. The earliest clinical studies demonstrated this versatility, and this has been confirmed by the numerous studies in subsequent years.

Biological testing showed that early glass-ionomers were acceptable for use in close proximity to the pulp, since the set cement exhibited no adverse effects in cell cultures (Dahl and Tronstad 1976; Meryon et al. 1983; Kawahara et al. 1979). Incompletely set cements were found to be more biologically active, with some possible indication of cytotoxicity (Dahl and Tronstad 1976; Meryon et al. 1983). However, later studies suggest that such effects are minimal in clinical situations (Oliva 1998).

Conclusion

The invention of glass-ionomer dental cements followed on from important and pioneering studies on the setting and structure of dental silicates. Armed with the knowledge won from these studies, Wilson and his team were able to make the key inventive steps and develop glass-ionomer cements as workable materials. Fundamental studies of these materials followed rapidly, and soon the essential features of their setting and maturation were established. Clinical applications were also developed early on. Later work has refined much of the details of our understanding of these materials, but the broad picture has changed very little. This is a tribute to the wisdom and insight of the early pioneers, especially their inventors Alan Wilson and Brian Kent, but also to those clinicians who identified the necessary techniques to make them successful and promoted them to the profession, most notably John McLean and Graham Mount. The place of glass-ionomers among current restorative dental materials owes much to them all.

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