A study of cements formed by aqueous lactic acid and aluminosilicate glass

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A study is reported of the formation of cements from aqueous lactic acid and aluminosilicate glass of the type used in dental glass–ionomer cements. These cements were found to set quickly, and were shown by infrared spectroscopy to have undergone a neutralization reaction to yield mainly calcium lactate. They were very soluble in water at 1 h, but became progressively less so over time; when matured for 6 h before being placed in water, they had become almost insoluble. No spectroscopic differences could be detected between the cements at 1 h or 6 h, indicating that insolubilization arises from a reaction that does not alter the part of the infrared spectrum examined. This suggested that a wholly inorganic reaction between the ion-depleted glass fragments is responsible for the formation of the insoluble structure. After 24 h, the cements were found to have compressive strengths in the range 9–35 MPa, the actual value varying with concentration of lactic acid used to form the cement, and there was no statistically significant increase in strength for the strongest of these after one month.
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Introduction

The set glass–ionomer dental cement consists of unreacted glass particles in a complex matrix. For many years, the matrix has been known to include calcium and aluminum polyacrylates, since these were detected by infrared spectroscopy in some of the earliest studies of this cement [1]. More recently, an additional component of this matrix has been suggested, namely an inorganic silicate and/or phosphate material derived from the ion-depleted glass [2–4].

The existence of this inorganic network has been postulated to explain the fact that glass-forming elements such as silicon have been found throughout the matrix when the material was examined by transmission electron microscopy [5], and also that stable cements can be prepared from a standard glass when it is reacted with acetic acid and allowed to mature for at least 6 h prior to immersion in water [2]. Additional evidence for the formation of such a network was found in a study using infrared and NMR spectroscopy [6].

This network has been suggested to be responsible for maturation processes within the cement which lead to increased compressive strength, improved translucency and increased binding of water into the structure [4]. Against this, the polymer has been shown to influence the toughness of the set cement, with toughness varying with increasing molecular weight [7, 8]. This has led some

workers to conclude that the properties of the set cement can be explained almost entirely by the formation of ionically crosslinked polymer chains [9]. Indeed, a number of recent authors have considered only the neutralization and crosslinking of the polymer in their studies of the setting of glass–ionomers [10, 11].

Following our recent work on the interaction of aqueous lactic acid with set glass–ionomers [12], we have become interested in the possibility of forming cements from glass and this acid only, without any polymer. A study of this of this possibility is now reported.

Materials and methods

The materials employed were glass G338, obtained from First Scientific Limited (Roseheyworth Business Park, Abertillery, Blaenau Gwent, Wales), the pre-firing composition of which is shown in Table I, and lactic acid (AnalaR grade, BDH, Poole, Dorset, England). Three different concentrations of lactic acid in water were used, namely 25%, 50% and 75% mass/volume (i.e. for 25%, 25 g of lactic acid was made up to 100 cm³ in a measuring cylinder).

Cements were prepared by spatulating glass powder and lactic acid solutions together at a powder to liquid ratio of 3 g to 1 cm³ on a ceramic tile using a metal

TABLE I Details of G338 glass used in cements

Pre-firing composition	%
SiO_2	24.9
Al_2O_3	14.2
Na_3AlF_6	19.2
CaF_2	12.8
AlF_3	4.6
$AlPO_4$	24.2
Other oxides	0.1

Ground to a fine powder, mean particle size: approximately 4 μm (87.7% at 10 μm or less).

mixing spatula. In the first series of experiments, five small batches of cement 75% lactic acid/glass were prepared and allowed to age in air for time periods of 1, 2, 3, 6 and 24 h. At the end of this time, they were dropped into water, and whether or not they were soluble determined by inspection.

For compressive strength determination, six specimens were prepared for each cement, of cylindrical geometry, 6 mm diameter × 12 mm height, by placing freshly mixed pastes in split metal molds. Specimens were allowed to harden in the molds for 1 h at 37 °C, then removed and stored for a further 23 h at 37 °C in glass vials at ambient humidity. An additional set of cements were prepared from 75% lactic acid and allowed to mature for one month after removal from the molds. After storage, samples were tested for compressive strength using a Universal Testing Machine (Type 1193; Instron, High Wycombe, UK) at a crosshead speed of 1.0 mm/min. Loads at failure were converted to compressive strength values, and means and standard deviations were determined for each cement composition. Differences were assessed for significance using 1-way ANOVA, followed by the non-parametric Mann–Whitney U test.

Infrared spectroscopy was carried out using a type 983G infrared spectrometer (Perkin–Elmer, High Wycombe, UK) with specimens prepared as thin films on calcium fluoride plates. Spectra were recorded for the following specimens: (i) aqueous lactic acid (75%), (ii) an experimental cement of 75% aqueous lactic acid with G338 glass at 1 and 6 h, (iii) calcium lactate and (iv) aluminum lactate.

Samples of calcium and aluminum lactate were prepared as follows: For calcium lactate, 0.74 g of calcium hydroxide was dissolved in 25 cm³ water. A slight excess of pure lactic acid was added dropwise, and the mixture allowed to evaporate to low volume in the air over the next few days. The resulting viscous solution was applied to a calcium fluoride plate using a small paint brush, and allowed to evaporate to dryness, after which the infrared spectrum was recorded. For aluminum lactate, 1.33 g of aluminum chloride was dissolved in 25 cm³ water, and this was added to a solution of sodium hydroxide (0.4 g in 25 cm³). A gelatinous white precipitate formed immediately, but gradually redissolved over the next 2–3 days. After this time, a slight excess of lactic acid was added, and the whole mixture allowed to evaporate to low volume. As before, the resulting viscous solution was applied to a calcium fluoride plate, and allowed to evaporate to dryness, after which the infrared spectrum was recorded.

Results and discussion

The solubility studies gave clear results, and quantification of solubility was thus not appropriate. The cement that was 1 h old disintegrated completely immediately on being placed in water, rapidly leaving only the glass undissolved. The 2 and 3 h old cements each took longer to disintegrate, but both dissolved similarly. The 6 h cement showed some signs of dissolution, with the water becoming cloudy from dispersion of fine particles of glass released from the cement, but the bulk of the specimen was still intact after overnight storage in water. The cement aged for 24 h before exposure to water also showed only slight signs of solubility, but again survived extended storage in water substantially intact. These results show that reaction of lactic acid with G338 eventually leads to an almost insoluble product, but that the process is slow. This is similar to previous findings for cements prepared from acetic acid [2].

Results from infrared spectroscopy are shown in Table II. We interpret them as indicating that lactic acid and G338 undergo a reaction to reduce the free acid and form mainly calcium lactate. Absorption bands are consistent with this suggestion, and the glass itself showed no absorption in the relevant region of the infrared spectrum. Infrared spectroscopy suggests that the neutralization of the aqueous acid by the basic glass powder is essentially complete at 1 h, and shows no sign of further progress after 6 h.

Infrared spectroscopy thus suggests that the insolubilization process is distinct from the neutralization reaction, a similar finding to that reported previously for acetic acid–glass cements [2]. This is consistent with the hypothesis, advanced previously, that there is a secondary setting reaction in cements formed from these glasses [6]. This latter reaction involves the formation of an inorganic network from the ion-depleted species left behind after the acid has reacted with calcium and aluminum from the glass. The formation of such a network, which may be a type of silicate or mixed silicate/phosphate, explains how such cements are so relatively insoluble, despite containing highly soluble metal lactate salts.

Results of the study of compressive strength are shown in Table III. These findings show that the compressive

TABLE II Infrared spectroscopic data

Specimen	Bands cm^{-1}	Interpretation
Lactic acid	1735	Free acid
	1637, 1458	Carbonyls
Calcium lactate	As acid, plus:	Lactate carbonyls of
	1604, 1479	varying structure
	Shoulders at 1546, 1575	
Aluminum lactate	As acid plus:	Lactate carbonyls of
	1631, 1658	varying structure
Cement (75% acid) plus G338	1724 (slight)	Residual free acid
	1636 (very broad)	
	Shoulders at 1540, 1561,	Similar to calcium
	1575	lactate (except 1561)
	1474	cf. 1479 of calcium lactate
	1460	cf. 1458 of calcium lactate

TABLE III Compressive strengths of lactic acid/G338 cements

Acid concentration (%)	Age	Compressive strength (MPa)	Standard deviation (MPa)
25	24 h	9.4	2.4
50	24 h	17.2	3.8
75	24 h	35.1	14.8
75	1 month	37.3	13.4

strength of all cements are much lower than would be expected for dental cements made from this glass, which have compressive strengths of at least 80 MPa, depending on powder : liquid ratio. Our results also show that the concentration of acid has a significant effect on compressive strength (to at least $p < 0.01$ from one-way ANOVA). Application of the Mann–Whitney U test to these data showed that the cements made from 75% lactic acid were significantly stronger than those made from 50% lactic acid ($p < 0.003$), which were in turn significantly stronger than those made from 25% lactic acid ($p < 0.009$). A similar influence of acid concentration on compressive strength has been reported previously for glass–ionomer cements [13]. By contrast, there was no significant increase in compressive strength after 1 month for the cement made from 75% aqueous lactic acid.

Although the strengths of the lactic acid–glass cements were low, they did show that a material with structural integrity could be made from the reactants. This suggests that the proposed inorganic network has the capability of playing a structural role in these cements, and also that glass–ionomer cements which are derived from G338 or similar glasses are likely to derive at least some of their physical properties from the presence of this network. Unfortunately, data from the present study do not allow any conclusions to be drawn about how important the influence of this network might be, and these findings need to be balanced against the strong evidence for the importance of the polymer component on mechanical properties [8, 9].

Conclusions

Cements have been prepared by reaction of aqueous lactic acid with G338, a glass which has been widely used in dental glass–ionomer cements. These lactic acid–glass cements were found to set quickly, and infrared spectroscopy showed them to have undergone a neutralization reaction to yield mainly calcium lactate.

These cements were very soluble in water at 1 h, but became progressively less soluble with time, so that they could survive substantially intact if left 6 h before being placed in water. Infrared spectroscopy showed no differences between the cements at 1 h or 6 h, suggesting that insolubilization is the result of reactions of species that do not absorb in the relevant part of the infrared spectrum. This implies a wholly inorganic reaction of the ion-depleted glass fragments to form a network, as has been suggested previously [2, 6]. Parent metal lactates were shown to be very soluble in water, which also demonstrates that these entitites are not responsible for the insolubility of the fully set cements. After 24 h, the cements had sufficient structural integrity to have reasonable but low compressive strengths, i.e. in the range 9–35 MPa, the actual value varying with acid concentration in the original cement-forming liquid, but for the formulation tested (75% aqueous lactic acid), this strength did not increase significantly over one month.

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