

Studies in the setting of polyelectrolyte cements

Part I *Effect of methanol on zinc polycarboxylate*

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Specimens of zinc polycarboxylate dental cement have been prepared with methanol or methanol/water mixtures as solvent. Such cements set at a reduced rate compared with those activated by water alone, and final materials are about 50% weaker in compression. Methanol reduces the dielectric constant of the solvent system compared with water alone and such a reduction inhibits ionic reactions and causes the polyacid to adopt a coiled configuration in solution. Both of these effects are assumed to contribute to the observed reduction in setting rate. The reduction in setting rate was confirmed using infrared spectroscopy.

1. Introduction

Zinc polycarboxylate cement was introduced into dentistry by Smith in 1968 [1]. It consisted of a modified zinc oxide powder, heat treated to make it very slightly non-stoichiometric [2], and an aqueous solution of poly(acrylic acid). More recently, versions have become available in which the zinc oxide powder is combined with a dried powder of polyacid, and the whole mixture activated by the addition of water.

Although many years have passed since zinc polycarboxylate was first described as a dental material, studies on its structure are still continuing. In 1988, Nicholson *et al.* [3] showed, using Fourier transform infrared spectroscopy, that, contrary to previous reports, zinc ions were partly chelated to the carboxylate groups of the polymer. In 1991, Hill and Labok [4] showed that these cements behave in many ways like thermoplastic composites with very weak crosslinks between the polyacrylate chains. This study, which involved determining the relationship between the molar mass of the polymer and the fracture toughness of the cement, supported conclusions obtained some years previously concerning the relatively plastic nature of this cement [5].

More recently still, Nicholson *et al.* [6] have studied the role of water in zinc polycarboxylate cements. They showed that these cements are relatively poorly hydrated, particularly by comparison with the closely related glass-poly(alkenoate) cements. Water seems to occupy co-ordination sites around the zinc ions, but does not have any other structural rôle. Little or no differences were seen in the hydration, setting or

strength properties of the materials regardless of whether they were made from aqueous acid with zinc oxide or from a water-activated mixture of polyacid plus ZnO.

The current study was aimed at further extending understanding of these materials. In particular, it is concerned with the effect of altering the dielectric constant of the reaction medium on the setting properties by comparing cements made with solvent systems based on water/methanol mixtures with those made, respectively, from pure water and pure methanol. The findings are of interest in a wider context, given the recent development of light-curable glass-poly(alkenoate) cements [7]. In light-curable glass-poly(alkenoates), significant levels of organic compounds are added to the aqueous poly(acrylic acid) component which is eventually mixed with the powdered inorganic base [8]. However, the effect of adding organic molecules to such a cement has not previously been the subject of a systematic study.

2. Materials and methods

A commercially available water-activated zinc polycarboxylate dental cement, Aquaboxyl (Davis Schottlander and Davis Ltd.) was used in the powder/liquid ratio 10:1 by mass.

The cement samples were prepared by adding appropriate mass of water, 50:50 water/methanol, or methanol to the ZnO/polyacid powder and mixing by spatulation on a glass block. Six specimens of each cement were prepared by placing freshly mixed cement

in cylindrical moulds of dimensions 12 mm high \times 6 mm diameter. The specimens were stored in their moulds for 1 h at 37°C, and then in water, also at 37°C, for a further 23 h. This storage regime is that specified in the British Standard for zinc polycarboxylate dental cements [9]. However the specimens prepared from methanol alone had not set after 1 h in the mould, consequently the standard storage regime could not be used for these cements, and hence directly comparable compressive strengths could not be determined.

Working and setting times were determined using the oscillating rheometer, whose design and mode of operation has been described in detail elsewhere [10]. Infrared spectra of cements were recorded using Attenuated Total Reflectance on a commercial infrared spectrophotometer (model PE983G, ex. Perkin Elmer).

Differences in compressive strength were assessed for significance using Student's *t*-test.

3. Results and discussion

Results for working and setting time determination are shown in Table I.

It can be seen that the introduction of methanol significantly reduced the setting rate. The cement, which set after 22 min when activated with water, took over 5 h to set with pure methanol.

We attribute this reduction in reaction rate to the smaller dielectric constant of methanol compared with that of pure water, i.e. at 25°C, 32.63 compared with 78.54 (water) [11]. This smaller dielectric constant disfavours ionic reactions because solvated ions in methanol are of higher energy than solvated ions in water. The lower dielectric constant also causes the poly(acrylic acid) to enter solution in a more coiled configuration than in water, hence making the carboxylic groups less available for reaction, and less able to ionize. Methanol is known to be a poor solvent for poly(acrylic acid) in terms of the Flory-Huggins theory of polymer solutions [12], and therefore the methanol/poly(acrylic acid) system is closer to precipitation than the water/poly(acrylic acid) one. Previous experimental work on methanol/water mixtures as solvents for poly(acrylic acid) were carried under so-called semi-dilute conditions, but we see no reason why the conclusions concerning methanol as a solvent for poly(acrylic acid) should not apply under the higher concentration conditions of our experiments.

Methanol/water mixtures have previously been considered as the solvent system for poly(acrylic acid) in experimental glass-poly(alkenoate) cements [13].

TABLE I Effect of liquid on working and setting times

Liquid	Time (min)	
	Working	Setting
Water	5.8 s = 0.4	22.0 s = 0.4
Water/MeOH	20.1 s = 6.5	55.8 s = 0.1
MeOH	–	≈ 330

s = standard deviation.

However, only low levels of methanol were used (5%), and at such levels no significant changes in working or setting times were found. In their paper, Crisp *et al.* [13] attributed the effect of methanol to esterification of the carboxylic acid groups, but this seems unlikely on equilibrium grounds. Moreover, in our experiments, using cements whose setting reaction is activated by the addition of water or water/methanol mixtures, it seems improbable that any such esterification could occur quickly enough to affect the setting rate.

The fact that solvent systems of lower dielectric constant reduce overall setting rate can be used to give insight into the processes occurring at the activation step. Many years ago, Hughes and Ingold [14] formulated their rules on solvent effects, and stated that where the activation step involves the development of

TABLE II Effect of liquid on strength

Storage Liquid	Time (h)	CS (MPa)
Water	24	182 s = 18
Water/MeOH	24	117 s = 18
MeOH	Not determined	

s = standard deviation.

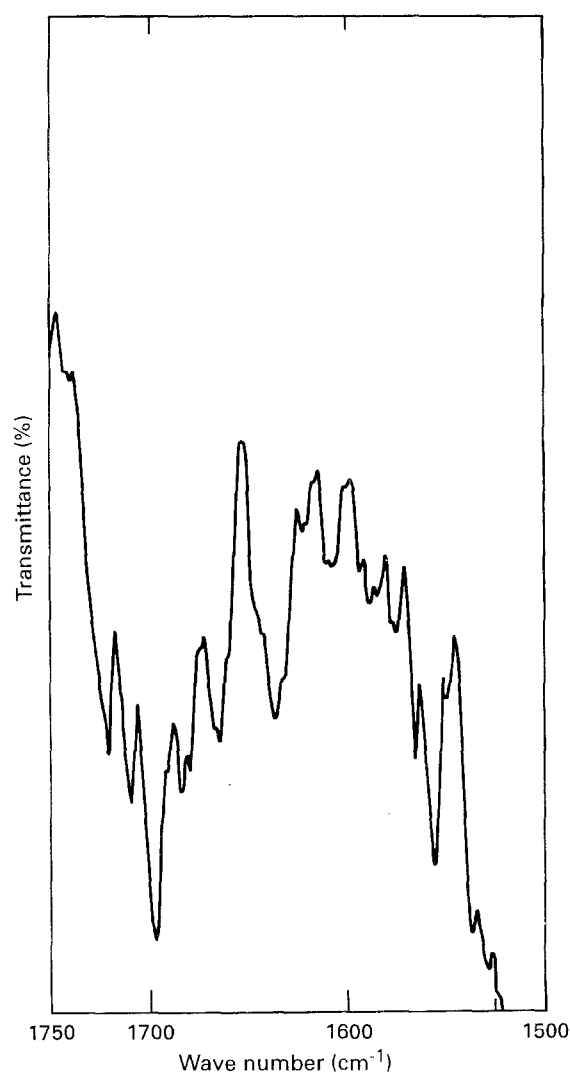
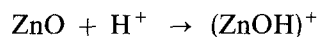


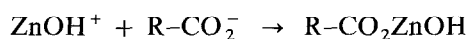
Figure 1 Infrared spectrum of Aquaboxyl, mixed with water, 5 min after the start of mixing.

electronic charge, polar solvents increase the rate of reaction. In the current reaction, we see a faster rate with the more polar solvent system, so can conclude that the activation step involves the development of electronic charge.

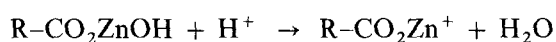
The most probable initial step in the setting of zinc polycarboxylate cements is protonation of the surface of the ZnO particles by the aqueous polyacid:



This step seems likely to be more favoured in pure water than in pure methanol, or even water/methanol mixtures. The removal of the $(\text{ZnOH})^+$ species from the surface of the particle, followed by immediate reaction with the carboxylate group on the polymer could result in the formation of a transient neutral species, which in acid solution might continue to react as follows:



Then:



and:



The effect of these solvent systems on the strength of the resulting cements is shown in Table II. The cement prepared from the 50/50 methanol/water mixture was weaker than that prepared from water alone, a difference that was significant at the 99% confidence level.

These findings are similar to those found previously for methanol/water mixtures in glass-poly (alkenoates). For these materials, both compressive strength and hardness were significantly reduced by the presence of only 5% methanol in the water.

Finally, infrared spectroscopy has been used to determine the extent of reaction in cements formulated from pure water and pure methanol. Spectra are shown in Figs 1 to 4.

These results show a number of features. First, cements that were an hour old both showed a reduced acid band at ca. 1700 cm^{-1} , but the reduction was much greater in the cement activated with water. This confirms that the slower rate of setting as determined rheologically in the methanol-activated cement is a consequence of slower chemical reaction.

A second clear feature of these spectra is that the 1 h cements show a variety of bands in the region $1520\text{--}1570 \text{ cm}^{-1}$, the region which has previously been assigned to carboxylate absorptions of different

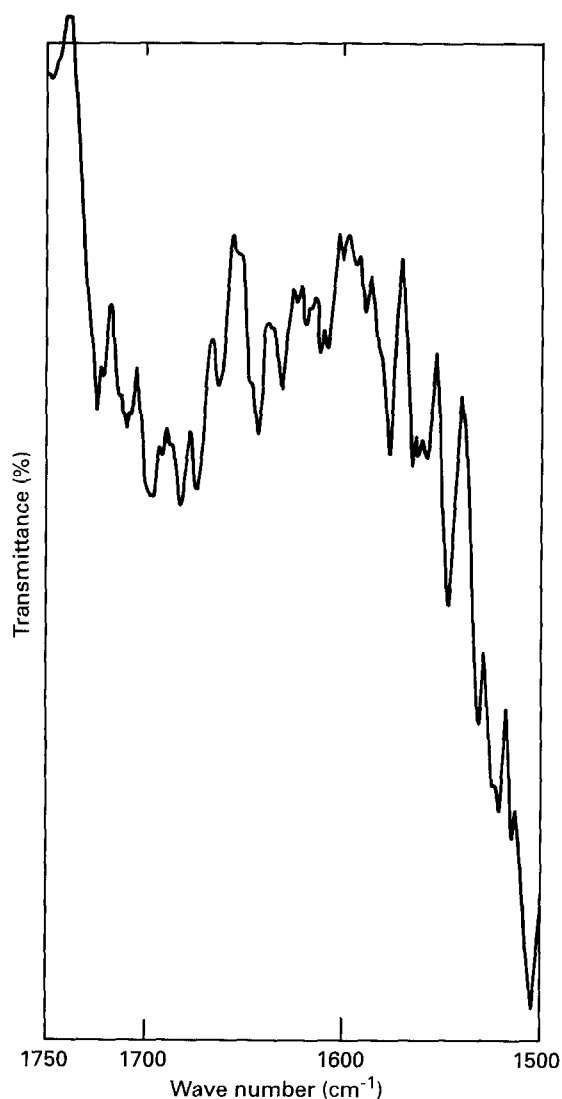


Figure 2 Infrared spectrum of Aquaboxyl, mixed with water, 60 min after the start of mixing.

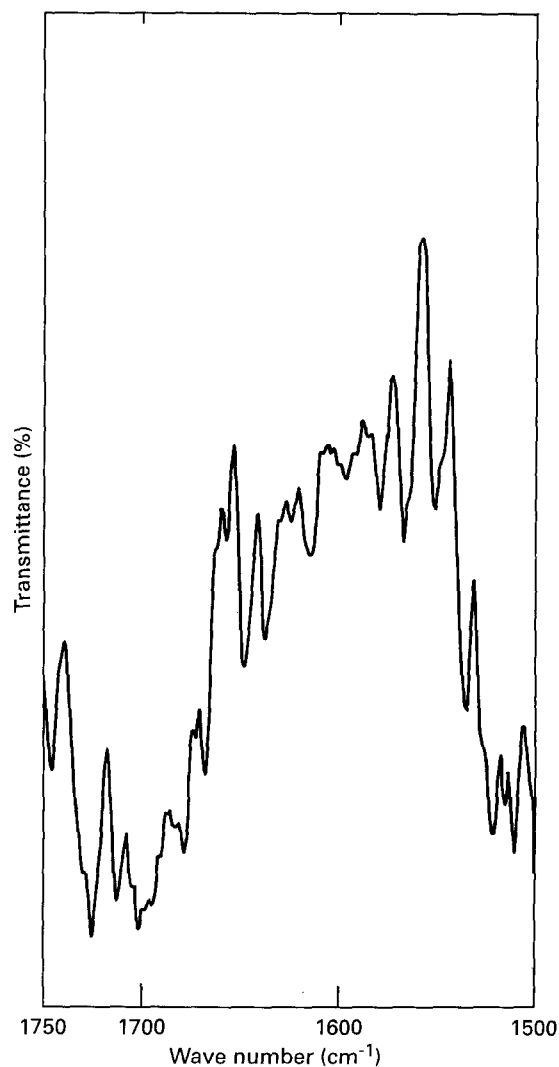


Figure 3 Infrared spectrum of Aquaboxyl, mixed with methanol, 5 min after the start of mixing.

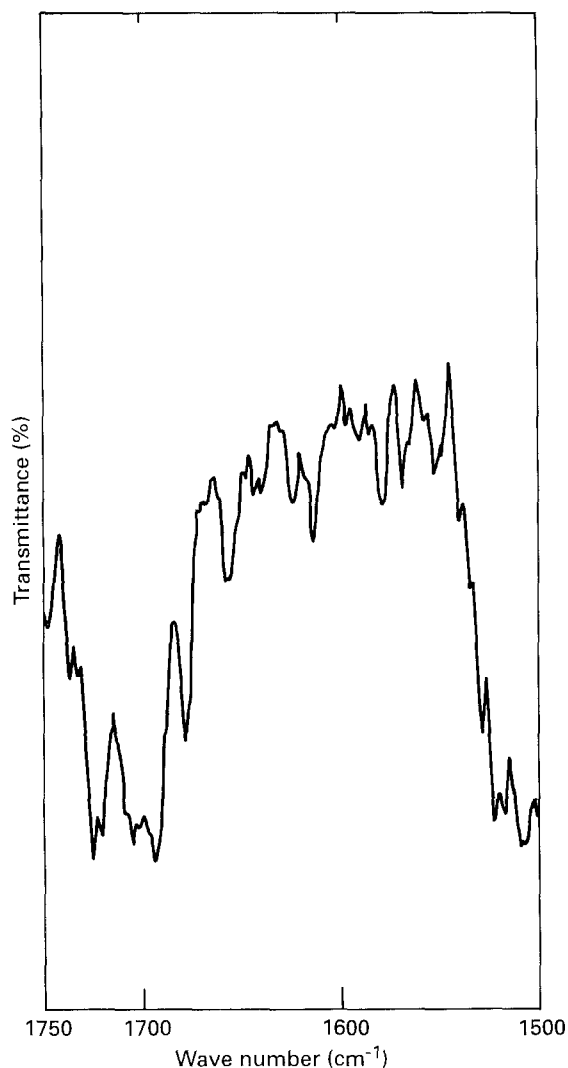


Figure 4 Infrared spectrum of Aquaboxyl, mixed with methanol, 60 min after the start of mixing.

kinds [3]. Table III lists the absorptions in the hour-old spectra in this region, together with assignments based on this previous study.

From Table III it is clear that the major chelated and ionic zinc carboxylate structures are present in both cements, but that some of the individual bands in the water-activated cement become split into two in the methanol-activated cement. These bands probably arise due to replacement of water molecules by methanol in hydration sites around the carboxylate groups, which modify their frequency of vibration slightly. Either way the presence of these bands shows that, even when formed in methanol, zinc polyacrylate is a complex species, comprising a range of zinc-carboxylate interactions, not a simple ionic compound as was once thought [15].

4. Conclusions

We have shown that zinc polycarboxylate dental cement prepared with methanol or methanol/water mixtures sets more slowly than with water to give weaker final materials. The reduction in speed of set arises due to the reduced dielectric constant of the organic solvent compared with water. This reduced dielectric constant inhibits ionic reactions and causes the poly-

TABLE III Infrared bands and their assignments (from Nicholson et al. [3])

Band	Water-activated cement	Methanol-activated cement	Assignment
1528	–	Present	–
1533	Present	Present	Unidentate carboxylate
1538	–	Present	–
1546	Present	Present	Bidentate carboxylate
1552	–	Present	–
1557	Present	Present	Bidentate carboxylate
1563	Present	Present	Ionic carboxylate?
1565	Present	Present	Ionic carboxylate?
1568	–	Present	–

acid to adopt a coiled configuration in solution, both of which would be expected to slow down the setting process. These findings are similar to those reported previously for experimental glass-poly(alkenoates). The inhibition of the ionic reactions by organic molecules in aqueous solution is clearly of importance in the setting of the recently developed light-curable glass-poly(alkenoates).

We have shown that the reduction in setting rate as determined by change in rheological properties correlates with slower changes in the infrared spectra of the setting cements. Infrared results have also confirmed previous findings that a range of chelated zinc carboxylate structural types exist in the set cement, even in the methanol-activated materials.

References

1. D. C. SMITH, *Brit. Dent. J.* **125** (1968) 125.
2. N. N. GREENWOOD and A. EARNSHAW, "The chemistry of the elements" (Pergamon Press, Oxford, 1984).
3. J. W. NICHOLSON, P. J. BROOKMAN, O. M. LACY, G. S. SAYERS and A. D. WILSON, *J. Biomed. Mater. Res.* **22** (1988) 623.
4. R. G. HILL and S. A. LABOK, *J. Mater. Sci.* **26** (1991) 67.
5. J. M. PADDON and A. D. WILSON, *J. Dent.* **4** (1976) 183.
6. J. W. NICHOLSON, S. J. HAWKINS and E. A. WASSON, *J. Mater. Sci. Mater. Med.* **4** (1993) 32.
7. A. D. WILSON, *Int. J. Prosthodont.* **3** (1990) 425.
8. H. M. ANSTICE and J. W. NICHOLSON, *J. Mater. Sci. Mater. Med.* **3** (1992) 447.
9. British Standards Institution, "Dental zinc polycarboxylate cements", BS 6814:1987.
10. A. D. WILSON and J. W. NICHOLSON, Ch 10, "Acid-base cements; their biomedical and industrial applications" (Cambridge University Press, 1993).
11. N. R. LANGE (ed.), "Handbook of chemistry" (McGraw-Hill, New York, 1961), p. 1221.
12. N. T. M. KLOOSTER, F. van der TROUW and M. MANDEL, *Macromolecules* **17** (1980) 2087.
13. S. CRISP, A. J. FERNER, B. G. LEWIS and A. D. WILSON, *J. Dent.* **3** (1975) 125.
14. N. S. ISAACS, "Physical organic chemistry" (Longman Scientific and Technical, Harlow, Essex, 1987).
15. M. A. MOHARRAN, H. ABDEL-HAKEEM, H. SHAHEEN and R. M. IBRAHIM, *J. Mater. Sci.* **21** (1986) 1681.

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