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Investigation of the post-hardening reaction in glass-ionomer cements based on poly(vinyl phosphonic acid)

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In this study the behaviour of two PVPA-based glass-ionomer cements was investigated. The first cement was prepared from PVPA homopolymer and glass, together with a reaction modifier. In the second cement a modified version of the polymer was used instead of the homopolymer. The modification was achieved by the treatment of the polymer with a small quantity of zinc fluoride. The effect of ageing under different conditions on the strength, mass and volume of the cements was determined. The ZnF_2-containing system behaved in a fairly straightforward manner, showing a gradual increase in strength with time (up to 3 months) that was similar to glass-ionomer cements based on poly(acrylic acid). By contrast the unmodified material did not increase in strength with time, a feature that was attributed to extensive crosslinking of the material, causing it to become more brittle and hence more sensitive to defects in the specimens. With regard to the effect on mass and volume, both types of cement behaved like typical set glass-ionomers, displaying a sensitivity to dessication but little, if any, sensitivity to aqueous media.

1. Introduction

Glass-ionomer cements (glass polyalkenoate cements) are acid-base reaction cements formed by the action of a concentrated solution of a polymeric acid on an ion-leachable glass [1]. Originally the polyacid used was poly(acrylic acid), PAA, but now many commercial materials are formulated with copolymers of itaconic or maleic acids with acrylic acid [2].

Recently, it has been shown that poly(vinyl phosphonic acid), PVPA, the phosphorus analogue of poly(acrylic acid), can be used in the preparation of glass-ionomer cements with strength and handling properties that are comparable with commercial materials [3, 4]. The most recent PVPA-based cements have been formulated using a modified version of the acid. The modification was achieved by the incorporation of zinc fluoride (ZnF_2) into the acid during its preparation. The effect of the modification was to alter the working and setting times and compressive strengths of the resulting cements, the extent of the change in these properties depending on the degree of modification of the polymer. The means of action of the ZnF_2 has not been demonstrated conclusively, but it is thought to act by crosslinking the polymer chains.

The rationale for the incorporation of a phosphonic acid-based material is the observed increase in adhesive bond strength [5] and the potential for anticariogenic activity [6]. The proposed mechanism for the observed increase in adhesion is the exchange of phosphonate anions in the material with phosphate anions of the surface of the dental hydroxyapatite [7], while the anticariogenic activity of these materials is thought to be due to their absorption on to and subsequent modification of the surface of the tooth. Another advantage of the phosphonic acid-based materials is their improved biocompatibility compared with that of cements based on PAA [8], as demonstrated in *in vitro* cell culture tests.

The principal setting reaction of a glass-ionomer is the slow neutralization of an acidic polymeric solution which results in the formation of a polysalt matrix [1]. However, other processes, including the possible formation and hydration of a silicate network, may also be involved in the setting process [9]. It has been observed that glass-ionomers mature for at least the first 24 h after mixing. This maturation has been observed as an improvement in the translucency and in measured compressive strengths of the cement. The maturation extends far beyond the time when the cement is hard and can be considered to be set. In some cases the observed increase in strength continues beyond a year after preparation of the cements [1].

Studies by Williams and Billington [10] have shown that the polymer used to form the cement can affect the long-term behaviour of that cement. Some of

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the commercial glass-ionomer materials that they investigated were found to peak in strength and then get weaker with time. The decrease in strength was significant compared with the maximum value recorded for the cement and in some cases it was also significant with respect to the initial strength value recorded at 24 h. This behaviour was restricted to those materials that were based on copolymers of acrylic and maleic acids and the authors attributed the effect to hydrolytic instability of the cement. In accordance with earlier observations [1] the poly(acrylic acid) based materials maintained or increased in strength with time.

The purpose of this paper is to investigate the change in behaviour with age of PVPA-based cements and to see whether the post-hardening development of strength follows the same pattern as in cements prepared from poly(acrylic acid) or as cements prepared from co-polymers of maleic acid.

2. Method

The study was carried out on both a simple PVPA homopolymer cement ("unmodified") and a cement in which the polymer had been modified by the incorporation of 10% zinc fluoride (ZnF_2) ("modified"). The homopolymer was prepared as described elsewhere [11]. Dequest 2010 (hydroxy ethyl diphosphonic acid) [Monsanto Ltd.] was included in the formulation at the 5% (by mass of polymer) level as a reaction inhibitor. The structure of Dequest 2010 is shown in Fig. 1. Dequest controls the setting reaction of the cement by inhibiting its early stages. The inhibition occurs because of the chelation of the ions required for crosslinking the polymer chains as they are extracted from the glass. It continues until all the Dequest has been used up. The action of Dequest in this application is similar to that of tartaric acid in the conventional PAA-based glass-ionomer in that it extends the effective working time of the cement paste.

The modification of the polymer was achieved by the addition of 10% by mass of zinc fluoride to a 50% by mass solution of PVPA in water. With heating and stirring the modifying species, ZnF_2, dissolves. Then the new solution was spray-dried and the modified polymer obtained as a fine powder. Fluorine (^{19}F) NMR (nuclear magnetic resonance) of the polymer after modification indicates that there has been a change in the fluorine environment on reaction suggesting that some of the polymer chains have been crosslinked by the zinc fluoride [12]. This modified polymer has been shown to yield cements having superior properties to those prepared from unmodified polymer [4].

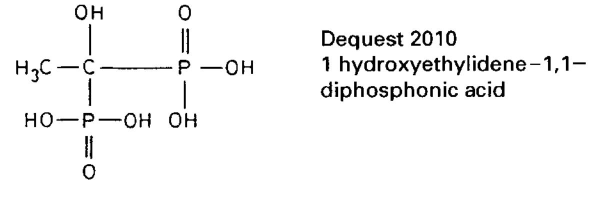

Figure 1 Structure of Dequest D2010.

TABLE I Prefiring composition of the ion-leachable glass

Component	wt %
Al_2O_3	23.0
SiO_2	43.7
CaF_2	12.9
AlF_3	–
$AlPO_4$	2.9
Na_3AlF_6	17.5

TABLE II Relative composition of powder component of modified PVPA cement (by mass)

modified PVPA (10% ZnF_2)	5.00
Dequest D2010 (freeze-dried)	1.38
Glass (HT – 450 °C/90 min)	28.00

Unmodified cements were prepared by mixing a 50% solution of PVPA (containing a further 5% of Dequest D2010) with a heat-treated ion-leachable glass (450 °C for 90 min) at a powder to liquid ratio of 3:1 (by mass). The prefiring composition of the glass is given in Table I.

The modified cements were mixed at a powder to water ratio of 9.5:1 (by mass) where the powder was of composition as shown in Table II. The glass used in the formulation was as before. For each specimen 1.00 g of powder was mixed with 0.105 g of water.

British Standard [13] size (12 mm high × 6 mm diameter) compressive strength specimens were prepared. The specimens were stored in moulds for 1 h at 37 °C. They were then weighed on an analytical balance to 0.001 g and measured with a micrometer to 0.001 cm before storage in the various media, both aqueous and desiccating, for up to 90 days. The media chosen were air, dry air, water and physiological saline (0.154 M NaCl). The specimens were stored for 1 day, 1 week, 1 month or 3 months. After the appropriate storage time the change in mass and volume upon storage was determined and the load at failure in compression was measured using a universal testing machine (Instron 1185).

Six specimens were prepared for storage under each set of conditions. The result for a specific set of conditions is expressed as the mean and standard deviation of the six specimens' results. Any differences between sets of results were tested for significance using the Student's *t* test.

3. Results

The results for the effect of storage on compressive strength, mass and volume are given in Tables III, IV and V, respectively.

The standard deviations in the compressive strengths were quite large. This is probably a reflection of the difficulties experienced in mixing the cements and a possible lack of homogeneity in the modified polymer.

The cements prepared from the modified PVPA were significantly stronger (at the 99% confidence level) than similar specimens prepared from the

TABLE III Effect of storage on compressive strength[a]

Storage medium	Storage duration (days)	Compressive strength	
		Unmodified acid (MPa)	Modified acid (MPa)
Air	1	125 (13)[b]	163 (7)
	7	114 (17)	175 (37)
	30	134 (25)	184 (28)
	90	156 (15)	227 (18)
Dry air	1	73 (10)	97 (23)
	7	55 (4)	114 (5)
	30	47 (10)	98 (6)
	90	59 (3)	92 (4)
Water	1	84 (15)	158 (15)
	7	67 (7)	166 (6)
	30	146 (25)	174 (29)
	90	112 (9)	226 (35)
Saline	1	87 (7)	145 (25)
	7	62 (7)	156 (26)
	30	134 (24)	172 (37)
	90	118 (22)	188 (27)

[a] The values quoted are the mean of the six results obtained for each set of conditions

[b] Values in parentheses are standard deviation (MPa)

TABLE IV Percentage change in mass upon storage

Storage medium	Storage duration (days)	Percentage change in mass	
		Unmodified PVPA	Modified PVPA
Air	1	− 0.41 (0.07)	− 0.28 (0.06)
	7	− 0.74 (0.14)	− 0.26 (0.12)
	30	− 0.98 (0.13)	− 1.26 (1.04)
	90	− 1.68 (0.25)	− 0.80 (0.32)
Dry air	1	− 9.97 (0.30)	− 5.33 (0.16)
	7	− 13.07 (0.23)	− 7.70 (0.13)
	30	− 12.94 (0.36)	− 9.07 (0.23)
	90	− 12.61 (0.36)	− 9.21 (0.41)
Water	1	0.25 (0.25)	0.48 (0.18)
	7	0.12 (0.12)	0.63 (0.34)
	30	0.74 (0.09)	0.70 (0.11)
	90	0.36 (0.18)	0.34 (0.13)
Saline	1	0.09 (0.14)	0.28 (0.04)
	7	0.70 (0.30)	0.55 (0.19)
	30	0.90 (0.20)	1.00 (0.57)
	90	0.77 (0.14)	0.81 (0.13)

A positive value indicates an increase in mass upon storage
A negative value indicates a decrease in mass upon storage
The values quoted are the mean of the six results obtained for each set of conditions and values in parentheses are standard deviations

TABLE V Percentage change in volume upon storage

Storage medium	Storage duration (days)	Percentage change in volume	
		PVPA	PVPA
Air	1	− 1.32 (0.52)	− 1.95 (1.68)
	7	− 0.84 (0.60)	− 1.42 (1.54)
	30	− 1.39 (0.89)	− 2.01 (2.05)
	90	− 3.51 (1.19)	− 1.43 (0.18)
Dry air	1	− 7.62 (0.44)	− 4.61 (1.27)
	7	− 8.86 (0.77)	− 5.74 (1.33)
	30	− 8.53 (0.58)	− 8.53 (0.58)
	90	− 9.49 (1.71)	− 4.89 (1.39)
Water	1	1.57 (0.58)	− 1.67 (1.87)
	7	0.55 (0.72)	− 0.20 (1.19)
	30	1.16 (0.76)	0.72 (1.78)
	90	0.63 (1.35)	0.82 (1.46)
Saline	1	2.51 (1.28)	− 0.11 (0.60)
	7	1.84 (1.01)	0.13 (0.77)
	30	0.28 (1.06)	− 0.28 (1.06)
	90	1.52 (1.43)	− 0.26 (0.27)

A positive value indicates an increase in mass upon storage
A negative value indicates a decrease in volume upon storage
The values quoted are the mean of the six results obtained for each set of conditions and values in parentheses are standard deviations

unmodified acid. The modified acid cements easily exceed the British Standard compressive strength requirement of 125 MPa for type II (restorative) glass-ionomer cements [13].

The unmodified polymer cements stored in air became progressively stronger over the 3-month storage period. Results for 1 day and 3 months were significantly different at the 99% confidence level. However, there was no significant difference in strength for the specimens tested at consecutive time intervals. This would imply that the acid-base reaction is progressing very slowly and that most of the matrix was laid down in the first 24 h period. The specimens stored in dry air became weaker with time. The values obtained at 1 day were significantly stronger (at the 99% confidence level) than those obtained at 1 week or 3 mon ths. This indicates that the cement is sensitive to desiccation.

The behaviour of the specimens stored in aqueous media is less straightforward. The specimens stored in water and saline behaved in a similar manner. The cements appear to achieve their maximum strength at 1 month and then, as with some other non-poly(acrylic acid) cements, the compressive strength decreases [10]. Thus the maximum strength was recorded at 1 month, with the specimens aged 1 week and 3 months being significantly weaker (significant at at least the 95% significance level).

The behaviour of the specimens with regard to their change in mass and volume was very much as would be expected for a glass-ionomer cement [14]. The specimens stored in desiccating environments were observed to lose weight (due to the loss of water from the cement). This loss in mass was also accompanied by a reduction in the volume of the cement. The specimens stored in aqueous media showed no significant change in volume on storage. The slight increase in mass on storage could be due to a small uptake of water, but is also (at least in part), due to the fact that the specimens were still damp when measured.

The behaviour of the modified system is very different from that of the PVPA/Dequest system. The strength of the modified system is not adversely affected by the presence of aqueous media. Similarly it is not affected by the slight desiccation provided by storage in air. There is a general, if not always statistically significant, increase in strength upon storage in air, water or saline for these modified materials. This implies that the acid-base reaction is continuing within the material, even 1 month after the start of mixing. In comparison the PVPA/Dequest system appeared to peak and then decrease in strength. The modified PVPA cements lost weight when stored in desiccating environments, but the associated reduction in volume of the specimens was only significant for the dry air stored cements. There was a statistically significant change in volume for the aqueous stored cements, and the slight increase in mass could be associated with insufficient drying of the specimens prior to weighing.

4. Discussion

The results obtained in this study give an insight into the nature of the post-hardening reaction in the PVPA cements.

4.1. Effect of storage on compressive strength

The modified PVPA cements were significantly stronger than the unmodified materials. The modified cement had a significantly longer working time than the unmodified material. Consequently a possible reason for part of the observed increase in strength could be due to improved wetting of the components in the cement paste prior to the setting of the cement. If the cement paste sets too fast it is hard to ensure that all the material has been incorporated and once incorporated it is not possible to ensure that the paste is a homogenous mixture of the components.

The modified materials showed a progressive increase in strength upon storage in air indicating that there was a post-hardening reaction within the set cement. The increase in strength was very slow. There was no significant change in compressive strength between successive storage periods implying that the ongoing reaction is very slow and that the bulk of the ionic matrix is laid down in the first 24 h after mixing of the cement. This result is not too surprising because the PVPA cements react much faster than their PAA-based counterparts and the modified material is already significantly crosslinked prior to reaction.

The modified PVPA cements behave as would be expected of a conventional glass-ionomer cement on storage in an aqueous medium. The samples increased in strength on storage in air, indicating that the acid-base reaction continues after the initial set of the cement. This ageing reaction is also demonstrated in the aqueous stored materials. The samples become progressively stronger with time, although the difference in strength between successive storage periods is not always significant. The cements were still increasing in strength 3 months after their preparation.

The results for the storage of the unmodified PVPA-cements are less straightforward. There is no steady variation in strength for these materials over the storage period. All the specimens stored for 1 week, in any of the four storage media, were significantly weaker than their 1-day or 1-month-old counterparts. This dip was statistically significant at at least the 95% level. If the reduction is strength continued beyond the first week, it would be more easily explicable. It could then be stated that the maximum strength of the PVPA cement was achieved at 24 h and that the cement deteriorated after that time. As Williams and Billington found it is not unusual for certain conventional glass-ionomers (e.g. those prepared from copolymers of acrylic and maleic acids) to reach a maximum strength at a specific time after preparation and from this peak to decrease in strength with time [10]. The explanation that they offer for this phenomenon is the hydrolytic instability of the cement. However, this would seem to be unlikely in this study because the decrease in strength was also observed in the air and dry air stored samples. A more likely explanation would appear to be that proposed by Hill [15], who suggested that the reduction in compressive strength was due to the continued development of crosslinking within the cement. As the polymer becomes more crosslinked the set cement becomes more brittle and as the brittleness of the specimen increases, the sensitivity of the compressive strength to the presence of flaws in the test piece also increases. The structure of maleic acid based polymers allows for extensive crosslinking through the carboxylate groups, whereas a poly(acrylic acid) based material will have far less crosslinking and the unreacted carboxylic acid groups present in the set cement observed by Nicholson and coworkers [16] will instill a measure of plasticity to the material, thus reducing its sensitivity to the presence of flaws.

If this argument is then applied to the (unmodified) PVPA cements, the reduction in compressive strength after 1 week can be explained. PVPA is a stronger acid than PAA [3] consequently it could be expected to give rise to a more crosslinked set cement structure. Also as a lower molecular weight species ($M_w \approx 5000$) [3], PVPA will retain its mobility within the cement for longer than the larger PAA molecules ($M_w \approx 30{,}000$) [1]. This mobility will ensure yet further crosslinking of the material. Another consideration is that the unmodified cement is very fast setting, and the components are quite hard to incorporate into the paste. Consequently the likelihood of the presence of flaws or inhomogeneities in the specimens is increased. The modified PVPA does not exhibit the reduction in strength. This can be explained because the pre-crosslinked material is likely to have some acid groups that are blocked off and as such are unavailable for reaction. Hence some measure of plasticity is retained within the cement.

The unmodified PVPA cements did not peak in strength at 1 day, but instead the strength at 1 month shows a significant increase over the values obtained for 24 h. This 1-month strength would appear to be a maximum, because the compressive strengths after 3 months are lower, if not always significantly so, than the 1-month values. The observed increase in strength could be due to the post-hardening reaction described by Wasson and Nicholson as the formation and hardening of the silica gel in the material [17]. A possible explanation for the subsequent reduction in strength would be some sort of hydrolytic instability in the set cement, since, in this case, the effect was not observed upon storage in air. Perhaps the hydration of the metal–oxygen bond could be responsible.

The results for the storage of both types of cement, both modified and simple, over concentrated sulphuric acid indicate that the PVPA-based materials are very sensitive to desiccation. The compressive strength of the desiccated materials was always significantly less than that of the air stored (i.e. slightly desiccated) materials. This sensitivity to desiccation has clinical implications; a restoration must not be allowed to dry out while other clinical procedures are being carried out. A similar sensitivity is observed in commercial glass-ionomer cement [1]. If the cement is subjected to a desiccating environment the water that is only loosely held in the set cement (sometimes referred to as the unbound water) will be lost. If the unbound water is lost then an inferior cement, with only a partially hydrated network will result. The desiccation of PVPA cements probably also results in the loss of "unbound" water from the cement matrix.

4.2. Effect of storage on mass and volume

The percentage changes in mass and volume of the two types of specimen on storage in the desiccating environments reflect the loss of unbound water from the cements (Tables IV and V). The specimens shrank by a significant percentage of their original volume and there was a significant decrease in mass. An interesting observation to note with the percentage change in mass results, is the time over which the specimens became lighter. The unmodified cement showed no significant change in mass after the first week of storage, i.e. all the unbound water that was lost was removed in the first week of storage. The modified material was less susceptible to desiccation. The water was lost over the first month rather than the first week of storage. This would imply that the "unbound" water is more tightly bound in the modified material. At this stage it is interesting to note that the unmodified material was mixed as an aqueous solution of the polymer whereas the modified material was mixed in a freeze-dried form. It is surprising, taking into consideration the percentage of the total mass of the cement that has been lost during desiccation, that the specimen was still intact after the 3-month test period.

When considering the effect on mass and volume of storage in aqueous media, the specimens, both modified and unmodified systems, behaved in the expected way. The percentage increase in mass upon storage in aqueous media was very small. This would be due, at least in part to insufficient drying of the specimen prior to weighing. It is very difficult to dry a glass-ionomer cement specimen without causing some degree of desiccation, and since these specimens were to be used in compressive strength testing, it was safer to error on the side of caution and under, rather then over dry the specimens. Nevertheless it is possible that the cements have taken up a small amount of water, perhaps for use in hydration of the ionic matrix or solvation of the polymer in the freeze-dried system. The solvation of the polymer is indicated because the percentage change in mass for the freeze-dried (modified) system was higher than that of the aqueous (unmodified) material in the early stages of the storage study. An uptake of water at the level observed in these results is not clinically significant.

The percentage change in volume on storage in aqueous media was variable, but the change in volume was rarely statistically significant. The variability in the results could reflect a variation in the porosity of the samples. This in turn could be a result of incomplete mixing of the components of the cement. A slight increase in volume upon storage under such conditions would not be unexpected for a glass-ionomer cement and the unmodified material did perhaps show an increase in volume. There was no progressive increase in volume with time.

5. Conclusions

This study has shown that modifying PVPA with zinc fluoride prior to reaction with glass leads to cements which behave differently on long-term storage compared with cements prepared from the unmodified homopolymer. The modified cements stored in water show a gradual increase in strength analogous to that exhibited by glass-ionomers based on poly(acrylic acid). By contrast, unmodified cements show a peak in strength at 24 h, followed by a decline at 1 week, an increase at 30 days and a further decline at 90 days. These effects may be explained by assuming two setting processes, one immediate, one longer term, that are more discrete than those that occur in conventional glass-ionomers. That they are not due to hydrolytic instability was shown by their occurrence in air at ambient humidity and in heavily desiccated air.

The behaviour of the specimens with regard to their change in mass and volume was very much as would be expected for a glass-ionomer cement. The specimens stored in dessicating environments were found to lose weight (due to the lose of water from the cement), the loss in mass was also accompanied by a reduction in the volume of the cement. The aqueous media stored specimens showed no significant change in volume on storage, the slight increase in mass on storage could be due to a small uptake of water, but will also (at least in part), be due to the fact that the specimens were still damp when measured.

Overall we conclude that if clinically useful cements are to be developed from the PVPA system, the modified rather than the simple acids should be investigated further.

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