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Studies in the setting of polyelectrolyte materials

Part III *The effect of sodium salts on the setting and compressive strength of glass-polyalkenoate and zinc polycarboxylate dental cements*

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Water-activated versions of zinc polycarboxylate and glass-polyalkenoate dental cements have been used in a study of the effect of electrolytes on setting behaviour and properties. In addition to pure water, 1 M solutions of NaCl, NaF, Na_2SO_4 and $NaNO_3$ have been used to activate setting. The setting reaction of the zinc polycarboxylate was found to be profoundly affected by the presence of such electrolytes, with the working time generally being shorter, and the overall set sharper. The setting reaction of the glass-polyalkenoate was less affected: there was generally no change in the working time, though the set was slightly less sharp. After 24 h at 37 °C most of the zinc polycarboxylates had compressive strengths of about 90 MPa, with differences between the different specimens not being statistically significant. The exception was the cement made with aqueous sodium sulphate, which had a compressive strength of 56.8 MPa. By contrast, the strengths of the various glass-polyalkenoates fell into three groups: water- and NaF-activated at 80–85 MPa, Na_2SO_4- and $NaNO_3$-activated, at 65 MPa, and NaCl-activated, at 53 MPa. These differences were significant at least the 99% confidence level. They are discussed in terms of the effect of the electrolytes on the conformation adopted by the reacting poly(acrylic acid) molecules in solution. It is concluded that the differences in response to the presence of sodium salts between the zinc polycarboxylate and the glass-polyalkenoate confirm the view that these cements set to give substantially different microstructures.

1. Introduction

The polyelectrolyte cements, zinc polycarboxylate and glass-polyalkenoate, were invented in the late 1960s [1]. Since then, they have become widely used in dentistry. They are similar materials, in that they are acid-base cements formulated from a water-soluble polymeric acid, usually poly(acrylic), and they set by a neutralization process [1]. In the case of zinc polycarboxylate the base is a heat-treated zinc oxide containing a small amount of magnesium oxide [2]; in glass-polyalkenoates, the base is a powdered fluoro-alumino-silicate glass containing calcium [3]. Both of these cements are available in anhydrous forms. *i.e.* where the dry polymeric acid is incorporated into the base as part of the powder, and reaction is initiated by the addition of water [4].

Recently, studies have been carried out on the effect of organic compounds on the setting of both zinc polycarboxylates and glass-ionomers. These studies were prompted by the development of light-curable versions of the glass-polyalkenoate cement [5], which include various organic species in order to confer photocurability to the cement. The inclusion of organics raises questions about the ease with which the ionic setting reactions may occur, and the stability of the setting cement with respect to phase separation [6]. In the study of methanol [7], either alone or in aqueous solution, as the activator for an anhydrous zinc polycarboxylate, it was found that the cements set significantly more slowly than with water, and were weaker [7]. Similarly, using either aqueous methanol or hydroxyethyl methacrylate, HEMA, to activate the setting of an anhydrous glass-polyalkenoate cement led to slower setting reactions and weaker cements [8].

The reason for using methanol is that information is available on the conformation of poly(acrylic acid) in the presence of this solvent [9]. Fundamental studies have been carried out using water–methanol mixtures in the semi-dilute concentration range, rather than at the high concentrations used in dental cements. However, since molecular overlap occurs in this region [10], the findings concerning the effect of methanol on poly(acrylic acid) should be broadly relevant to what occurs in the cements. Methanol, being a relatively poor solvent, causes the polymer to adopt a more coiled and less solvated conformation [11], and this in turn reduces the ease of ionization [9]. Coiling, coupled with the effect of decreasing dielectric constant on the ionic processes involved in the setting reactions, resulted in the observed reduction in the speed of setting [7]. The presence of the organic compounds also altered the composition of the set material, which were consequently weaker [7].

The current study aims to extend this earlier work by using electrolytes rather than organic compounds to influence the conformation of the poly(acid). The effect of these compounds on the setting chemistry and final properties of the cements have been examined. As before, information is available on the effect of these compounds on the conformation of poly(acrylic acid) but it is limited, being restricted to the dilute or semi-dilute regions and to relatively high concentrations of salt. Any conclusions from these studies therefore involves extrapolation to the concentrations employed in the cements.

2. Materials and methods

The cements used in this study were Aquakent, a water-activated glass-polyalkenoate luting cement, and Polykent, a water-activated zinc polycarboxylate (both ex. Kent Dental Ltd, UK), both of which are formulated from poly(acrylic acid). Each was mixed by hand at the powder:liquid ratio recommended by the manufacturer (Aquakent, 3.6:1 by mass; Polykent, 7.5:1).

For the aqueous phase, either demineralized water or an aqueous solution of 1 M electrolyte was used. The details of the electrolytes employed are given in Table I; the 1 M solutions were made up accurately, using Grade A volumetric glassware.

Working and setting times at 21 °C were determined in duplicate using the oscillating rheometer, as described previously [1]. The working time was taken as the point at which the oscillation reached 95% of its initial amplitude; the setting time, the point at which it reached 5%.

Compressive strengths were determined by the method described in the British Standard for glass ionomer dental cements [12]. In this method the compressive strength was determined at 24 h using a set of six samples of size 12 mm high × 6 mm diameter, stored initially in the mould at 37 °C for 1 h, then removed and stored in water, again at 37 °C, for a further 23 h. Specimens were tested on a Universal Testing machine (Instron 1180), using a crosshead speed of 1 mm/min. Compressive strength was determined from load at failure under these conditions.

Statistical analysis of the strength data was carried out using Student's t-test.

3. Results

The working and setting times for the glass-polyalkenoate cements activated with various aqueous solutions are shown in Table II. The ratio of setting time to working time can be taken as a measure of the sharpness of the set.

From this Table, it can be seen that NaCl and $NaNO_3$ did not affect the working time, but slightly extended the setting time, and hence reduced the sharpness of the set. On the other hand, both NaF and Na_2SO_4 increased the working time, as well as the setting time, and both also reduced the sharpness of the set.

The working and setting times for the zinc polycarboxylate cements are shown in Table III.

By contrast with the results for the glass-polyalkenoate, Table III shows that the sodium salts either speeded up and sharpened the set, or left it unaffected. Thus NaCl, Na_2SO_4 and $NaNO_3$ all reduced both the working and setting times, and reduced the ST:WT ratio. On the other hand, NaF did not affect the working time and had only a marginal effect on reducing the setting time, which resulted in a fractional sharpening the set.

Results for compressive strength are shown in Tables IV and V for the glass-polyalkenoate and zinc polycarboxylates, respectively.

Results in Table IV are grouped into three sets: pure water as activating liquid gave a compressive strength of 85.3 MPa, which did not differ in a statistically significant way from the 79.9 MPa of the cement made from aqueous NaF. Cements made from aqueous Na_2SO_4 and $NaNO_3$ had a strength of just a little over 65 MPa, and constituted a second set. Finally, NaCl-containing cements had a compressive strength of 53.1 MPa, a value that was significantly different from the others, and constituted the third set. Table VI shows the significance levels of the differences from the pure water and NaCl cements, which can be seen to have been at the 99% level in most cases.

Table V shows compressive strength results for the zinc polycarboxylate cements. With the exception of those made from aqueous Na_2SO_4, they are all at around 90 MPa, and as Table VII shows, any differences are not statistically significant. The cements containing Na_2SO_4, by contrast, were found to be significantly weaker.

TABLE I Electrolytes used in the preparation of cements

Electrolyte	Grade and supplier
NaCl	AR, ex. Fisons, Loughborough
NaF	SLR, ex. Fisons, Loughborough
Na_2SO_4 (anhydrous)	AR, ex. BDH, Poole
$NaNO_3$	AR, ex. BDH, Poole

TABLE II Working and setting times of glass-polyalkenoate

Activating liquid	Working time, WT (min)	Setting time, ST (min)	ST:WT
Pure water	3.3	14.5	4.4
1 M NaCl	3.3	16.2	4.9
1 M NaF	4.1	21.7	5.3
1 M Na_2SO_4	4.7	23.4	5.0
1 M $NaNO_3$	3.4	16.9	5.0

TABLE III Working and setting times of zinc-polycarboxylate

Activating liquid	Working time, WT (min)	Setting time, ST (min)	ST:WT
Pure water	3.5	13.9	4.0
1 M NaCl	3.0	7.9	2.7
1 M NaF	3.5	12.7	3.6
1 M Na_2SO_4	2.6	7.3	2.8
1 M $NaNO_3$	4.6	11.7	2.6

TABLE IV Compressive strength of glass-polyalkenoate

Activating liquid	Compressive strength (MPa)	Standard deviation (MPa)
Pure water	85.3	9.5
1 M NaCl	53.1	4.7
1 M NaF	79.9	7.6
1 M Na_2SO_4	65.3	6.8
1 M $NaNO_3$	65.2	3.5

TABLE V Compressive strength of zinc polycarboxylate

Activating liquid	Compressive strength (MPa)	Standard deviation (MPa)
Pure water	95.2	7.1
1 M NaCl	87.2	7.5
1 M NaF	89.2	3.1
1 M Na_2SO_4	56.8	3.2
1 M $NaNO_3$	90.8	3.6

TABLE VI Significance level of differences between compressive strengths of glass-polyalkenoates

Activating liquid	Compared with water	Compared with 1 M NaCl
1 M NaCl	99%	-
1 M NaF	not significant	99%
1 M Na_2SO_4	99%	99%
1 M $NaNO_3$	99%	99%

TABLE VII Significance level of differences between compressive strengths of zinc polycarboxylates

Activating liquid	Compared with water	Compared with 1 M NaCl
1 M NaCl	not significant	-
1 M NaF	not significant	not significant
1 M Na_2SO_4	99.9%	99.9%
1 M $NaNO_3$	not significant	not significant

Cement specimens have their diameter measured as part of the determination of compressive strength, and all specimens were found to have mean diameters that did not differ from each other in a statistically significant way. In other words, the presence of the sodium salts did not cause swelling. On the other hand, testing of the water in which the NaCl specimens had been stored with 10% $AgNO_3$ gave a white precipitate, showing that chloride had leached out of the cements.

4. Discussion

The fact that all specimens were the same size (any differences being not statistically significant) indicates that the effect of the sodium salts is not to make the cements weak through swelling. Instead, they seem to exert their effect by interfering with the setting reactions, whose rates in many cases was measurably affected, and which may therefore lead to the formation of critically different microstructures. Discussion of the setting chemistry in terms of the effect of the sodium salts on the poly(acrylic acid) is complicated for three reasons: (i) little is known about the behaviour of polyelectrolyte molecules in the highly concentrated region employed in dental cements [13]; (ii) where studies have been made on the effect of added salt, it has always been done at relatively high salt concentrations, *i.e.* those in which the following condition holds

$$C_s > ZC_p$$

where C_s and C_p are the concentrations of the salt and the polymer, respectively, and Z is the degree of polymerization. In other words, the extensively studied systems have all had sufficient salt to at least match the concentration of functional groups on the polyelectrolyte chain. This has tended to have the effect that the polyelectrolytes are shielded electrostatically, and hence retain a coiled conformation [13]; finally, (iii) at high salt concentrations, solvent quality is affected. This has hardly been studied at all, but undoubtedly exercises a distinct effect on polyelectrolyte conformation [13].

Of the salts employed in this study, NaCl was used because it has been widely used to suppress conformational change in poly(acrylic acid) and other polyelectrolytes. There is thus the possibility of extrapolating from fundamental studies to the concentration region of interest, and thus of accounting qualitatively, at least, for the observed effect of NaCl on the reaction rate and properties of the final material. The other salts have been less widely used, but it is known that SO_4^{2-} and NO_3^- ions have very different effects on the solubility of polymers in aqueous solution, and appear at widely separated intervals within the so-called lyotropic series [14]. Basically, NO_3^- acts as a solubilizing additive ("salting in"), while SO_4^{2-} acts as an insolubilizing additive ("salting out"). The origin of this effect is not clear [14], but it is well supported experimentally. The consequent solvating power of the respective aqueous solutions means that polyelectrolytes will adopt an expanded, well-hydrated conformation in aqueous SO_4^{2-}, but a more coiled and less hydrated conformation in NO_3^-.

Sodium fluoride has been used in studies of additives on the setting of glass-polyalkenoates, but at very low levels [15]. Hill and Wilson [15] found that the addition of NaF at a level of 1% increased the working and setting times of glass-polyalkenoate cements made from certain glasses. They attributed this to the formation of soluble metal fluoride complexes that were stable under the conditions within the cement. There is also the possibility of forming very strong hydrogen bonds to the carboxylic acid groups [16]. In the present study, inhibition of the setting reaction was observed in the glass-polyalkenoate, but to only a slight extent. By contrast, there was no comparable inhibition of the setting of the zinc polycarboxylate. For both cements, compressive strength was unaffected by the presence of NaF.

For zinc polycarboxylate, in all cases, the presence of the sodium salts sharpened the set. Looking at individual compounds, we see that the presence of relatively low amounts of $NaNO_3$, caused a slowing down of the setting reaction. This is a "salting in" compound and might therefore be expected to result in an expanded coil conformation of the poly(acrylic acid). The presence of Na_2SO_4, a "salting out" compound, by contrast increased the rate of the setting reaction. Sodium sulphate probably causes the polyacid to adopt a contracted coil conformation. At the same time, in these two solvent systems, the product, zinc polyacrylate, will vary in solubility. The effect of this on the mechanical stiffening of the cement paste is difficult to predict, but may explain the deviation from the intuitive view that the more soluble, expanded conformation of poly(acrylic acid) should undergo neutralization more readily than the coiled conformation, due to the more diffuse charge in the former. Certainly, the effect of sodium chloride, which is in the middle of the lyotropic series (hence neither "salting in" nor "salting out") would support this idea. At higher relative concentrations, it is known to screen the polyacid electrostatically [13, 17] and therefore assist coil expansion. In the current series of experiments, it has been shown to speed up the setting reaction of the zinc polycarboxylate.

Despite the effects on the speed of the setting reaction, in general these sodium salts do not affect the strength of the set cements. Since the only possible product of the reaction is zinc polyacrylate, with unreacted zinc oxide as filler, it may be that the speed of matrix formation does not matter. Provided the cement has reacted as far as it can, the structure formed is identical, and the strength will be the same. The reason that the cement made from 1 M Na_2SO_4 was the exception is not clear. It may be that in this case the coiled polymer configuration, while not affecting the initial setting reaction, did significantly slow down the post-hardening process.

Turning attention next to the glass-polyalkenoate cements, results for the setting reactions can be seen to be generally completely opposite to those for the zinc polycarboxylate. All of the sodium salts made the set less sharp. The "salting in" compound $NaNO_3$ made only the slightest difference to the speed of the reaction, whereas Na_2SO_4, the "salting out" compound, slowed the reaction down considerably.

The compressive strengths fell into three broad groups. The highest values (around 80–85 MPa) were obtained with pure water and with aqueous NaF. Next, both $NaNO_3$ and Na_2SO_4 gave values of about 65 MPa, despite the fact that the solvents are widely separated in the lyotropic series, and hence the cements were probably formed from poly(acrylic acid) in very different conformational states. Finally, the lowest value of all, 53.1 MPa, was obtained with 1 M NaCl as the activating liquid.

The fact that these salts made such a difference to the strengths of the glass-polyalkenoates implies that, unlike the zinc polycarboxylates, these materials set to give cements which have significantly different compositions of the matrix. Recent studies have indicated that the setting of glass-polyalkenoates is more complex than that of zinc polycarboxylates [18, 19]. It seems likely that solubilized fragments of glass containing silica, phosphate, sodium ions and other inorganic species play a part in the setting and hardening of these cements [20]. It is likely that, in the presence of the additional sodium salts, the rates at which individual components of the matrix form will differ and also that with variations in the solvent quality of the water, there will be variations in the hydration states of the inorganic part of the matrix. This would account qualitatively for the observed variations in strength. These results thus support the emerging view that the setting of glass-polyalkenoates involves more than simple neutralization, and differs in important ways from the setting of zinc polycarboxylates.

One practical consequence arising from these results is that a second reason has become apparent for protecting setting glass-polyalkenoate cements from saliva during clinical use. Not only does this prevent the washing out of matrix-forming ions, but also it stops the ingress of saliva. The ionic content of saliva would disturb the sequence and extent of the setting reactions, and result in weak cements.

5. Conclusions

The addition of sodium salts at a concentration of 1 M to the water used to activate the setting reaction of zinc polycarboxylates and glass-polyalkenoates has been shown to affect both the rate of setting and final strength in different ways.

The rate of the setting reaction of the zinc polycarboxylate was found to be profoundly affected by the presence of the sodium salts. The working time was generally shorter, and the overall set sharper than without them. By contrast, the setting reaction of the glass-polyalkenoate was less affected. Working time was generally unaffected, though setting time was slightly longer, thus making the overall reaction slightly less sharp.

In general, the presence of the sodium salts did not affect the strength of the zinc polycarboxylate cements, which had compressive strengths of about 90 MPa. The one exception was the cement made with aqueous sodium sulphate, which had a compressive strength of only 56.8 MPa. Again, the results for glass-polyalkenoates were different. Compressive strengths fell into three groups: water- and NaF-activated at 80–85 MPa, Na_2SO_4- and $NaNO_3$-activated, at 65 MPa, and NaCl-activated, at 53 MPa.

The salts are known to have different effects on the quality of water as a solvent, which in turn will mean that the poly(acrylic acid) molecule will have different and more or less well-solvated conformations depending on which salt is present. For zinc polycarboxylate, the relatively poor solvent, 1 M Na_2SO_4, speeded up the setting reaction but yielded a weak cement. On the other hand, the relatively good solvent, 1 M $NaNO_3$, slowed the setting reaction down, but yielded a cement of the usual strength. For the glass-polyalkenoate, the effects on setting were exactly the opposite: the poor solvent (1 M Na_2SO_4) slowed the setting reaction down, whereas the good solvent (1 M $NaNO_3$) speeded it up. Both solvents gave cements of the same strength, albeit lower than for cements made from pure water.

Interpretation of these results is difficult, but they clearly provide further evidence that the processes by which zinc polycarboxylates and glass-polyalkenoates set are very different, despite superficial similarities in their chemistry.

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