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The role of glass composition in the behaviour of glass acetic acid and glass lactic acid cements

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Abstract Cements have recently been described, made from glass ionomer glass reacted with acetic and lactic acid instead of polymeric carboxylic acid. From their behaviour a theory relating to a possible secondary setting mechanism of glass ionomer has been adduced. However, only one glass (G338) was used throughout. In this study a much simpler glass ionomer glass (MP4) was compared with G338. This produced very different results. With acetic acid G338 formed cement which became resistant to water over a period of hours, as previously reported, MP4 formed cement which was never stable to water. With lactic acid G338 behaved similarly to G338 with acetic acid, again as reported, but MP4 produced a cement which was completely resistant to water at early exposure and unusually became slightly less resistant if exposure was delayed for 6 h or more. These findings indicate that the theories relating to secondary setting in glass ionomer maturation may need revision.

Introduction

For more than 150 years cements based on acid/base reactions have been used in dentistry. The initial cements used very strong acids (hydrochloric or sulphuric acids) reacted with zinc oxide. In the 1870s these were replaced by the somewhat weaker and less aggressive phosphoric acid to produce the zinc phosphate cement (ZC). In the 1903 the zinc oxide powder was replaced by a glass powder derived from the formulations used in dental porcelain production to produce the dental silicate cement (DSC). In the 1960s the phosphoric acid in ZC was replaced by polyacrylic acid to produce zinc polycarboxylate cement (ZPC). In the 1970s a similar replacement was made in DSC resulting in the glass ionomer cement (GIC). The setting mechanism of all these cements results from cation release from the powder under the acid attack. In the phosphoric acid based cements, as the pH increases with neutralisation of the acid, insoluble species such as zinc phosphate and aluminium phosphate are precipitated. With the polymeric acid based cements it is reported [1] that di- and tri-valent ions such as calcium and aluminium react with the pendant carboxyl groups to form ionic crosslinks between the polymer chains.

Unlike the other three types of cement described above, some GICs show changes in physical properties over prolonged periods (i.e. >24 h). In an attempt to study this change in long-term properties, Wasson and Nicholson [2] made model cements using GIC glass mixed with acetic acid solution (replacing polyacrylic acid). For the first few hours the cement formed was not hydrolytically stable but after 24 h it resisted water.

From this they adduced that some other setting mechanism might also occur since the acetates of all the cations (i.e. Na, Ca, & Al) were readily soluble. More recently Nicholson and Czarnecka have evaluated model cements using lactic acid in place of acetic [3, 4]. The mechanisms discussed involve the production of a complex silicate polymer network. Matsuya et al. [5] reported changes in both infrared and NMR spectra which appeared to support the formation of this secondary silicate network in the GIC

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matrix phase. More recently, De Maeyer et al. [6] using infrared spectroscopy on the glass phase alone found that effect of acid on this component could account for the spectral changes observed. In addition, the particular glass used with both acetic acid and lactic acid [2–4] had certain characteristics that made it unsafe to draw general deductions from results obtained on it alone. Although commercially successful glass ionomer dental restorative cements have been based on this glass (G338) they do not show changes in either compressive or flexural strength at periods >24 h [7, 8]. The composition of G338 is not entirely typical of other GIC glasses as it has high levels of both F and P. Both elements can form anions which have insoluble salts with Ca and Al.

To elucidate the possible role of silicate network formation this studies aims to compare the behaviour of G338 glass with that of MP4 which is a simple oxide glass containing 28%SiO_2; 35%Al_2O_3; 26%CaO; 11%Na_2O. Although cements based on MP4 were developed for orthopaedic splinting where hydrolytic stability was not needed, these cements are known to be perfectly stable in water [9] and have been used in comparisons with dental glass ionomers.

Since this glass contains neither F nor P the potential for insoluble salt formation, apart from silicate is eliminated. The objectives are to evaluate the hydrolytic stability of the reaction products formed from the two glasses each with acetic and lactic acid and to examine the effects of maturation time on all four materials. In addition the infrared spectra will be evaluated to compare with those reported by De Maeyer et al. [6].

Materials and methods

Glasses used were the G338 and MP4. Compositions of both these glasses are shown in Table 1.

For cement formation lactic and acetic acids were used at a concentration of 75% and 45% respectively and a P:L ratio of 3:1 and 4:1 respectively. Optimization studies have shown G338 to produce water stable cements after at least 24 h with these acid concentrations and powder liquid ratios [2, 4]. Cements were prepared by spatulating glass powder and acid solution on a glass slab for not more than 30 s. After this time the mix was packed, under pressure, into circular moulds 1 mm thick and 10 mm in diameter. Under this condition, the cements were allowed to set for 1, 2, 3, 6 and 24 h. After these times the cements were dropped into 40 mL of deionised water to assess there hydrolytic stability. Assessment was performed by visual examination based on a point score system (Table 2).

Table 1 MP4 and G338 composition

Glass	Al	Ca	F	Na	O	P	Si
G338	16.9	6.6	19.7	6.3	32.5	6.2	11.8
MP4	18.5	18.6	–	8.2	41.6	–	13.1

Table 2 Point system

Score	Features
1/5	Fully intact
2/5	Fully intact with minor surface defects including minor fissures
3/5	Massive fissuring but no disintegration
4/5	Disintegrates into large chunks
5/5	Disintegrates into fine powder

A similar protocol as described above was used for zinc lactate cements prepared by mixing ZnO powder and 75% lactic acid at a P:L ratio of 3:1.

To observe salt formation ATR-FTIR analysis was performed using Perkin Elmer Infrared Spectrometer using a diamond crystal.

Results

G338 glass formed hydrolytically stable cements, with both acetic and lactic acid, when allowed to mature for at least 6 h. Cements immersed in water before this time disintegrated completely turning the solution cloudy and did not retain their disc form. The time taken by the cement to disintegrate was directly proportional to its maturation time. Unlike with acetic acid G338 formed translucent cements with lactic acid however these cements instantly turned chalky white on immersing in water.

The MP4 glass showed different results with lactic acid and with acetic acid. With lactic acid it formed hydrolytically stable cements when allowed to mature for just 1 h. The cements showed no sign of disintegration/solubility except for cracking observed for cements with maturation time of 6 and 24 h. With the acetic acid, MP4 failed to give hydrolytically stable cement throughout the experiment (Table 3; Fig 1). Although the cements had a perfect disc form when taken out from the moulds, but soon after

Table 3 Points scored

	1	2	3	6	24	Total points
G338 (lactic)	4/5	4/5	2/5	2/5	2/5	2.8
MP4 (lactic)	1/5	1/5	1/5	3/5	2/5	1.6
G338 (acetic)	4/5	4/5	1/5	1/5	1/5	2.2
MP4 (acetic)	5/5	5/5	5/5	5/5	5/5	5

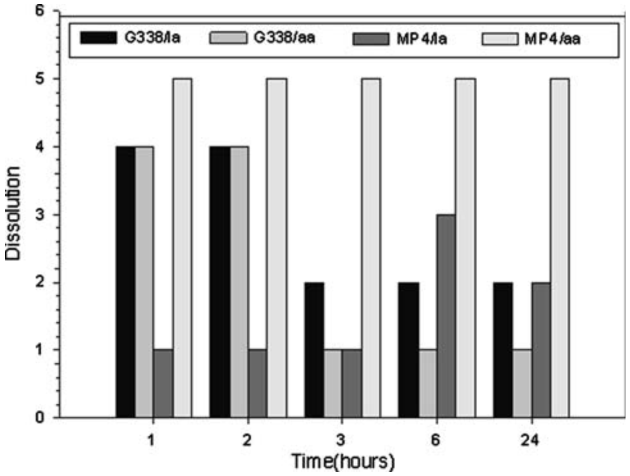

Fig 1 Bar chart depicting dissolution of cements based on the point score system (aa = acetic acid cements; la = lactic acid cements)

immersing in water the cements disintegrated in to fine powder.

To further the solubility/disintegration analysis the immersing solutions were slowly evaporated to dryness in an incubator kept at 37 °C. A residue was observed in all instances except for MP4/lactic acid cements.

Zinc-lactate cement showed hydrolytic stability similar to that of MP4-acetic acid cements.

FTIR-ATR analysis showed rapid salt formation up to 3 h after which no additional salt formation was observed (Fig 2).

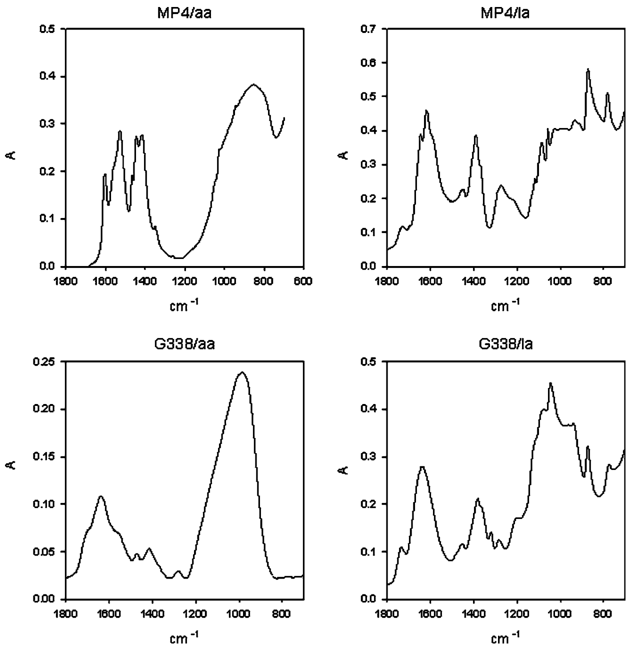

Fig 2 FTIR-ATR scans at 6 h (aa = acetic acid cements; la = lactic acid cements)

Discussion

The results on acetic acid cements demonstrate the hypothesis that maturation of GICs is caused by formation of a silicate network in the polyacid matrix is not viable. MP4 contains the same amount of silica as G338 but does not form an insoluble cement with acetic acid. In contrast, G338 does behave in this way as reported previously by Wasson and Nicholson [2]. Examination of the differences between MP4 and G338 (Table 1) show other elements present in the latter that may account for the formation of hydrolytically stable cements. Both P and F are present in high levels (compared to most GIC glasses). If the initial formation of soluble acetates occurs with acid attack on the glass, as the pH increases these elements may provide anions that could precipitate calcium salts. CaF_2 is very insoluble as are various phosphates such as tricalcium phosphate, calcium pyrophosphate, hydroxylapatite or fluorapatite. The formation of such compounds is analogous to the processes involved in the setting of ZP and DSC materials.

The setting reaction as shown by FTIR traces (Fig. 2) is similar to those found when GICs are examined by this technique.

Understanding the mechanism by which improvements produced by maturation in GICs is potentially of importance since both heat and ultrasound have been used to attempt accelerate this process [7, 8, 10]. Also an understanding of the mechanism may enable GICs with enhanced properties initially to be formulated. However, the maturation of GICs is a complex area. Whereas strength may increase for some materials [11–13] it can also remain unchanged for maturation times beyond 24 h or can increase and then reduce at even longer times [12, 14]. In contrast, resistance to erosion by an impinging jet of lactic acid improves for all GICs tested [15]. Also the resistance to abrasion, under the conditions of three body wear established by ACTA, appears to improve for all GICs tested with maturation times greater than 24 h [16, 17]. Any changes in model cements should therefore be evaluated in respect to the type of property change with maturation observed in the GIC from which the model cement is derived. A number of theories relating to changes in the cement structure have been proposed. Changes in bound to free water have been reported to relate to mechanical property changes in a range of cements including GICs [18, 19]. Changes in the nature of interchain crosslinks have also been suggested to be associated in maturation changes in properties [1, 20]. Although the replacement of Ca ionic crosslinks by Al based ones are discussed no reference is made to the possibility that many of the –COOH groups may first be converted to –COONa. Most of the GIC glasses studied contain this element and it is very mobile.

The replacement of these neutralised but not crosslinking carboxyl groups by Ca or Al (by analogy with the setting mechanism of alginate) may occur in maturation. Another possible maturation mechanism relates to water content. Young suggests [21] that water is required to the extent of 5.6 moles for every mole of acidic group neutralised and that only when additional water is absorbed can full neutralisation occur. Although this appears an interesting theory, improved strength with maturation in oil matches that in water at short times and exceeds it considerably at longer times [11].

De Maeyer et al. [6] reported that G338 treated with acetic acid showed silicate related absorption peaks at 800 and 1,073 cm^{-1} but the former is not shown in our study and the latter would be masked by the carboxylate peaks at 1,000 cm^{-1} (Fig. 2). Our findings agree with the conclusion of De Maeyer et al. that the “silica gel phase is formed as a surface layer on the glass particles and not as a hydrated silicious matrix....” [6].

The behaviour of lactic acid based cements differs from acetic acid based ones. This is not surprising as lactic acid is not as weak an acid as acetic (pKs of 3.86 and 4.76 respectively). Also lactic acid has the possibility forming chelate structures. This difference is clearly indicated in the FTIR spectra which have peaks in areas not shown by acetic acid cements or GICs (see Figs. 2 and 3). In contrast to acetic acid and polyacid in cements the lactic acid concentration used here (the optimum found by Nicholson and Czarnecka [3]) is much higher. Calcium lactate is only moderately soluble [19]. As Nicholson and Czarnecka [3] state in their investigation of lactic acid based cements, “Following our recent work on the interaction of aqueous lactic acid with set glass-ionomers we have become interested in the possibility of forming cements from glass and this acid only...” Although the lactic acid cements have been evaluated as a direct comparison between the behaviour of G338 and MP4 glasses, the lactate cements are plainly not models for GICs in the way that acetic acid [2] or propionic acid [22]ones are; nor were they intended as such. We did, however, note that cement made from zinc polycarboxylate powder and lactic acid was soluble as Nicholson et al reported the acetic acid one to be [3]. Both zinc and magnesium lactates are readily soluble.

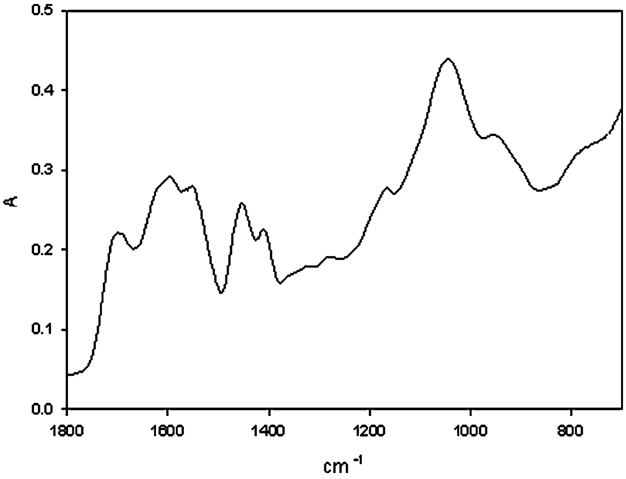

Fig 3 Characteristic FTIR-ATR spectrum of G338 cement with 40% polyacrylic acid

The most interesting aspect of this study is the comparison of MP4 cements with the two different acids. The total failure to form hydrolytically stable cements with acetic acid contrasts with the initial hydrolytic stability of the lactate cements. This latter is a very unusual phenomenon, most dental cements exhibit the reverse behaviour. It would appear that the relatively early exposure to water enhances the cements stability. Possibly the cement may take up water to produce an improved structure; as noted above the lactic acid concentration is very high. The initial hydrolytic stability of the MP4:lactic acid cement suggest that it may have a possible application as a temporary dental cement.

It is concluded that the comparison of the simple GIC glass MP4 with G338 enables some of the theories on GIC maturation to be eliminated. The behaviour the novel MP4 lactic acid cement may provide a mechanism for improving dental cements.

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