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Chemical characterization of *in vivo* aged zinc polycarboxylate dental cements

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The chemical composition of zinc polycarboxylate dental cements aged *in vivo* was studied. Thirty samples aged from one to 17 years were investigated using X-ray diffraction, infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry. Evidence for the presence of zinc oxide, amorphous zinc polycarboxylate and water of hydration was found. No correlation with age concerning either the chemical structure of the components or their relative amounts was found. Zinc polycarboxylate dental cements show very good chemical stability on long-term use.

1. Introduction

Since Smith [1] introduced zinc polycarboxylate cements in dentistry in 1968, few fundamental studies on their chemical evolution have been undertaken. Smith [1] and Wilson and coworkers [2–4] essentially focused on the understanding of the setting reaction. Crisp *et al.* [5], Mortimer and Tranter [6] and Williams *et al.* [7] investigated the chemical changes occuring *in vitro* in zinc polycarboxylate cements with time. The few *in vivo* studies that have been reported [8, 9] involved the clinical evaluation of these dental cements without any description of their chemical characteristics. All of these investigations were performed over relatively short periods (from some hours up to three years).

Nearly three decades after the introduction of zinc polycarboxylate cement, it is now possible to investigate long-term chemical changes of zinc polycarboxylate dental cements aged in the oral environment as had been done for zinc phosphate dental cements [10]. Investigations of structural and chemical changes in zinc polycarboxylate cements were performed on powdered samples using X-ray diffraction (XRD), infrared (i.r.) absorption spectroscopy and thermoanalytical techniques: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). These techniques were applied to both cements aged *in vivo* for up to 17 years and freshly prepared cements (48-h-old) for comparison.

2. Experimental procedure

2.1. Cement samples

2.1.1. In vivo cement

Some 30 samples of cements were taken after removal of fixed prostheses. All the cement present in each prosthesis (inside and outside the crown) was used as sample. None of the occlusals of these prostheses were perforated. A minimum of 30 mg of cement was necessary to perform all the different manipulations. The mean age was 6.8 years, the oldest being 17 years and the most recent one year. Fig. 1 shows the distribution of samples relative to their age. All samples were identified by XRD analysis and i.r. spectroscopy as zinc polycarboxylate dental cements.

2.1.2. In vitro cement

Two typical commercial dental polycarboxylate cements were prepared for comparison with *in vivo* cements. Bondex (De Trey) whose powder (72% zinc oxide, 7% magnesium oxide and 13% polyacrylic acid) was mixed with liquid (distilled water) according to the manufacturer's instructions; and Durelon (ESPE) whose powder (zinc oxide, tin fluoride)[§] was also mixed with the liquid (aqueous polyacrylic acid)[§] according to the manufacturer's instructions. All the analyses were performed after at least a 48-h delay (to ensure that the cements were chemically stabilized).

Both the *in vivo* and *in vitro* samples were dried in air under ambient conditions (20 °C, 65% relative humidity) and ground to obtain fine powders.

2.2. Chemical characterization

Powder XRD patterns were obtained with an automatic Philips diffractometer controlled by an IBM PC (100 acquisitions, 3–35 °θ, 1600 points, acquisition delay 500 ms) using an anticathode CuK_α (0.154 18 nm) with a nickel filter.

I.r. absorption spectra were registered on a Perkin Elmer 983 G spectrometer in the 4000–400 cm^{-1}

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[§] The exact composition was not given by the manufacturer.

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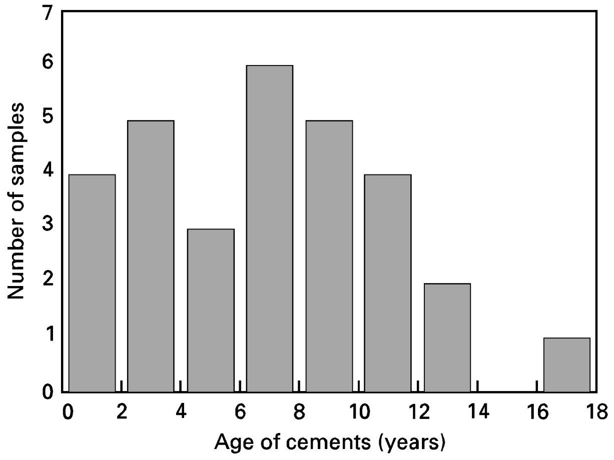

Figure 1 Distribution of the number of cement samples tested versus their age.

range. Samples were diluted (1%, wt wt^{-1}) in vacuum-dried KBr (Aldrich Chemicals, spectroscopic grade), and pellets 13 mm diameter and 0.2 mm thick were made under 9 kN cm^{-2} pressure.

TGA was performed using a Setaram thermobalance, with continuous registering by means of a B 601 Ugine–Eyrand system and a temperature controller RT 64. The heating rate was 2.5 °C min^{-1}.

DSC was performed using a DSC4 Perkin–Elmer computer-managed calorimeter. The calometric and thermometric reference was indium. All experiments were executed under nitrogen flow on 2–3 mg samples in closed aluminium pellets. The heating rate was 20 °C min^{-1}.

3. Results

3.1. XRD

The X-ray diffractograms of the fresh commercial cements are shown in Fig. 2a and b (Bondex and Durelon, respectively). Fig. 2c and d shows XRD diagrams of two typical old cements aged *in vivo* chosen as examples. All the diffractograms showed sharp peaks corresponding to crystalline material and a large band in the $9° < \theta < 19°$ domain.

3.2. I.r. spectoscopy

The i.r. spectra of the two fresh cements are very similar, that of Bondex is shown in Fig. 3a, and a typical spectrum of a 12-year-old cement aged *in vivo* is shown for comparison in Fig. 3b.

3.3. Thermal analysis

For the fresh Bondex and Durelon cements, a 6–8% weight loss is observed in the TGA curve, beginning at 40 °C and ending at about 120 °C. No other change is observed at higher temperatures until the end of the scanned domain is reached at 300 °C. These results are in good agreement with those reported earlier [11] for fresh cements.

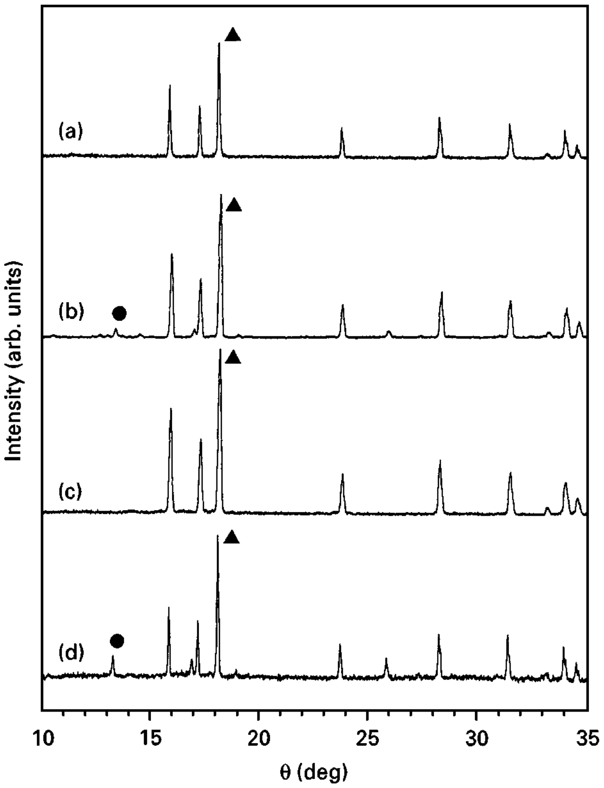

Figure 2 XRD patterns of fresh dental polycarboxylate cements: (a) Bondex, and (b) Durelon; and examples of *in vivo* cements: (c) a seven-year-old dental cement, and (d) a 17-year-old dental cement. Main peaks of the residual oxides are indicated, and their corresponding Miller plane indices, [*h k l*] are given: (▲) ZnO, (●) SnO_2.

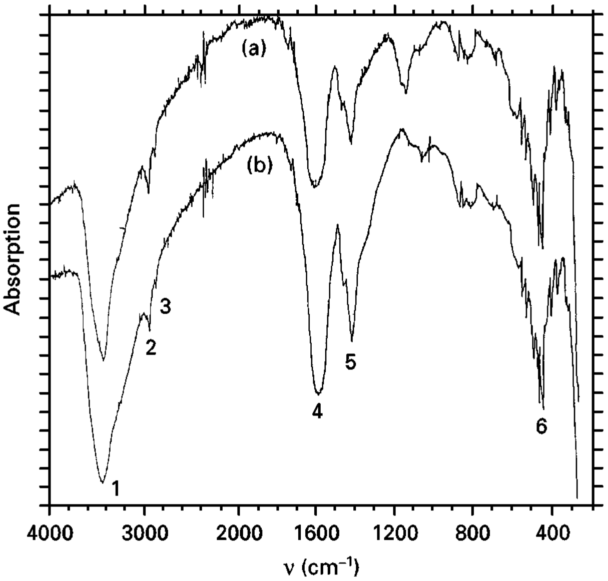

Figure 3 I.r. spectra of: (a) a fresh dental zinc polycarboxylate cement (Bondex), and (b) an *in vivo* 12-year-old dental cement chosen as an example. Bands numbered one to six are indicated in Table II.

For old cements, the shape of the TGA curve is the same. Weight losses of 4–12% beginning at 40 °C and ending at about 120 °C are observed. The average weight loss for cements aged from one to 17 years is 10%. The TGA curve of a 17-year-old cement is given as an example (Fig. 4b).

The DSC curve of the same 17-year-old cement appears in Fig. 4a. The shape of this curve is typical of both fresh and old cements. The fresh cements show one endotherm between 50 and 180 °C; $\Delta H = 50\,\mathrm{J\,g^{-1}}$. Old cements all show one endotherm, typically in the same temperature range (50–180 °C), whose value ranged between 48 and $284\,\mathrm{J\,g^{-1}}$, the mean value being $160\,\mathrm{J\,g^{-1}}$.

4. Discussion

4.1. XRD

Table I shows that the systems of diffraction lines observed by XRD corresponds to (i) ZnO, as is clearly shown by comparison with ASTM card No. 36–1451; and (ii) SnO_2 (ASTM card No. 41–1445). In a few cements studied MgO (ASTM card No. 30–794) was present. The presence of tin oxide depends on the commerical cement initially used: it is present in small quantities in some cements, i.e. Durelon, and not in others, i.e. Bondex. The diffuse band in the 9–19 °θ domain is typical of non-crystalline materials, and thus can be attributed to the amorphous zinc polycarboxylate matrix. Therefore, the cement must be a composite of unreacted oxides [ZnO (mainly), MgO and SnO_2] and the amorphous zinc polycarboxylate matrix resulting from the setting reaction of these oxides with polyacrylic acid and water. These results are in accordance with the core-link structure proposed for such cements [12, 13].

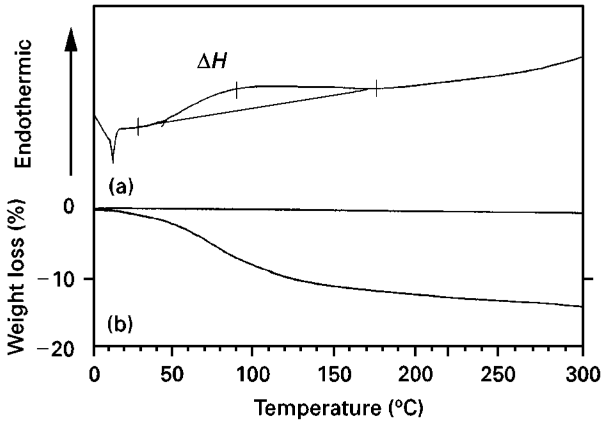

Figure 4 Thermal analyses of an *in vivo* 17-year-old dental cement: (a) DSC curve, and (b) TGA curve. The endotherm is labelled ΔH.

TABLE I Indexation of the XRD lines of a 17-year-old zinc polycarboxylate dental cement[a]

Cement	ZnO^b		SnO_2^c	
d_{hkl} (nm)	d_{hkl} (nm)	$[hkl]$	d_{hkl} (nm)	$[hkl]$
0.335			0.335	100
0.282	0.281	100		
0.264			0.264	101
0.261	0.260	002		
0.248	0.248	101		
0.237			0.237	200
0.191	0.191	102		
0.176			0.176	211
0.167			0.167	220
0.163	0.162	110		
0.148	0.148	103		
0.140	0.141	200		
0.138	0.138	112		
0.136	0.136	201		

[a] Reticular distances, d_{hkl} are in nanometres and the $[hkl]$ are the Miller indices of the corresponding planes.
[b] Values from ASTM card No. 36–1451.
[c] Values from ASTM card No. 41–1445.

4.2. I.r. spectroscopy

According to Wilson [3] and literature data, the main vibration bands observed in Fig. 3a and b are attributed as shown in Table II. The main carboxylate band was seen at about $1590\,\mathrm{cm^{-1}}$. It is an intense, relatively broad signal, and according to Nicholson *et al.* [4] it seems to be composed of two or more signals. An attempt was made to quantitate roughly the relative amounts of water, carboxylic groups and unreacted zinc oxide in order to plot them against time. The method consisted of dividing the $\nu(H_2O)$ and $\nu_{as}(CO_2^-)$ absorption values for each sample by the $\nu(ZnO)$ absorption value (which was chosen as an internal reference). No correlation between these resulting values and the age of the cements was observed, as shown in Fig. 5, indicating that the relative amounts of water, carboxylate matrix and zinc oxide do not change over the years.

4.3. Thermal analysis

The TGA analyses showed that weight losses were observed below 120 °C whatever the sample; they were attributed to a loss of water. The absence of weight loss after 120 °C indicated that no drastic structural change occurred in the cements on heating. Fig. 6 gives the weight losses versus the age of the cements. No evidence of a correlation was found.

DSC analyses showed that both fresh and old cements presented one endotherm (Fig. 4a), which must be that of the trapped water departure as shown by the close correspondence with weight loss observed in the same temperature range by TGA (Fig. 4b). The ΔH evolved from $50\,\mathrm{J\,g^{-1}}$ for fresh cements to an average value of $160\,\mathrm{J\,g^{-1}}$ for old cements. This fact implies that there is an increase in water content between freshly-set cements and old ones, as we had already observed for zinc phosphate cements [10]. Plotting

TABLE II Main i.r. absorption bands for zinc polycarboxylate cements

$\nu(\mathrm{cm^{-1}})^a$	Vibration		Peak number[b]
3420	$\nu(H_2O)$	Water	1
2930	$\nu_{as}(CH_2)$	Asymmetric C–H stretch	2
2850	$\nu_s(CH_2)$	Symmetric C–H stretch	3
1590	$\nu_{as}(CO_2)$	Asymmetric C–O stretch	4
1405	$\nu_s(CO_2)$	Symmetric C–O stretch	5
470	$\nu(ZnO)$	Zinc oxide	6

[a] Approximate wave numbers.
[b] Corresponds to Fig. 3.

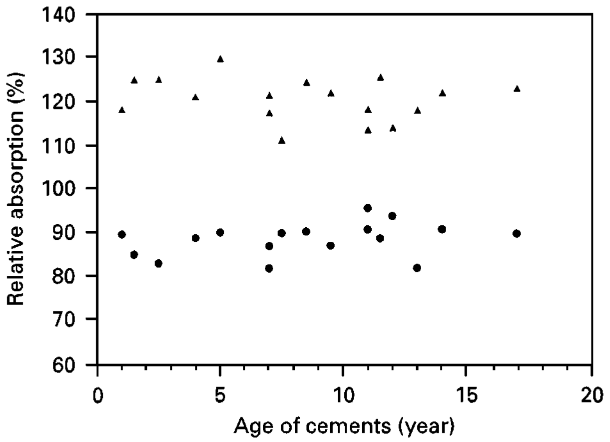

Figure 5 Relationship between the relative values of characteristic i.r. absorption bands of (▲) water, $\nu(H_2O)$, and (●) carboxylate matrix, $\nu_{as}(CO_2^-)$, and the age of the cements. Relative values were obtained by dividing them by the $\nu(ZnO)$ absorption value, chosen as an internal reference for each sample, and taken as equal to 100%.

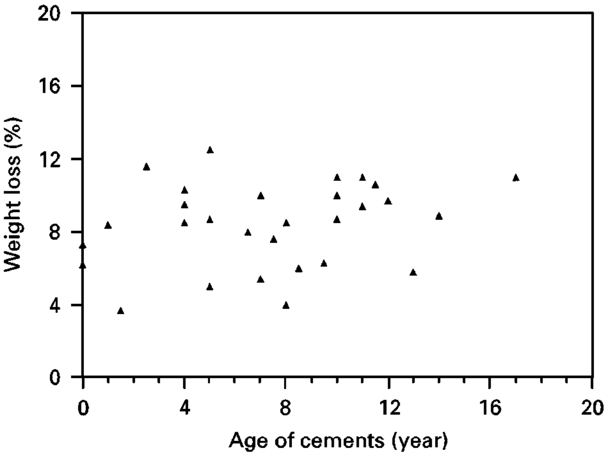

Figure 6 Relationship between the weight loss, as measured by TGA, and the age of the cements.

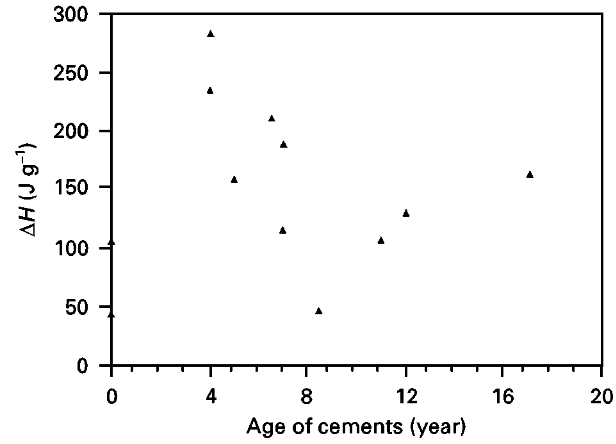

Figure 7 Relationship between the endotherm, ΔH, as measured by DSC, and the age of the cements.

the ΔH values of this endotherm versus the age of the cements (Fig. 7), no statistical relationship was observed. This long-term investigation shows that once the final water content is reached, it remains unchanged for years.

5. Conclusions

The present report illustrates the contribution of conventional structural analytical techniques to a better understanding of the *in vivo* behaviour of zinc polycarboxylate dental cements over a long period.

The fresh, 48-h-old, zinc polycarboxylate dental cements investigated mainly contained amorphous zinc polycarboxylate, unreacted zinc oxide and water. Old cements aged *in vivo* have a similar structure, but with a greater amount of water. The composition of the cements (unreacted zinc oxide, zinc polycarboxylate matrix and trapped water) is found to be independent of their age. So, zinc polycarboxylate dental cement is found to be chemically very stable over the time period investigated, namely, from one to 17 years.

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