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Studies on the setting of polyelectrolyte cements

Part VI *The effect of halide salts on the mechanical properties and water balance of zinc polycarboxylate and glass–ionomer dental cements*

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A study is reported in which a zinc polycarboxylate and a glass polyalkenoate dental cement, respectively, were prepared from aqueous solutions of NaCl, KCl, KBr and KI, all at 1 mol dm^3 concentration, as well as from pure water. For the zinc polycarboxylate, setting as determined by oscillating rheometry was speeded up and water uptake was enhanced by the presence of the salts. Conversely, compressive strength at 24 h was unaffected. On the other hand, for the glass polyalkenoate, the setting reaction was slowed down, water uptake inhibited and compressive strength at 24 h reduced (from 94.3 MPa with pure water to 59.8 MPa with NaCl, 65.8 MPa for KCl, 67.0 MPa for KBr and 81.1 MPa for KI). Previous work with polyelectrolytes in aqueous solution suggests that the halides probably enhance the rate of the neutralization process. For the zinc polycarboxylate, this leads to a more rapid setting reaction. By contrast, for the glass polyalkenoate, it results in slower setting and weaker cements. This result is attributed to inhibition of the secondary setting reaction, involving the formation of the silicate/phosphate network, by enhanced neutralization, a process which is consequently concluded to occur earlier in the overall setting of these cements than had been assumed previously. © *1998 Chapman & Hall*

1. Introduction

Both zinc polycarboxylate and glass polyalkenoate cements are widely used in clinical dentistry [1]. Their uses include cavity lining beneath either amalgam or composite resin restorations, fixation of orthodontic appliances and, in the case of the glass polyalkenoate, restoration of erosion lesions along the gum line, so-called Class V cavities. Initially, these cements were assumed to have very similar microstructures, and to set by similar reactions [2]. However, detailed studies have cast doubt on this. For example, the hydration states of the two classes of cement have been shown to differ markedly. Not only have the zinc polycarboxylates been shown to be poorly hydrated, but also that hydration state has been shown to change hardly at all on ageing [3, 4]. Mechanical properties are different, too. By comparison with the glass polyalkenoate, the zinc polycarboxylate is more plastic [5–8] and reaches full strength more rapidly [9].

Finally, and most recently, the addition of sodium salts has been found to cause very different effects in these two cements. In zinc polycarboxylates, such salts made a significant difference to the setting rate, either speeding it up or slowing it down but, with the exception of sodium sulphate, made no difference to the strength [10]. On the other hand, in glass polyalkenoates, these salts did not affect the rate of the setting reaction to any measurable extent, but led to significant reductions in compressive strength [10, 11].

The current paper reports work that was aimed at extending the understanding of the effect of metal salts on these two types of cement. A series of halides, NaCl, KCl, KBr and KI, was used, selected because the respective anion and cations vary in known ways in size and hydration state in aqueous solution. Each of these salts was used at 1 mol dm^{-3} in water to form cements, and their effect on setting reaction and mechanical properties were determined. In addition, a study was made of the nett water uptake at 24 h in these cements.

2. Materials and methods

Commercially available water-activated dental cements were used, namely a zinc polycarboxylate, PolyF Plus, and a glass polyalkenoate, AquaCem (both ex. Dentsply Ltd, Konstanz, Germany). The

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TABLE I Halides used as additives

Halide	Grade	(Supplier)
NaCl	General purpose reagent	(BDH, Poole, UK)
KCl	AnalaR	(BDH, Poole, UK)
KBr	Analytical reagent	(Fisons, Loughborough, UK)
KI	Analytical reagent	(Fisons, Loughborough, UK)

powder: liquid ratio was as recommended by the manufacturers, i.e. 5 : 1 by mass for the zinc polycarboxylate, 3.3 : 1 for the glass polyalkenoate. Samples were prepared by spatulating together the appropriate amount of powder (deactivated ZnO or glass plus dried polymer) with water or aqueous 1 mol dm^{-3} solution of metal halide on a ceramic tile using a metal mixing spatula. Details of the salts used are given in Table I.

Compressive strengths were determined for cements activated with water and with the halide solutions at 24 h. Six specimens of each cement were prepared by placing freshly mixed cement paste in cylindrical moulds of dimensions 12 mm high × 6 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 similar to that specified in the current British Standard for water-based dental cements, except that larger specimen sizes were used [12]. These larger specimens have been shown to give the same value of compressive strength as the smaller ones of the current Standard specification [13, 14].

After the storage period, samples were tested for compressive strength using a universal testing machine (Type EU500, ex. Howden, Leamington Spa, UK) at a crosshead speed of 0.1 cm min^{-1}. 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 one-way ANOVA.

Working and setting times were determined for cements set by water activation and by activation with each of the metal halide solutions. All determinations used the oscillating rheometer [9] at ambient temperature (21–23 °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

The values for working and setting time for each activating liquid are shown for zinc polycarboxylate and glass polyalkenoate respectively in Tables II and III. From these figures, it can be seen that for the zinc polycarboxylate, the halide salts made setting more rapid, with the effect declining as halide ion increased in size. By contrast, for the glass polyalkenoate, the halides made the setting slower, especially the later stages indicated by the setting time. Again the effect was more pronounced with chloride ions than with bromide or iodide, as shown in the series of potassium salts.

TABLE II The influence of metal halides on the setting characteristics of zinc polycarboxylate

Liquid	Working time (min)	Setting time (min)	Sharpness
Water	3.0	7.9	2.63
1 M NaCl	2.5	4.7	1.88
1 M KCl	2.2	4.6	2.09
1 M KBr	2.8	6.2	2.21
1 M KI	2.7	7.2	2.67

TABLE III The influence of metal halides on the setting charateristics of glass polyalkenoate

Liquid	Working time (min)	Setting time (min)	Sharpness
Water	4.2	12.4	2.95
1 M NaCl	4.2	15.6	3.71
1 M KCl	4.4	17.8	4.05
1 M KBr	4.2	16.0	3.81
1 M KI	4.6	16.0	3.48

The effect of these solutions on compressive strength is shown in Tables IV and V. None of the differences between the results for the zinc polycarboxylate was significant, thus confirming previous observations that the addition of salts does not, in general, influence the strength of zinc polycarboxylates [10]. By contrast, there were significant dfferences in compressive strength between the varying glass polyalkenoate formulations. The NaCl, KCl and KBr cements differ in strength from the pure water cement at $P < 0.001$, and the KI cement differs at $P < 0.02$. The difference between the KI cement and the KBr or KCl cement is significant at $P < 0.01$. Finally, the effect of varying cation size is shown by the cements containing NaCl and KCl respectively, and between these the difference in compressive strength is significant at $P < 0.05$.

These results again confirm previous observations [10]. In the case of the glass polyalkenoate containing NaCl, strength was reduced to 63% of that of the equivalent cement containing only water; the previous report, using a different brand of cement, was of a fall to 62% of the original strength [10].

The values of nett weight gain for the various cements are shown in Tables VI and VII. In all cases, the weight change can be assumed to be due to the combined effect of dissolution of a proportion of the cement and compensating sorption of water. The addition of halide salts would be expected to increase the total solubles content of the cements, but as can be seen from Tables VI and VII, they did not necessarily cause weight loss. For example, for the zinc polycarboxylates, there was a negligible weight change for water-activated cements, but a clear gain for the cements containing the various metal halides. For the series KCl, KBr and KI, all weight gains were

TABLE IV Compressive strength at 24 h of zinc polycarboxylate cements with metal halides (standard deviations in parentheses)

Liquid	Compressive strength (MPa)
Water	86.0 (13.8)
1M NaCl	82.9 (11.3)
1M KCl	77.2 (5.5)
1M KBr	85.3 (3.4)
1M KI	83.8 (7.0)

TABLE V Compressive strength at 24 h of glass polyalkenoate cements with metal halides (standard deviations in parentheses)

Liquid	Compressive strength (MPa)
Water	94.3 (8.3)
1M NaCl	59.8 (4.4)
1M KCl	65.8 (3.5)
1M KBr	67.0 (4.1)
1M KI	81.1 (5.3)

TABLE VI Nett weight gain at 24 h for zinc polycarboxylate cements with metal halides (standard deviations in parentheses)

Liquid	Water uptake (%)
Water	0.08 (0.11)
1M NaCl	0.32 (0.22)
1M KCl	0.52 (0.14)
1M KBr	0.53 (0.12)
1M KI	0.64 (0.16)

TABLE VII Nett weight gain at 24 h for glass polyalkenoate cements with metal halides (standard deviations in parentheses)

Liquid	Water uptake (%)
Water	1.77 (0.34)
1M NaCl	1.74 (0.30)
1M KCl	1.20 (0.24)
1M KBr	0.54 (0.27)
1M KI	− 0.17 (0.20)

significantly greater ($P < 0.001$) than for pure water, and though the gain followed the sequence KCl < KBr < KI, the differences were not statistically significant. The weight gain for the cement containing NaCl was also greater than for the halide-free cement, but only at $P < 0.05$.

By contrast, for glass polyalkenoates, weight gain was greatest for the water-activated cement, and least for the KI-activated cement. There was actually a slight weight loss in the latter cement, and the difference between the two sets of cements was highly significant ($P < 0.001$). The difference between the gains for water and NaCl were not significant, but between water and KCl, and between water and KBr were highly significant ($P < 0.001$). The difference between KCl and KBr was significant at $P < 0.01$ and between KBr and KI was significant at $P < 0.001$.

4. Discussion

This study has examined the effect of metal halides in glass polyalkenoates and zinc polycarboxylates on the setting rate, compressive strength and water uptake. For all three aspects, glass polyalkenoates and zinc polycarboxylates show opposing behaviour. Halides in zinc polycarboxylate increase the speed of the setting reaction and increase the water uptake, but leave the compressive strength unaffected. By contrast, in glass polyalkenoates, they reduce the speed of the setting reaction, reduce the water uptake and reduce the compressive strength. The greatest strength reduction occurred with NaCl, the least with KI. In general, for both types of cement, there were clear trends in properties for the series KCl, KBr and KI, suggesting that the explanation for their contrasting effects lies in the well-established solution chemistry of the halide ions.

Alkali metal halides have well-documented effects on polyelectrolytes in aqueous solution. Specifically, they are known to screen electrostatic interactions leading to a favouring of conformations with high charge-density, generally the helix, and allowing the polyelectrolyte to develop increased ionization [15]. This kind of behaviour has been demonstrated for both NaCl [16] and NaBr [17], though in both cases, under so-called *abundant-salt* conditions, i.e. where the concentration of metal halide is at least equal to, and preferably greater than, the equivalent concentration of carboxylic acid groups on the polymer [18]. In principle, similar behaviour would be expected for all of the metal halides used in the present study.

The main effect to be anticipated from this favouring of highly charged conformations by metal halides is increased ease of neutralization, which in the simplest case would lead to an increase in the rate of setting. This behaviour is shown by the zinc polycarboxylate. The fact that these altered setting rates yield cements of unaltered compressive strength is a further reflection of the simplicity of the zinc polycarboxylate system. Regardless of how fast the cement is formed, it consists only of a matrix of zinc polyacrylate with unreacted zinc oxide particles embedded in it. In the set zinc polycarboxylate cement, metal halides exercise a hydrophilic effect and cause a slight but significant increase in water-uptake. That, however, is the limit of their effect once the cement has set.

For glass polyalkenoates, opposite effects are observed. In the case of speed of setting, stabilization of the more highly charged polyelectrolyte conformations must still occur, but it does not result in an increased setting rate. On the contrary, there is a slight reduction in the setting rate. The overall hardening of these cements is now considered to include both neutralization of the polyelectrolyte molecules and development of a silicate/phosphate network from the glass component [19]. The latter would not necessarily be expected to be affected by the presence of metal halides in the setting cement. On the other hand, if the neutralization were to occur more rapidly, the resulting stiff structure might inhibit the formation of the inorganic network, as diffusion of the silicate or phosphate moieties was able to occur less readily. This slowing of the inorganic network formation, and probable alteration in the balance of neutralized polymer to network, may explain the relative weakness of the halide-containing glass polyalkenoates.

As glass polyalkenoates mature, they increasingly bind water into their structure. This has the effect of raising the ratio of bound to unbound water [9], and is probably an effect of the slow hydration of the silicate/phosphate network. This water uptake is critical if these cements are to develop optimum properties. This being so, it is difficult to explain why the halide which most inhibits water uptake, KI, should have the least effect on compressive strength.

In general, however, the broad trend in effects among the metal halides can be explained in terms of their different hydration states, and corresponding subtly different effects on the solvating power of water. When individual ions dissolve in water, they become associated with specific water molecules. A number of techniques have been used to estimate the number of water molecules that associate with individual ions, including the classical determinations from transport numbers [20] and compressibility [20] and the more recent techniques of mass spectrometry [21] and neutron scattering [22]. The actual hydration number varies according to the technique used, because they tend to be concerned with different time scales over which the water molecules may be considered to be associated with the specific ion. However, there are generally agreed trends, most techniques showing $Na^+ > K^+$ and $I^- > Br^- > Cl^-$. Thus, of the substances used in this study, KI would bind the greatest number of water molecules. Such binding would reduce the availability of water for solvation of other species. At the same time, the high hydration number, together with the increased ionic size, would have the effect of reducing the charge density on either ion, which in turn would reduce the effectiveness of KI in screening charge development on the poly(acrylic acid) molecules. Such behaviour is consistent with the observed relatively long working and setting times for KI in zinc polycarboxylate. It is also consistent with the observed differences between KCl and NaCl in the zinc polycarboxylate. Among the series of halides, similar effects occur for the glass polyalkenoate. The major difference here is that all give longer setting times than the halide-free cement, reasons for which have already been discussed.

5. Conclusions

The addition of metal halides has been shown to have strikingly different effects on glass polyalkenoate and zinc polycarboxylate cements. In glass polyalkenoates, setting was slowed down, strength was reduced and water uptake inhibited; in zinc polycarboxylate, setting was speeded up, strength unaltered and water uptake enhanced. Consideration of other results from the field of polyelectrolyte physical chemistry suggests that metal halides are likely to stabilize high charge-density polyacrylate molecules, thus enhancing the rate of neutralization. This leads to the observed faster setting with zinc polycarboxylate. We suggest that the reason similar behaviour was not seen with the glass polyalkenoate is that the secondary setting reaction, i.e. the one leading to the formation of the silicate/phosphate network, is adversely affected by the rapid neutralization. If this suggestion is correct, then silicate/phosphate network formation must contribute to the overall setting process at an earlier stage than has previously been assumed.

Differences between the individual halides has been found to follow clear trends based on their relative position on the Periodic Table. For example, setting time for zinc polycarboxylate was shown to increase in the order KCl, KBr, KI. These results may be correlated with known differences in ionic size and hydration state of the individual alkali metal and halide ions.

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