JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 4 (1993) 32–35

A study of the structure of zinc polycarboxylate dental cements

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Two examples of zinc polycarboxylate dental cement were studied, one of which was prepared from an aqueous solution of poly(acrylic acid) together with the zinc oxide powder, the other being prepared by adding water to a mixture of dried polyacid and zinc oxide powder. The changes in the properties of the resultant cements with length of storage in various media were determined. In all cases the maximum strength was achieved fairly rapidly, usually at 1 week, after which there was little or no increase. Cements stored in water achieved the lowest compressive strengths, whereas cements stored in highly desiccating conditions, over concentrated sulphuric acid, achieved very high (if variable) compressive strengths. There appeared to be very little difference between the water-activated and conventional cements. These results confirm previous findings that zinc polycarboxylate cements are relatively poorly hydrated compared with other polyelectrolyte biomaterials. This in turn implies that water does not play a structural role in these cements.

1. Introduction

The use of zinc polycarboxylate cement as a dental material was first described by Smith in 1968 [1], that early report highlighting the good adhesion to tooth materials and the low irritancy. Since 1968 zinc polycarboxylate cements have been widely used clinically, including as cavity liners, as adhesives for the placement of crowns and for the adhesion of orthodontic appliances [2].

Zinc polycarboxylate cement belongs to the class of materials known as acid–base reaction cements [3]. The components are a polycarboxylic acid, usually poly(acrylic acid), and a modified zinc oxide powder [2]. The modified zinc oxide is prepared by mixing pure zinc oxide with small amounts of magnesium oxide and fusing the mixture at 1100–1200 °C. This process reduces the reactivity of the zinc oxide towards the acid, so that, in clinical use, the cement paste sets sufficiently slowly to be mixed and placed. The heat treatment causes the zinc oxide to become slightly yellow in colour. This is due to evaporation of oxygen to give a non-stoichiometric material corresponding to $Zn_{1+x}O$, where $x \leqslant 70$ p.p.m. [4].

The setting process involves the formation of zinc polyacrylate units, as has been shown in numerous infrared spectroscopic studies [5–8]. The nature of the set cement was also considered in these studies, although there is some controversy about the conclusions reached. Wilson [5], Moharan *et al.* [7] and Rabie *et al.* [8], on the basis of conventional dispersive infrared spectroscopy, all concluded that the zinc carboxylate units are wholly ionic. By contrast, Nicholson *et al.* [6], using Fourier-transform infrared spectroscopy (FTIR), concluded that there were a number of types of zinc carboxylate unit, including the purely ionic but also including a variety of covalent structures. Covalent structures of the type proposed have previously been found for a variety of monomeric zinc carboxylates [9], and were suggested as possible structures in an early review by Wilson [10]. FTIR has a better resolving power than dispersive infrared spectroscopy and, since the spectra reported by Nicholson *et al.* [6] had numerous discrete bands in the region conventionally assigned to carboxylate absorptions, there is strong evidence that the set cements do indeed involve a complex array of zinc–carboxylate interactions.

Apart from these spectroscopic studies there have been few reports of other work on the structure of zinc polycarboxylates. Crisp *et al.* [11] carried out a study of the erosion of commercial zinc polycarboxylates in water. They found that zinc and magnesium ions were leached out of the cement early in its life, but such leaching ceased as the setting processes approached completion. In another study Cook [12] followed the early stages of the setting process, using conductivity measurements. He showed that the reaction between zinc oxide and poly(acrylic acid) was almost quantitative and that the rate of diffusion of Zn^{2+} ions within the set matrix is low. This was consistent with the conclusion of Crisp *et al.* [11] that the loss of these ions from the cement ceased upon ageing. The lack of zinc ion mobility was also consistent with the findings of Nicholson *et al.* [6] concerning the site binding of these ions within the matrix.

More recently Hill and Labok [13] investigated the effect of the molecular weight of the poly(acrylic acid) on the fracture of these cements. They concluded that these cements behaved in many ways like thermoplastic polymer composites, with very weak crosslinks between the chains, a view which supported conclusions previously obtained by Paddon and Wilson [14]. However, Hill and Labok maintained that their results disagreed with the conclusions of Nicholson *et al.* [6] concerning the essentially covalent nature of these cements. This is not necessarily the case, because the covalent structures postulated could be intramolecular and hence would not contribute to crosslinking.

The study reported in this paper was carried out in order to gain an improved understanding of the final chemical structure of zinc polycarboxylate cements. One particular aspect that we considered in detail is the role played by water in these materials. Water has a number of possible functions. It is the solvent in which the setting reaction takes place, it is one of the products of the reaction between zinc oxide and poly(acrylic acid) and is known to be retained in the final structure [10]. In the set cement it may occupy co-ordination sites around the metal ions, it may hydrate the polyanion and it may act as plasticizer [15].

In a previous study the ratio of bound to unbound water in these cements was determined as a function of age [16]. This ratio was determined by weighing a cement disc before and after removal of the unbound ("evaporable") water following storage under vacuum over anhydrous magnesium perchlorate. This study showed that the ratio of bound to unbound water rose as the zinc polycarboxylate cement was aged, but this change was slight compared with those in glass-ionomer (glass–polyalkenoate), zinc phosphate or dental silicate cements. Wilson *et al.* [16] concluded that these cements were the least hydrated of the dental cements studied, and that the main role of the evaporable (unbound) water was that of plasticizer.

In this paper we report results for an extensive study of two zinc polycarboxylate cements, one conventional and one water-activated. We examined changes in various properties that occur as these cements are aged under different storage conditions, the properties we studied being compressive strength, mass and volume. From the results obtained we have been able to extend the understanding of the relationship between the structure and properties of zinc polycarboxylate cements and, in particular, to understand further the role played by water in these materials.

2. Materials and methods

Two commercially available zinc polycarboxylate cements were employed in this study, Aquaboxyl (from Davis, Schottlander and Davis Ltd) and Lumicon (from Bayer Dental, FRG). The first of these is a water-activated cement in which the powder consists of a mixture of the zinc oxide component (including a small amount of magnesium oxide) and dried polyacid; the cement is prepared by incorporation of the appropriate amount of water. The second cement is prepared conventionally by mixing the zinc oxide component with an aqueous solution of the polyacid.

The two zinc polycarboxylate cements were mixed according to the manufacturers' instructions. Aquaboxyl cements were mixed as directed for cementation, i.e. one scoop of powder to two drops of water. These quantities were found to give a mass ratio of 6:1. In the case of Lumicon the cement was mixed at the ratio recommended for use as a liner for pulp protection, i.e. 4.6 g powder to 1 ml liquid.

Following mixing, the cements were placed in 6 mm (diameter) × 12 mm (height) cylindrical moulds. They were stored for 1 h at 37 °C, then weighed and the length and diameter were measured with a micrometer screw gauge. Sets of six pellets of each cement were prepared and stored under different conditions for different lengths of time. The storage conditions were in water, in air at ambient humidity, in a desiccating atmosphere over concentrated sulphuric acid and in cottonseed oil. Storage times ranged from 24 h to 6 months.

After the storage time had passed, the specimens were weighed and their length and diameter were measured again. The compressive strengths of the various cement specimens were tested using a universal testing machine (Instron 1185) at a crosshead speed of 1.0 mm min^{-1}.

3. Results and discussion

Results of the measurements of compressive strength, shrinkage and weight gain are shown for the two zinc polycarboxylates in Tables I and II.

To determine whether the changes in strength recorded in Tables I and II were significant, Student's *t*-test was applied to the data. For the conventional zinc polycarboxylate, Lumicon, the increase in strength from 1 to 7 days was significant at the 99% confidence level under all conditions except storage in cottonseed oil. In the case of storage in the desiccating atmosphere over concentrated sulphuric acid there was also a significant change in strength between 7 and 30 days at the 99% confidence level. None of the other changes was significant at the 99% confidence level.

For the water-activated zinc polycarboxylate, Aquaboxyl, the situation was more complicated. In air at ambient humidity and in cottonseed oil the increase in compressive strength was significant at the 99% confidence level between 1 and 7 days. The change in compressive strength between 1 and 7 days for specimens stored in dry air over concentrated sulphuric acid was significant only at the 95% confidence level. For samples stored in water the change between 1 and 7 days was not statistically significant at either the 99% or 95% confidence level, but the change between 1 and 30 days was significant at the 99% confidence level.

As was found for Lumicon, the apparent slight increases in compressive strength of samples of Aquaboxyl from 7 to 180 days were not statistically significant under any of the storage conditions. The one exception to this was for storage in water, as mentioned above. However, for this medium, too, there was no significant change in strength between 30 and 180 days.

TABLE I. Mean (s.d.) changes in strength, volume and weight for Lumicon brand of zinc polycarboxylate (samples of this cement were mixed according to the manufacturer's instructions for pulp filling)

Storage time (days)	Compressive strength (MPa)	Volume change (%)	Weight change (%)
Storage conditions: Air at ambient humidity			
1	82 (4)	-0.9 (0.6)	-0.79 (0.04)
7	89 (3)	-1.7 (0.7)	-1.00 (0.06)
30	92 (12)	-1.9 (0.4)	-1.10 (0.2)
90	109 (8)	-3.8 (0.7)	-2.40 (0.4)
180	116 (18)	-3.3 (0.4)	
Storage conditions: Water			
1	73 (4)	-0.4 (0.4)	0.21 (0.09)
7	80 (2)	-0.9 (1.7)	0.03 (0.11)
30	81 (3)	-0.3 (0.7)	0.20 (0.10)
90	79 (5)	-0.4 (0.2)	0.30 (0.20)
180	87 (6)	-1.2 (0.3)	
Storage conditions: Cottonseed oil			
1	95 (6)	0.3 (0.3)	-0.58 (0.06)
7	93 (5)	-1.8 (0.8)	-1.02 (0.04)
30	91 (9)	-2.2 (0.5)	-1.13 (0.03)
90	115 (4)	-3.0 (1.0)	-1.50 (0.10)
180	114 (11)	-4.2 (0.6)	-2.40 (0.20)
Storage conditions: Dry air			
1	152 (10)	-4.3 (0.6)	-6.8 (0.4)
7	183 (6)	-9.0 (1.0)	-10.1 (0.2)
30	144 (46)	-8.7 (0.6)	-10.5 (0.3)
90	191 (17)	-7.0 (1.0)	-11.0 (1.0)
180	164 (16)	-9.6 (0.5)	-10.0 (1.0)

TABLE II Mean (s.d.) changes in strength, volume and weight for Aquaboxyl brand of zinc polycarboxylate (samples of this cement were mixed according to the manufacturer's instructions)

Storage time (days)	Compressive strength (MPa)	Volume change (%)	Weight change (%)
Storage conditions: Air at ambient humidity			
1	98 (9)	-1.6 (0.6)	-0.7 (0.1)
7	116 (8)	-1.8 (0.6)	-1.3 (0.1)
30	115 (13)	-2.6 (0.3)	-1.5 (0.3)
90	142 (31)	-4.0 (2.0)	-5.0 (3.0)
180	145 (17)	-4.4 (0.5)	
Storage conditions: Water			
1	93 (14)	-0.7 (0.4)	-0.3 (0.1)
7	105 (7)	-0.7 (0.2)	-0.1 (0.1)
30	112 (2)	-1.2 (0.2)	0.4 (0.3)
90	107 (14)	-0.4 (0.5)	0.4 (0.2)
180	118 (5)	-0.8 (0.7)	
Storage conditions: Cottonseed oil			
1	89 (6)	-1.6 (0.4)	-0.8 (0.1)
7	110 (8)	-1.4 (0.6)	-0.9 (0.1)
30	125 (10)	-2.6 (0.4)	-3.2 (0.8)
90	135 (5)	-3.1 (0.9)	-1.9 (0.1)
180	143 (11)	-5.0 (1.0)	
Storage conditions: Dry air			
1	107 (32)	-6.7 (0.2)	-10.5 (0.8)
7	159 (31)	-10.5 (0.6)	-11.3 (0.2)
30	142 (23)	-12.2 (0.3)	-11.8 (0.3)
90	168 (20)	-12.7 (0.4)	-12.3 (0.3)
180	180 (43)	-12.0 (2.0)	-12.0 (0.4)

Under all storage conditions, except water, the two zinc polycarboxylates underwent shrinkage and reduction in weight. This included storage in cottonseed oil, an essentially hydrophobic medium, showing that these materials have a strong tendency to lose a proportion of the water originally incorporated into them. Storage in water led to a slight weight gain for Lumicon at each duration and for Aquaboxyl at 30 and 90 days. For the two shorter periods Aquaboxyl showed slight weight losses.

The changes in weight and volume were most marked following storage in the desiccating medium of dry air over concentrated sulphuric acid. For both types of cement storage under these extremely dry conditions caused severe loss of water and, although the resultant cements showed very high compressive strengths, there was a large increase in the standard deviations recorded. These results imply that storing cements under such dry conditions causes them to become less homogeneous than cements stored in water, cottonseed oil or air at ambient humidity.

Figures for weight loss over concentrated sulphuric acid give an important insight into the state of water in these cements. These results cannot be compared with previous findings concerned with establishing the ratio of bound to unbound water, such as those obtained by Wilson *et al.* [16], for a number of reasons. First, conditions were much more desiccating than those used by Wilson *et al.* because the desiccant was stronger and the exposure period very much longer. Secondly, the specimen geometry was very different. However, despite this, our findings can be used to give information about the state of water in these cements.

The initial water contents of these cements were 12.4 wt % for Lumicon and 14.3 wt % for Aquaboxyl. The maximum weight losses upon storage over concentrated sulphuric acid were 11.0% and 12.3%, respectively. These imply that small amounts of water, viz. 1.4% and 2.0%, respectively, are particularly tightly bound within the cement structure. If we assume complete neutralization of the poly(acrylic acid), as has been demonstrated previously in zinc polycarboxylates by Cook [12], then these amounts of water correspond to 1.4 and 1.7 molecules of water per zinc or magnesium atom for Lumicon and Aquaboxyl, respectively. This water is almost certainly present within the co-ordination sphere of the metal ions. Such water is retained despite exposure to such a heavily desiccating environment.

4. Conclusion

This study showed that, unlike the closely related glass–polyalkenoate cements, the zinc polycarboxylates achieve their maximum strength fairly rapidly, usually by 7 days. After this time there is little or no increase in strength.

The development of strength was found to depend on the storage conditions. Cements aged in water achieved the lowest compressive strengths. On the other hand, cements stored under highly desiccating conditions over concentrated sulphuric acid achieved very high compressive strengths; results were, however, very variable, indicating that strongly desiccated cements lacked homogeneity. In all of these characteristics there appeared to be only slight differences between the conventional and the water-activated versions of the zinc polycarboxylate cement.

Finally, our results confirm previous findings that zinc polycarboxylate cements are relatively poorly hydrated, particularly in comparison with the closely related glass–polyalkenoate ("glass–ionomer") cements. We therefore conclude that, although water appears to occupy co-ordination sites around the zinc or magnesium ions within these cements, it does not play the same kind of structural role that it does in glass–polyalkenoate cements [17].

Acknowledgement

This work was carried out as part of the "Materials Measurement Programme", a programme of underpinning research financed by the United Kingdom Department of Trade and Industry.

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Received 31 July
and accepted 26 November 1991