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The effect of strontium oxide in glass–ionomer cements

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The reaction of strontium oxide powder with poly(acrylic acid) has been studied both alone and within glass–ionomer cements. Reaction was found to be slow and the strontium-carboxylate structure was found to be partially covalent in character, as determined by Fourier transform infrared spectroscopy (FTIR). These are similar to the structures formed by calcium in glass–ionomer cements, but are different from typical monomeric strontium carboxylates, which tend to be purely ionic. Strontium oxide powder introduced in two types of glass–ionomer cements, slowed down the setting reaction at both 21 °C and 37 °C, but at low levels (5 wt %), increased the compressive strength in both cement formulations studied. However, at higher levels, it was found to decrease the compressive strength. This study confirms the view that strontium is a cement-forming ion; but concludes that, except at very low levels, strontium oxide powder does not improve the properties of glass–ionomer cements.

1. Introduction

Glass polyalkenoate cements are widely used in clinical dentistry [1]. Applications range from use as restorative materials in Class V cavities to liners and bases beneath amalgam or composite resin fillings, as luting agents in the placement of crowns and bridges and adhesives for the fixation of orthodontic appliances.

Glass–ionomer cements are prepared by the reaction of an ion-leachable glass with an aqueous solution of a polymeric acid, typically poly(acrylic acid), the resulting setting reaction is an acid–base reaction which generates a polysalt that forms the initial matrix of the cement. Subsequently a post-hardening maturation process occurs which results in the formation of a silicon containing phase. The aqueous solution may be preformed, or formed *in situ* from a formulation prepared by mixing glass powder with dried acid powder. This latter type of cement is activated by the addition of water, which dissolves the polymer and thereby initiates the setting reaction. Glasses for these cements are typically complex phase separated materials formed by fusion of mixtures of silica, alumina, calcium fluoride and calcium oxide, often with minor components such as aluminum fluoride, aluminum phosphate and cryolite (Na_3AlF_6) [2]. In certain glasses, some or all of the calcium is replaced by lanthanum, strontium or barium, to confer radiopacity on the final cement, an important requirement in the standards for glass-ionomers. The glass component not only acts as a source of ions for initial crosslinking, but also provides the inorganic species required for post-hardening. The nature of the glass governs the setting rate and is also responsible for the development of translucency in the cement. However, the effect of substituting calcium with these ions on setting has not been fully investigated and it is not clear what structure is formed when an ion such as strontium interacts with poly(acrylic acid).

The current work was carried out to determine what happens when strontium oxide reacts with poly(acrylic acid), in order to assess the cement forming characteristics of strontium ion. Given the fact that the ionic radii of Ca^{2+} and Sr^{2+} are quite close [3] it is important to examine the effect of inclusion of strontium oxide alone and as a solid additive to glass–ionomer cements. Previous studies of the inclusion of solid additives have met with varied success. For example, metal powders such as stainless steel or silver–tin alloy have been included as reinforcing components in glass–ionomer cements [4]. These materials are available commercially, and there is some evidence that, at high enough loadings, the silver–tin alloy enhances the mechanical properties of the set cement [5], but conversely the mixing is more difficult [6]. Other substances studied as solid additives have been hydroxyapatite [7] and borax [8]. In both cases, they led to weaker cements and there were no advantages in incorporating either as fillers for glass–ionomer cements.

2. Materials and methods

Strontium oxide powder of the following specification was used: purity 99.5%, maximum particle size 150 μm

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TABLE I Pre-firing composition of G338 glass

Glass	SiO_2 (%)	Al_2O_3 (%)	ALF_3 (%)	CaF_2 (%)	NaF (%)	$AlPO_4$ (%)
G338	24.9	14.2	11.0	12.8	12.8	24.2

(Goodfellow, Cambridge, UK). Glasses employed were (i) a batch of so-called G 338, whose composition is given in Table I, (supplied by Laboratory of the Government Chemist, Teddington, UK) and (ii) glass from a commercial glass-ionomer, Fuji II (GC Corporation, Japan). Poly(acrylic acid) (Versicol E7, supplied by Allied Colloids, Bradford, UK) was employed as a 40% mass/mass solution.

Cements were prepared by spatulating together the powder and polymer solution on a glass block, the powder being either a glass, or a mixture of glass and strontium oxide prepared by replacing 5, 10 or 20% of the glass by mass with SrO. A powder : liquid ratio of 3 : 1 was maintained for all these cements. Cements were also prepared using pure strontium oxide in the same way, using liquid-powder ratios of 3 : 1, 2 : 1 and 1 : 1 ratio. In this case, specimens were prepared only to record infrared spectra, not determine compressive strength.

For glass–SrO mixtures, working and setting times were determined in duplicate both at 21 and 37 °C using an oscillating rheometer which has been described in detail previously [8]. The working time was taken as the the time at which the amplitude of oscillation reached 95% of its initial value; the setting time was taken at 5% of the initial value.

Compressive strengths were determined according to the ISO standard [10], except that specimens of size 12 mm height × 6 mm diameter were employed. Sets of six cylindrical specimens were prepared in split metal molds which were stored at 37 °C for 1 h. They were then removed and stored in water at 37 °C for 24 h. The specimens were tested for each group on a Universal Testing Machine (Howden Type EU500, UK), using a cross-head speed of 5 mm min^{-1}. Compressive strengths were determined from load at failure, the mean and standard deviations being calculated for each set of specimens. Differences between means were evaluated for significance where appropriate using analysis of variance (ANOVA).

Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Nicolet FT800 spectrometer using a photo-acoustic cell using cured discs in case of cements.

3. Results

Cements in three different ratios of 3 : 1, 2 : 1 and 1 : 1 containing pure strontium oxide and polyacrylic acid were prepared, the setting time ranged from 1, 3, and 10 h respectively. Results for working and setting times at both 21 and 37 °C are shown in Tables II and III for G338 and Fuji-GC glass, respectively. In all cases, progressive increases in the level of strontium oxide led to increases in both working and setting times, indicating that strontium oxide retarded the rate of reaction.

TABLE II Working and setting times of G338 glass containing cements

Glass:PAA 3 : 1	Working time at 21 °C (min)	Setting time at 21 °C (min)	Working time at 37 °C (min)	Setting time at 37 °C (min)
G338	3.0	15.0	2.0	7.6
G338 + 5% SrO	3.2	17.0	2.2	9.4
G338 + 10% SrO	3.4	19.0	2.6	12.4
G338 + 20% SrO	4.0	21.6	2.8	14.8

TABLE III Working and setting times of Fuji GC glass containing cements (P:L ratio 3 : 1)

Glass:PAA 3 : 1	Working time at 21 °C (min)	Setting time at 21 °C (min)	Working time at 37 °C (min)	Setting time at 37 °C (min)
Fuji-GC	1.8	14.0	1.4	6.0
Fuji-GC + 5% SrO	2.2	10.8	1.8	6.4
Fuji-GC + 10% SrO	2.6	11.6	2.0	7.6
Fuji-GC + 20% SrO	3.2	14.2	2.4	13.0

TABLE IV Compressive srengths of G338 containing cements

Cement	Compressive strength ± SD (MPa)
G338	73.0 ± 3.6
G338 + 5% SrO by wt	93.3 ± 3.9
G338 + 10% SrO by wt	73.3 ± 5.0
G338 + 20% SrO by wt	49.8 ± 4.6

TABLE V Compressive strengths of Fuji II GC glass containing cements

Cement	Compressive strength ± SD (MPa)
Fuji-GC glass	59.00 ± 6.5
Fuji-GC + 5% SrO by wt	66.37 ± 7.1
Fuji-GC + 10% SrO by wt	51.00 ± 3.1
Fuji-GC + 20% SrO by wt	39.00 ± 4.0

Results for compressive strength are shown in Tables IV and V. For cements containing G338 glass the increase in strength from 0–5% SrO was significant ($P < 0.01$), as were the reductions from 5–10% and from 10–20%. For Fuji II cements the increase from 0–5% was not significant, however, the decrease from 5–10% and from 10–20% SrO were each significant ($P < 0.02$ and $P < 0.01$, respectively). Major bands appearing in the infrared spectra of strontium oxide–poly(acrylic acid) and G338–poly(acrylic acid) cements are listed in Tables VI and VII, respectively.

4. Discussion

4.1. Working and setting times

The decrease in speed of setting caused by the addition of strontium oxide is similar to that found previously with

TABLE VI Observed major carbonyl (—C=O) bands in the FTIR spectrum of SrO-poly(acrylic acid)

Peak assignments	Band (cm^{-1})
Carbonyl from the carboxyl group	1685
Asymmetric stretch of C=O in carboxylate group	1550
Symmetric stretch of C=O in carboxylate group	1460

TABLE VII Observed major carbonyl (—C=O) bands in the FTIR spectrum of G338-poly(acrylic acid)

Peak assignments	Band (cm^{-1})
Carbonyl from the carboxyl group	1701
Asymmetric stretch aluminium carboxylate group	1614
Asymmetric stretch calcium carboxylate group	1551
Symmetric stretch of C=O in carboxylate group	1456

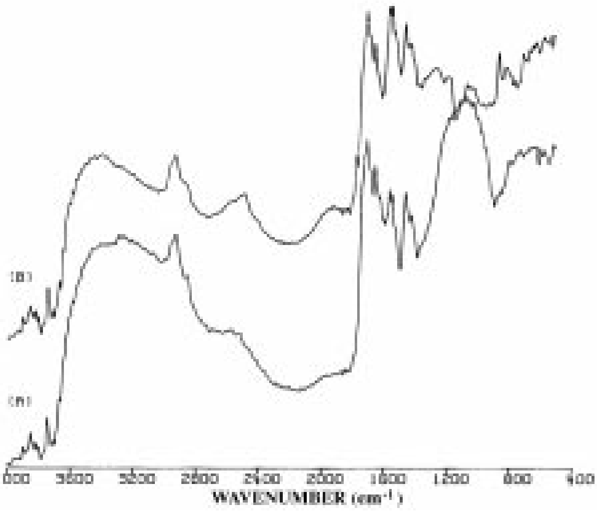

Figure 1 A comparison of the FTIR spectra of (A) G338 glass-ionomer cement and (B) strontium oxide–PAA cement.

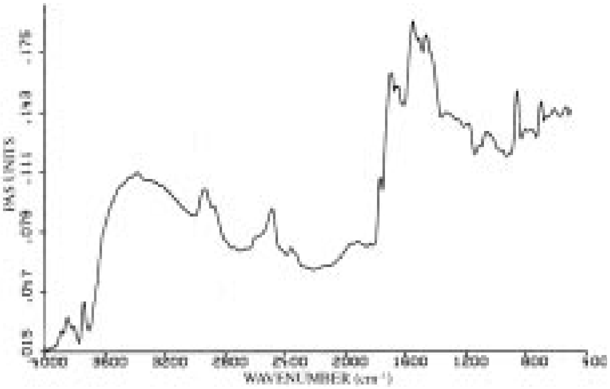

Figure 2 An FTIR spectrum of Fuji II glass-ionomer cement.

both hydroxyapatite [7] and borax [8]. It arises because of the dilution of the components of the main acid–base reaction, and occurs despite the fact strontium oxide will react with the acid. This is due to the relative slowness of the latter reaction. The slowness is presumably related to the kinetics of release of Sr^{2+} ions from the oxide, because there is no evidence that strontium containing glasses themselves react any slower with poly(acrylic) acid than equivalent calcium containing ones.

4.2. Compressive strength

Compressive strength of strontium oxide containing cements did not follow a consistent pattern and was not similar to the inclusion of hydroxyapatite or borax in which low levels caused an increase. An increase with low levels of SrO was observed with both glasses, but was statistically significant only for G338 cements. The reason for this observation is not clear, but it indicates that there must have been a possible modification of the fracture mechanism due to the presence of small amounts of SrO. However, this effect is reversed by further addition of SrO, since at 10% the compressive strength is essentially the same as with no additive, and at 20% SrO it is significantly lower. However, the well established correlation of slow setting with low compressive strength for glass–ionomers is also seen in these cements.

4.3. Infrared spectroscopy

The infrared spectra of both strontium oxide–poly(acrylic acid) and G338–poly(acrylic acid) are shown in Fig. 1. Two features can be taken into account, the position of the asymmetric carbonyl stretch, at $1550\,cm^{-1}$ and the difference between this and the symmetric carbonyl stretch at $1460\,cm^{-1}$, $\Delta\nu = 90\,cm^{-1}$. The precise position of the asymmetric carbonyl band is considered a more reliable indicator of structure than the $\Delta\nu$ values [12]. This band generally occurs between 1550 and $1620\,cm^{-1}$ for metal carboxylates and polycarboxylate salts, [13, 14] though it is found approximately at $1634\,cm^{-1}$ for the rare case of a monodentate structure [15]. For strontium polyacrylate, the band at $1550\,cm^{-1}$ is indicative of a chelating bidentate structure. This is partially covalent, thus differing from monomeric strontium carboxylates, which are ionic in nature. These typically have an asymmetric carbonyl stretch at about $1575\,cm^{-1}$, for example, it occurs at $1578\,cm^{-1}$ in strontium acetate [16].

The position of the asymmetric carbonyl band for strontium polyacrylate is consistent with a partially covalent character which is further confirmed by the relatively small $\Delta\nu$ value of $90\,cm^{-1}$. In general, large $\Delta\nu$ values ($150\,cm^{-1}$) are assigned to purely ionic structures, which have frequently been confirmed by X-ray crystallography. Purely ionic structures are rare for the lower members of Group II, barium, magnesium and calcium carboxylates all exhibiting a covalent character. Hence, in the polyacrylate salt, strontium behaves more like a typical Group II element than it does in monomeric carboxylates. The spectrum of the glass–ionomer cement shows asymmetric carbonyl stretches at 1551 and $1614\,cm^{-1}$ and by reference to previous results [17, 18] these bands arise from the calcium and aluminum polyacrylates respectively. A strong, broad intense peak centered at $1066\,cm^{-1}$ is observed in the glass–ionomer cement, much more so than in the spectrum of the strontium oxide cement. It probably arises from two sources, one from the silicate network formed as a cement matrix and similar bands have been observed previously in glass–ionomers [19], in hydrated silica gel [20] and they have been attributed to the Si–O–Si stretching vibration [19]. The phosphate stretching frequencies also arise in the same region, and as the G338 cement contains phosphate groups there is considerable overlap in this region.

5. Conclusions

Strontium oxide has been shown to react with poly(acrylic acid) in a relatively slow reaction to yield cements. Strontium has thus been shown to be cement forming ion. FTIR studies have revealed that the resulting strontium-carboxylate polysalt contains structures that are partially covalent in nature. These are similar to those formed by calcium in glass–ionomer cements, but are different from those occurring in typical monomeric strontium carboxylates.

The addition of strontium oxide was found to slow the setting reaction, as indicated by the working and setting times at both 21 and 37 °C. At the lowest levels of strontium oxide used, 5%, by weight, there was a significant increase in compressive strength for both cement formulations studied, which may be beneficial in some applications. However, this declined at higher levels, such that at 20% SrO the compressive strength was reduced to about two-thirds of the strength of the equivalent cement with no additive present.

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