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Studies in the setting of polyelectrolyte cements

Part V *The effect of organic acids on zinc polycarboxylate dental cements*

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Specimens of zinc polycarboxylate dental cement have been prepared from aqueous solutions of citric, lactic and (+)-tartaric acid respectively, and the effect of these acids on the setting characteristics and compressive strength determined. All three acids are stronger than poly(acrylic acid) yet, at 20% concentration, gave variable results in terms of their effect on setting: (+)-tartaric acid shortened the working time by comparison with pure water, whereas both citric and lactic acids extended it; all three extended the setting time. In all three cases, the setting profile was less sharp than with pure water, as quantified by the ratio of setting to working times. Similar results were obtained for (+)-tartaric acid at 10 and 15% concentrations, but at 5%, the working time was marginally longer than for pure water. Compressive strength at 24 h was determined for all three acids at 20% concentration, and found to be unaffected by the changes in setting chemistry, all being of the order of 90–95 MPa (i.e. the same as for pure water). The slight differences between the strengths for the different sets of cements were not statistically significant.

1. Introduction

Zinc polycarboxylate cement is widely used in the clinical dentistry [1], and has a number of applications, for example as liners beneath either amalgam or composite resin restorations, and as a cement for orthodontic appliances. However, although the zinc polycarboxylate was first described for clinical use many years ago [2], structural studies are still continuing. For example, the variety of possible co-ordinating structures involving zinc with carboxylate groups were not identified until 20 years after the original report on this cement [3]. More recently a study has shown that, unlike the apparently related glass polyalkenoate cement, these cements are poorly hydrated, and that the extent of hydration changes hardly at all on ageing [4]. Indeed, a clear finding that has emerged from these more recent studies is that, contrary to earlier assumptions [5], zinc polycarboxylate differs from glass polyalkenoate in many significant ways: it is more plastic, less hydrated, and reaches full strength more rapidly [6].

A further area of difference and similarity between zinc polycarboxylates and glass polyalkenoates is in their setting chemistry, and the factors that affect it. For example, both cements have been found to set more sluggishly and to be weaker when formulated from 50% aqueous methanol than with pure water [7, 8]. These findings were readily accounted for in the light of the known influence of methanol on both the conformation of poly(acrylic acid) in aqueous solution, and on the energetics of ionic reactions [7, 8]. By contrast, setting in the presence of sodium salts was more complex and not so easily explained. In general, for zinc polycarboxylates, sodium salts had a significant effect of setting rate, either speeding it up or slowing it down but, with the exception of sodium sulphate, they made no difference to the strength [9]. For glass polyalkenoates, reaction rate was not affected by any of the salts to a measurable extent, but compressive strengths were generally much reduced [9].

The aim of the current work is to extend understanding of the effect of additives on zinc polycarboxylate by examining the effect of organic acids, including (+)-tartaric acid, on the setting rates and compressive strength. (+)-Tartaric acid is of particular interest because of the effect it has on the setting of glass polyalkenoates. It is added to glass polyalkenoates to improve the handling characteristics, which it does by extending the working time and sharpening the later setting stage [10, 11]. Compressive strength is improved, too. For example, in the original paper describing this discovery, the unmodified cement had a compressive strength of 165 MPa, a figure that was raised to 181 MPa by the addition of 5% (+)-tartaric acid [9]. In the same study, citric acid was found to have similar effects in sharpening the setting reaction and raising the compressive strength, a value of 192 MPa being recorded for glass polyalkenoate cement containing 5% citric acid. This action of citric acid has never been exploited in clinical cements, possibly because there was some evidence

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that cements containing citric acid were more water-soluble than either the parent cements or those containing (+)-tartaric acid [11].

The mode of action of tartaric acid is not fully understood. There have been studies aimed at elucidating its role. For example, Prosser *et al.* [12] used ^{13}C NMR spectroscopy to examine the setting of cements based on the glass known as G-200, and in another study, Nicholson *et al.* [13] used Fourier transform infrared spectroscopy, this time to study the setting of a cement based on so-called G-309. Both studies came to similar conclusions, namely that tartaric acid totally changes the course of the cement-forming reaction. It reacts preferentially with the glass, presumably due to its lower pH, and forms chelate compounds with calcium ions released from the glass that are stable at relatively low pH, i.e. in the range 3 to 4. This means they are stable in the presence of poly(acrylic acid). Later, peaks in the spectra attributable to calcium tartrate disappear, presumably masked by the broader peaks of the metal polyacrylate salts that form more slowly. Although the increase in compressive strength was initially attributed to particular metal chelates of (+)-tartaric acid in the cement [9, 10], an alternative interpretation is that the acid, by delaying the early stages of the setting reaction, makes the cement easier to mix. This, in turn, aids incorporation of the glass powder into the cement, which is consequently more homogeneous and hence stronger.

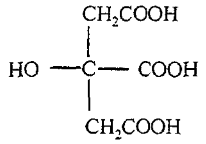
Despite these results, to date there has been no published account of this or any other organic acid on the properties of zinc polycarboxylate. The possible effect of such acids on zinc polycarboxylate is of interest for a number of reasons. First, as part of a more general assessment of the extent to which these cements are similar to glass polyalkenoates; second, as a test of the hypothesis that it is low pH of these organic acids that leads directly to their role as reaction rate modifiers in glass polyalkenoates; and third as a possible method of evaluating the link between slower setting rate and improved compressive strength. This study used (+)-tartaric acid and citric acid, in order to compare and contrast the behaviour of zinc polycarboxylates with glass polyalkenoates. It also considered an additional organic acid, namely lactic acid. Concentrations used in glass polyalkenoates have tended to be 5 or 10%; this study employed the relatively high value of 20% for the compressive strength study in order that any effects should be very pronounced.

2. Materials and methods

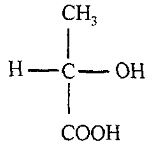
A commercially available water-activated zinc polycarboxylate dental cement, PolyKent (ex. Kent Dental Ltd, Gillingham, Kent, UK) was used. The powder–liquid ratio was as recommended by the manufacturers, i.e. 7.5:1 by mass. Samples were prepared by spatulating together the appropriate amount of powder (deactivated ZnO plus dried polymer) with water or aqueous acid solution on a glass mixing block. Details of the acids used are given in Table I, and their structures are shown in Fig. 1.

TABLE I Organic acids used as additives

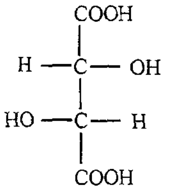
Acid	Grade (Supplier)
Citric acid	General Purpose Reagent (BDH, Poole, UK)
(±)-lactic acid	AnalaR (BDH, Poole, UK)
(+)-tartaric acid	Analytical Reagent (Fisons,Loughborough, UK)



Citric acid



Lactic acid



(+)-tartaric acid

Figure 1 Structures of organic acids

Compressive strengths were determined for cements activated with water and with the acids at 20% concentration. Six specimens of each cement were prepared by placing freshly mixed cement paste in cylindrical moulds of dimensions 6 mm high × 4 mm diameter. Specimens were stored in their moulds for 1 h at 37 °C, then in water at the same temperature for a further 23 h. This regime is as specified in the recently revised British Standard for water-based dental cements [14].

After the storage period, samples were tested for compressive strength using a universal testing machine (Type EU500 ex. R.D.P. Howden, Leamington Spa, UK) at a crosshead speed of 0.1 mm/min. Loads at failure were converted to strength values, and means and standard deviations were determined for each cement composition. Differences in compressive strength were assessed for significance using Student's *t*-test.

Working and setting times were determined for cements set by water-activation and by activation with each of the three acids at 20% concentration. In addition, for (+)-tartaric acid, working and setting times were determined for 5, 10 and 15% acid concentration. All determinations used the oscillating rheometer [6] at ambient temperature (24–25 °C), duplicate values being recorded. Working time was taken to be the point at which the amplitude of oscillation reached 95% of the initial (maximum) value; setting time as the point where amplitude was 5% of this value.

3. Results and discussion

The values for working and setting time, together with other information, for each liquid are shown in Table II. From these figures, it can be seen that there is no clear pattern of influence of acid on the setting reaction. The 20% tartaric acid gave a shorter working time and a less sharp set than water, whereas both 20% citric and 20% lactic acids gave longer working times, much longer setting times, and less sharp setting profiles.

The influence of (+)-tartaric acid did not vary linearly with concentration. The 10, 15 and 20% concentrations gave much shorter working times than pure water and also gave much longer setting times, which resulted in less sharp setting profiles. By contrast, the 5% concentration gave a slightly longer working time than pure water, and a sharper setting profile than all the other concentrations of tartaric acid studied. However, at all concentrations the setting profile was less sharp than with pure water, which demonstrates that tartaric acid has a different effect in zinc polycarboxylates than in glass polyalkenoates, where it sharpens the set and extends the working time.

The effect of these organic acids on compressive strength is shown in Table III. These results show that none of the acids affected the compressive strength of the set cement. This finding is similar to those found for simple sodium salts, where only sodium sulphate (1 M) affected the final strength, causing a reduction to 56 MPa, whereas NaF, NaCl and $NaNO_3$ had no influence on strength. This difference is surprising, given the considerable slowing in the early stages of the reaction in the presence of either 20% citric or lactic acids. In an unpublished study [15], the use of a turntable automixer was found to improve the compressive strength of this same brand of zinc polycarboxylate to around 105 MPa, a difference that was significant at $p > 0.025$. In other words, it is possible, by more efficient mixing of the initial cement paste, to improve the compressive strength of the finished specimens. However, such an improvement does not follow simply from slowing down the reaction by chemical means, a result that again contrasts with previous findings for glass polyalkenoates.

There are a number of possible mechanisms by which additives seem able to modify the setting reactions in acid-base cements. Organic molecules, such as methanol or HEMA, appear to act by altering the dielectric properties of the aqueous reaction medium [7, 8]. This, in turn, affects both the energetics of the ionic neutralization reaction and the conformation of the polymer. Simple salts, such as sodium chloride, by contrast might be expected to make very little difference to the energetics of the neutralization reaction, but are known to influence the conformation adopted by poly(acrylic acid) in solution [16, 17]. The conformation itself is expected to affect the neutralization reaction, since more tightly coiled conformations will ionize less readily than less tightly coiled ones due to the greater charge density in the former case [16]. In view of this, it was difficult to account for the fact that glass polyalkenoates showed no detectable change in working time, setting time or sharpness of set in the presence of these salts.

TABLE II The influence of organic acids on the setting characteristics of zinc polycarboxylate

Liquid	pH	Working time (min)	Setting time (min)	Sharpness
Water	–	2.4	5.6	2.3
20% citric acid	1.29	2.6	11.3	4.4
20% lactic acid	1.55	3.5	9.8	2.8
20% tartaric acid	1.05	1.4	7.9	5.6
15% tartaric acid	1.17	1.2	8.0	6.7
10% tartaric acid	1.35	1.3	8.0	6.2
5% tartaric acid	1.47	2.7	8.2	3.0

TABLE III Compressive strength at 24 h of zinc polycarboxylate cements with organic acids

Liquid	Compressive strength (MPa)	Standard deviation (MPa)
Water	93.6	9.4
20% citric acid	91.4	8.0
20% lactic acid	91.8	11.9
20% tartaric acid	90.1	5.0

In the case of (+)-tartaric acid, the additive has been shown to react preferentially with the glass in glass polyalkenoate cements [3]. A necessary condition for this effect is greater acidity (i.e. lower pH) than poly(acrylic acid). However, that this is not a sufficient condition is demonstrated by the results for citric and lactic acids in the current study. What other features of the acids are involved, though, is not clear from the present data.

4. Conclusions

Organic acids have been found to make a considerable differences to the course of the setting reaction of zinc polycarboxylate cements, but to have no effect on their ultimate compressive strength. This contrasts with the effect of such acids, particularly (+)-tartaric acid, on glass polyalkenoate cements, where not only is the setting reaction modified, but also the strength at 24 h is considerably improved. The previous assumption that this increase in strength is simply a consequence of the less rapid setting reaction is called into question by the present findings. Lactic acid was found to increase the working time by 1.1 min, and the setting time by 4.2 min, yet did not yield a stronger cement. Thus the mechanism of action of (+)-tartaric acid in glass polyalkenoates need to be reconsidered. The action of (+)-tartaric acid in zinc polycarboxylates was generally to shorten rather than lengthen the working time, to reduce the sharpness of the setting profile, and to make no difference to the compressive strength, all of which contrast significantly with the findings for glass polyalkenoate cements. This study has thus revealed further points of dissimilarity between these two classes of dental cement. The full significance of these results is not clear and investigations are continuing in order to try to clarify them.

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