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Studies in the setting of polyelectrolyte materials

Part II: *The effect of organic compounds on a glass poly(alkenoate) cement*

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The effect on a water-activated glass poly(alkenoate) dental cement of replacing the water with methanol, 50/50 water/methanol or 50/50 water/HEMA has been studied. The presence of the organic compounds caused the setting reaction to be substantially slowed down, and the resulting cements to be significantly weaker than those prepared with water. The use of water/HEMA had less effect on the speed of set than the use of water/methanol, but led to weaker cements. The post-hardening maturation processes that gradually increase the compressive strength of glass poly(alkenoate) cements were found to take place in both water/HEMA and water/methanol.

1. Introduction

As part of our studies on the fundamental chemistry of polyelectrolyte dental cements, we have recently reported the effect of using methanol to initiate the setting reaction of anhydrous zinc polycarboxylate cement [1]. Zinc polycarboxylate cement is made by reaction of poly(acrylic acid) with thermally-deactivated zinc oxide powder, and consists of a matrix of zinc poly(acrylate) with unreacted zinc oxide particles as filler [2]. The anhydrous or water-activated version of this cement is formulated to include both the zinc oxide and the poly(acrylic acid) within a single mixed powder. Setting is initiated by the addition of water in appropriate amounts [3].

In our recent paper [1], we reported that partial or complete replacement of water with methanol led to significant reduction in the speed of hardening of zinc polycarboxylate cement. This slower rate of hardening was shown, using infrared spectroscopy in the ATR mode, to be the result of a slower setting reaction. Methanol either alone or as a 50% (by mass) solution with water was thus shown to inhibit the reaction. Final cements were found, 24 h after mixing, to be significantly weaker in compression than those formed by reaction with water.

The present paper extends these studies in two ways. First, it covers the related glass poly(alkenoate) cements, and shows the effect of methanol on the setting chemistry and final compressive strength of these materials. Secondly, it explores the effect of adding hydroxyethyl methacrylate, HEMA, on the setting and strength of these cements.

Glass poly(alkenoates), which are also known by the trivial name of "glass-ionomers", are made by reaction of a water-soluble polymer, usually poly(acrylic acid) or a copolymer of acrylic acid, with powdered basic glass [4]. Like the zinc polycarboxylates, they are available as both anhydrous (water-activated) and hydrous versions, the latter being prepared from aqueous solutions of polymer. In both cases, the set cement comprises a multi-component matrix that is predominantly metal (mainly calcium) polyacrylate, with unreacted glass particles embedded in it [5, 6].

Recently, light-curable versions of these glass poly(alkenoate) cements have become available, which are hybrid materials that include a photocurable component. This photocurable component may be an unsaturated organic side chain grafted onto the poly(acrylic acid) backbone, and/or a separate organic precursor, such as HEMA or mixtures of HEMA with other acrylic monomers, that are capable of undergoing photopolymerization when irradiated by visible light. HEMA is thus an important constituent of these hybrid materials.

The presence of HEMA in these materials has been shown to cause the set cements to be slightly water swellable [7, 8]. This swelling was shown to depend on the chemical potential of the water in the surrounding medium, and was therefore more severe in pure water than in physiological saline. It also led to a significant reduction in the compressive strength of the specimens, and to a change in their failure mode from brittle to tough. These alterations in properties are consistent with the existence of a substantial hydrogel phase within the cured cements, which suggests that HEMA, well known to polymerize into a hydrogel material [9, 10], is the component responsible for these changes.

Our present studies were aimed at providing background information on the light-curable glass poly(alkenoates). In particular, we have investigated the effect of the organic species, including HEMA, on the acid-base chemistry and compressive strength of a glass poly(alkenoate). We have also studied the effect of these compounds on the post-hardening reactions known to take place in such cements when prepared from poly(acrylic acid).

2. Materials and methods

A water-activated type II restorative grade glass poly(alkenoate) cement was used (Opusfil W, ex. Davis Schottlander and Davis Ltd, London). It was mixed in accordance with the manufacturer's instructions i.e. 7:1 by mass powder to liquid. For the purposes of the present study the liquids used to make the cements were water, methanol, 50:50 water/methanol and 50:50 water/HEMA. Methanol was HPLC solvent grade (ex. Fisons plc, Loughborough); HEMA was 97% pure (ex. Aldrich Chemical Co., Gillingham, Dorset).

Working and setting times were determined using the oscillating rheometer, whose mode of operation has been described in detail elsewhere [11]. Working time is defined as the time for the amplitude of oscillation to reach 95% of the initial value; setting time is defined as the time to reach 5%.

The compressive strengths of the cements were determined as described in the British Standard specification [12], i.e. using cylindrical specimens of dimensions 6 mm diameter x 12 mm height. Specimens were stored at 37 °C in the mould for 1 h followed by 23 h in water at 37 °C. Six specimens were prepared for each set of conditions and loaded to failure in compression at a rate of 1 mm/min in a universal testing machine (Instron 1180). For each set of specimens, mean compressive strength and standard deviation were determined. To study the effect of organic compounds on the longer-term maturation processes, HEMA/water and methanol/water cements were also tested in compression at 7 and 30 days.

For all results, differences in values were tested for significance using Student's *t*-test.

3. Results

The results for the compressive strength and changes in volume and mass for the specimens of cement are given in Table I.

From Table I, it can be seen that cements prepared from a solvent system that includes organic species are weaker in compression, and show swelling on storage in water. The HEMA/water mixture was found to affect cements more than the methanol/water mixture. It gave cements that were weaker in compression and which took up greater amounts of water as shown by the larger increases in both mass and volume.

In the case of the cement activated with pure methanol, setting was so slow that the specimens could not be removed from the mould after 1 h at 37 °C. Instead, they were left in the mould for the full 24 h. The slowness of the setting also made it difficult to determine working or setting times from the rheogram, hence the quoted setting time is shown in Table II as an approximation only. Working and setting times for the other cements are also shown in Table II, from which it is clear that both methanol and HEMA inhibit the setting reaction, with HEMA showing the greater effect. In contrast, with compressive strength, methanol was found to have the more severe effect.

The statistical significance of the differences in Tables I and II are shown in Tables III and IV. Confidence levels below 95% were considered not significant, and are shown in Table IV as 'NS'. From Tables III and IV it is clear that the reductions in strength and the increases in working and setting times are all significant to at least the 99% level.

TABLE I Effect of organic compounds on measured compressive strength

Liquid	Storage time/days	Compressive strength/MPa	Change (% of initial value)	
			Volume	Mass
Water	1	230 s = 34	− 0.9 s = 1.0	1.0 s = 0.2
	7	281 s = 21	− 1.6 s = 1.2	− 1.2 s = 0.3
	30	303 s = 20	0.2 s = 1.0	1.6 s = 0.4
Water/MeOH	1	170 s = 18	0.9 s = 0.9	2.3 s = 0.2
	7	204 s = 20	0.2 s = 0.6	2.8 s = 0.3
	30	231 s = 13	0.4 s = 0.5	3.2 s = 0.2
Water/HEMA	1	147 s = 13	4.6 s = 0.9	2.2 s = 0.1
	7	147 s = 13	5.3 s = 0.7	3.5 s = 0.6
	30	168 s = 7	4.8 s = 0.6	3.3 s = 0.1
MeOH[a]	1	147 s = 13	–	–

[a] cement stored in mould for the 24 h prior to testing
s-standard deviation

TABLE II Effect of organic compounds on working and setting times

Liquid	Time (minutes)	
	Working	Setting
Water	3.6 s = 0.1	9.1 s = 0.6
Water/MeOH	12.8 s = 1.3	28.0 s = 2.4
Water/HEMA	6.6 s = 0.4	19.1 s = 0.1
MeOH	–	≈ 300

s-standard deviation

TABLE III Significance levels of differences between cements

Liquid	Compressive strength	Working time	Setting time	Volume change/1 day
Water cf Water/ MeOH	99%	99%	99%	99.9%
Water cf Water/ HEMA	99%	99%	99%	99.9%
Water cf MeOH	99%	–	99%	–

TABLE IV Significance levels of changes within cements

Liquid	Storage time/days	Compressive strength	Change in Volume	Mass
Water	0–1	–	99.9%	99.9%
	1–7	99%	NS	99%
	7–30	NS	98%	99%
Water/MeOH	0–1	–	99.9%	99.9%
	1–7	99%	NS	–
	7–30	99%	NS	99%
Water/HEMA	0–1	–	99.9%	99.9%
	1–7	no change	NS	99%
	7–30	99%	95%	NS

The various changes within the individual cements are generally significant to at least the 95% level. Thus the increase in strength with time for each cement, regardless of activating solvent, is highly significant, as are the changes in mass and volume, particularly over the first 24 h.

4. Discussion

It is clear from the results in Tables I and II that the glass poly(alkenoate) cement is affected by organic compounds in a similar way to zinc polycarboxylate. Setting reactions are slowed down, and compressive strength is reduced. The slowing down of the setting reaction is assumed to arise for similar reasons in both types of cement: (i) ionic reactions such as those involved in attack by acid functional groups on the powdered inorganic base are less favoured in organic solvents than in water, due to the reduction in dielectric constant [1]; and (ii) organic compounds are less good as solvents for poly(acrylic acid) in the thermodynamic sense, hence the polyacid enters the solution less readily and in a more tightly coiled configuration. Certainly, studies of poly(acrylic acid) in the semi-dilute concentration range have shown that the polymer adopts a more tightly coiled configuration in aqueous methanol than in water [13]. There seems no reason why similar effects should not occur in the more concentrated conditions of our experiments.

There has been some previous work on the inclusion of methanol in conventional glass poly(alkenoate) cement [14], but using lower levels than in the current study, i.e. 5%. A slight increase in working time and decrease in compressive strength were observed, and this was attributed to the esterification of some of the carboxylic acid groups of the polymer [14]. This seems a most unlikely explanation, particularly in our experiments, where there is insufficient time for such methylation to occur after mixing and where, anyway, similar effects are seen with HEMA.

HEMA, in fact, gave results that contrasted slightly with those of methanol. Used in a 50:50 mixture with water, it gave cements that set more quickly than those made with water/methanol, but which were weaker in compression. HEMA thus has comparable, though not identical effects to methanol.

Cement specimens were also tested for compressive strength at 7 and 30 days in order to determine whether post-hardening reactions occur. Such reactions were reported many years ago by Wilson *et al.* [15], and have recently been attributed to the formation of a hydrated silicate structure [5]. Other studies suggest that such an increase in compressive strength is not a property of all glass poly(alkenoates), but appears to be restricted to those formed from poly(acrylic acid) [16]. However, it was observed for our particular material in the current study, and was also seen in those cements activated with the organic/water mixtures. Thus it seems that whatever processes lead to this increase, they are affected only marginally, if at all, by the presence of methanol or HEMA.

The changes in volume and mass on storage for the conventional, water mixed system were similar to those observed previously for glass poly(alkenoate) cements. The slight increase in mass can be attributed, in the most part, to insufficient drying of the sample prior to weighing. The methanol/water activated materials showed no significant increase in volume on storage, but there was a significant increase in mass of about 3%. This implies that water has been taken up by the cement. The uptake of water continued throughout the month's storage, although the uptake over the first day was the highest. If the ionic matrix was in place, then this water could enhance and complete rather than contaminate, the acid-base reaction.

The effect of HEMA on the volume and mass of the specimen, mimicked the behaviour of the commercial light-cured glass poly(alkenoate)s. The specimens demonstrated a significant increase in both volume and mass. The increase in mass was equivalent to that observed for the alcohol/water mixed materials, indicating an equivalent uptake of water. The swelling, of about 5% of the initial volume, all occurred during the first day of storage. This swelling can be explained by the hydrophilic nature of HEMA. As with the commercial light-cured glass-ionomer cements [7] the HEMA has caused the cement to act like a hydrogel, hence the observed swelling. The swelling of the HEMA/water mixed cements, but not for the methanol/water mixed material, confirms the conclusions of earlier work [8].

These results show that this study is relevant to the recently introduced light-curable glass poly (alkenoates). They show that the presence of the organic species, which though necessary in these newer cements to bring about the photochemical part of the cure, slow down the acid–base setting reactions and lead to a weakening of the resulting matrix. However, the post-hardening maturation processes are still, in principle, able to occur. The extent to which they do will be governed by the ease of diffusion of the reactants through a set matrix that is partly organic in nature.

5. Conclusions

A water-activated type of glass poly(alkenoate) dental cement has been used in an experimental study in which setting was brought about using methanol, 50/50 water/methanol or 50/50 water/HEMA mixtures. These water/organic mixtures caused a substantial reduction in the rate of the setting reaction, and led to weaker cements that those prepared with water. Water/HEMA cements set quicker than water/methanol ones, but were weaker. These effects are assumed to arise for two reasons: (a) because the ionic setting reactions are not favoured in less polar organic solvent mixtures, and (b) because the organic-modified aqueous solutions are poorer solvents in the thermodynamic sense than pure water, hence the poly(acrylic acid) enters solution more slowly and in more tightly coiled configuration than in water.

Despite this adverse effect on solvent quality, the gradual increase in compressive strength with time previously reported for glass poly(alkenoate) cements containing poly(acrylic acid) was still found to take place in both water/HEMA and water/methanol mixtures.

In addition to the effect on strength and setting times, the inclusion of organics increased the uptake of water of the cements, and in the case of the HEMA/water mixed material the cement showed a significant swelling after storage in aqueous environments. The inclusion of organic species had reduced the effective level of water in the cement, consequently the increase in mass could be associated with the uptake of water to allow complete hydration of the matrix. The swelling of the HEMA/water mixed material reflected the hydrogel nature imparted to the material, by the inclusion of such a hydrophilic species in the formulation.

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