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An infra-red spectroscopic study of the setting reactions of a calcium hydroxide dental cement

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An infra-red spectroscopic study of a proprietary calcium hydroxide cement based on l-methyl trimethylene disalicylate and calcium hydroxide shows that a chemical reaction occurs, in the cement paste, between the acidic phenol groups and calcium hydroxide. The close proximity of the carbonyl and hydroxyl groups leads to very strong intramolecular hydrogen bonding in the ester and bidentate chelation in the cement. This chemical reaction results in the setting and hardening of the cement.

1. Introduction

One of the important uses of cements in dental practice is as a protective base underneath a restoration in a deep cavity, where there is insufficient dentine to protect the pulpal tissues of the tooth. The cement serves to protect the pulp from toxic chemicals, thermal and mechanical shock, but also to sterilize carious dentine and promote the growth of secondary dentine. Traditionally the zinc oxide–eugenol cement has been used since it has good physical and anti-bacterial properties. However, it does not promote the growth of secondary dentine. In the past 15 years, cements have been introduced to overcome this disadvantage [1]; these are based on calcium hydroxide which stimulates the remineralisation of carious dentine and hence the formation of a dentinal bridge over exposed pulp [2, 3]. The effectiveness of these materials in sterilizing carious dentine has been examined [4].

Chemical studies on the system have been confined to a recently published infra-red spectroscopic examination [5] of the constituents of one of these materials, Dycal [6]. This study was initiated to obtain information on the mode of setting and structure of this particular calcium hydroxide cement. Changes in the consistency and, after set, the hardness of the cement paste were related to the underlying chemical processes, which were recorded using infra-red spectroscopy.

2. Experimental details

2.1. Materials

Samples of Dycal (L.D. Caulk Co) were supplied as "base" and "catalyst" pastes. For some studies, the active components were extracted from the pastes in order to simplify interpretation of the results.

2.2. Chemical studies on components of the cement

X-ray diffraction studies of the constituents of the "base" and "catalyst" pastes, and set cement were obtained with a generator (Phillips PW 1009) using cobalt $K\alpha$ radiation. Carbon-13 nuclear magnetic resonance (nmr) spectra of the deuterochloroform solutions of the constituents of the "base" and "catalyst" pastes were recorded with a JEOL PFT-100 spectrometer operating at 25.03 MHz. Chemical shifts are quoted with respect to tetramethylsilane. Infra-red spectra were recorded with a Perkin Elmer 621 spectrophotometer with transmission scale expansion up to × 2.

2.3. Chemical studies of the reaction

Cements were prepared at 23° C and 50% r.h. by mixing the "base" and "catalyst" pastes for 1 min. In these studies, it was necessary to reduce the clinical setting rate to accommodate instrumental measurement. This was partly accomplished by conducting experiments at 23° C, instead of the

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nominal mouth temperature, 37° C, and also by mixing the "base" and "catalyst" pastes at a ratio of 3 : 1 by weight instead of the recommended ratio of 1.18 : 1.

For the study of the setting reactions, the cement paste was quickly transferred to an attenuated total reflectance (ATR) cell, which was then placed in the spectrophotometer at an angle of incidence of 55°. The ATR cell was a RIIC Model TR 5 with a hemispherical KRS-5 crystal (Thallium bromide-iodide). The setting reactions were also studied in the transmission mode by placing a thin film of cement paste on a potassium bromide plate which was then placed in the spectrophotometer.

2.4. Measurement of consistency and hardness change

The setting times of the cement pastes were measured using an oscillating rheometer first applied to dental cements [7] by Plant *et al.* The setting time is defined as the time required from the start of mixing for the rheometer to show zero amplitude. The hardening reactions of the cement were monitored with a Wallace Microindentation Tester. Hardness measurements were made on cement discs (20 mm diameter × 1.5 mm thick) which were stored at 23° C and 50% r.h. From the Wallace indentation number (I), determined 15 sec after placing a 300 g load, the Woxen hardness number (WHN) was calculated using the equation

$$\text{WHN (MPa)} = 1.532 \times 10^6/I^2$$

3. Results

3.1. Chemical composition and structure of the cement components

The formulation of Dycal is based on a published patent [6] which indicates that the active components of the cement-forming reaction are calcium hydroxide and 1-methyl trimethylene disalicylate. The presence of calcium hydroxide as a major constituent and zinc oxide as a minor constituent of the "catalyst" paste was confirmed by X-ray diffraction analysis. The organic component was identified by infra-red and nmr spectroscopy as a mixture of ortho and para *N*-ethyl toluene sulphonamides.

The fillers contained in the "base" paste were identified by X-ray diffraction analysis as titanium dioxide, calcium sulphate and calcium tungstate. The presence of 1-methyl trimethylene disalicylate, together with methyl salicylate was confirmed by the carbon-13 nmr spectrum (Fig. 1) and the infra-red spectrum (Fig. 2) of the dichloromethane extract of the "base" paste. The carbon-13 nmr spectrum shows broadened peaks at 169.5 ppm and 112.1 ppm because of the different chemical shifts of the carbon nuclei in the two esters. The small peak at 51.9 ppm arises from the methyl group of the methyl salicylate.

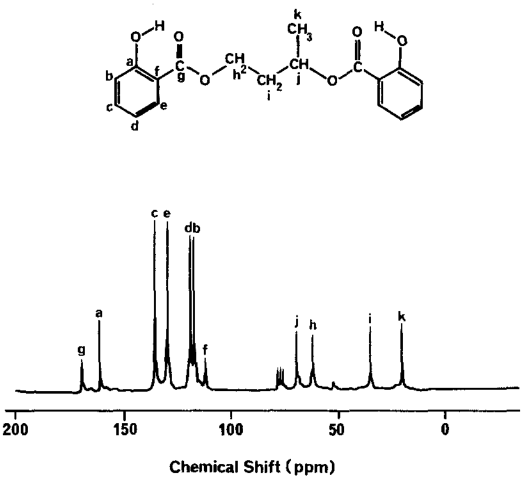

Figure 1 Carbon-13 nmr spectrum of the dichloromethane extract of the "base" paste of the Dycal cement.

3.2. Physical changes on cement formation

The setting time of Dycal cement was found to be 5 min at 23° C, when mixed at the recommended ratio for "base" : "catalyst" of 1.18 : 1 by weight. With the use of a "base" : "catalyst" ratio of 3 : 1 by weight, the setting time was extended to 8 min at 23° C to facilitate the recording of infra-red spectra of the setting cement paste. The development of hardness after set was recorded as the Woxen hardness number. Fig. 3 shows the development of hardness as the cement ages, and also the development of the optical density of the peak at 1540 cm^{-1} in the infra-red transmission spectrum of the cement. This peak shows significant changes during both the setting and hardening of the cement.

3.3. Infra-red spectroscopic changes on cement formation

The cement-forming reaction between "catalyst" and "base" pastes mixed in a ratio of 1 : 3 by weight was studied over a period of 5 days, following mixing, by the ATR technique. At this ratio, the infra-red spectrum of the cement paste before setting could be recorded. Spectra were also recorded in the transmission mode in order

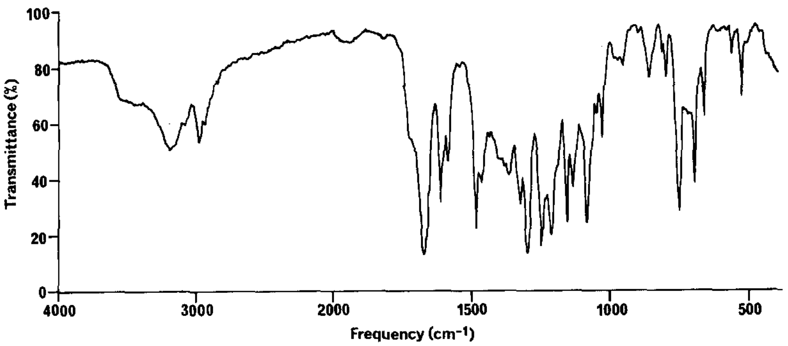

Figure 2 Infra-red spectrum of the dichloromethane extract of the "base" paste of the Dycal cement.

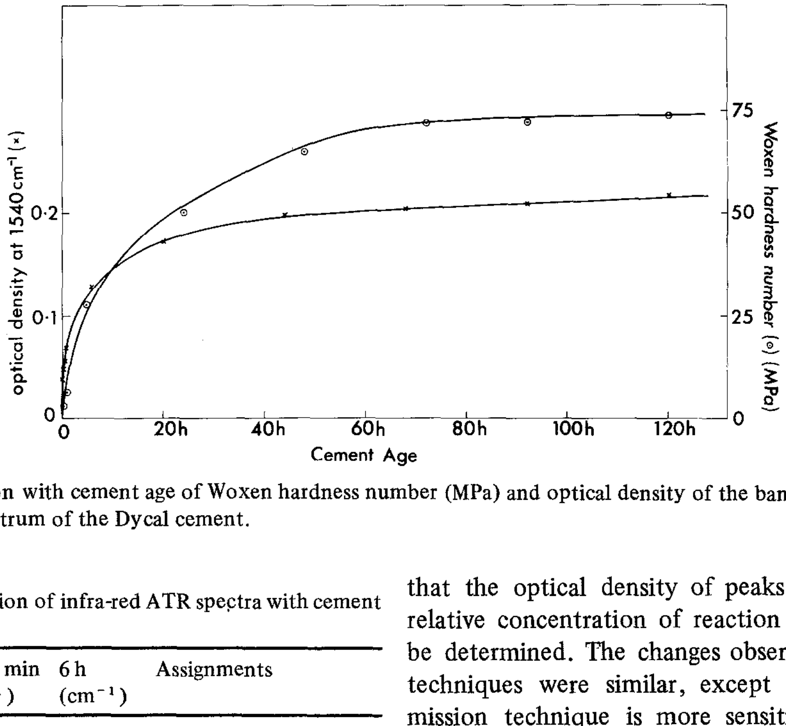

Figure 3 Variation with cement age of Woxen hardness number (MPa) and optical density of the band at 1540 cm^{-1}, in the infra-red spectrum of the Dycal cement.

TABLE I Variation of infra-red ATR spectra with cement formation

2–7 min (cm^{-1})	8–13 min (cm^{-1})	6 h (cm^{-1})	Assignments
1665 s	1660 s	1660 s	C=O stretch of ester
1612 m	1595 m	1595 m	Aromatic C–H bend
1590 w			
1535 w	1535 m	1535 m	Assymetric C–O stretch of chelate
1480 m	1480 w	1480 w	Aromatic C–H bend
1465 m	1465 m	1465 m	C–CH_2–C deformation and C–CH_3 bend
	1445 m	1445 m	
1380 w	1380 w	1380 w	Symmetric C–O stretch of chelate
1320 m	1320 m	1320 m	Ring stretch mode
1300 s	1300 sh		C.CO.O skeletal mode
1245 m	1250 w	1250 w	C–O stretch of ester
1210 s	1210 s	1210 s	O–H in-plane deformation and C–O stretch of chelate
720 sh			O–H out of plane deformation

s = strong, m = medium, w = weak, sh = shoulder.

that the optical density of peaks and hence the relative concentration of reaction products could be determined. The changes observed by the two techniques were similar, except that the transmission technique is more sensitive at 4000 to 2000 cm^{-1}. The significant ATR spectra are shown in Fig. 4, and the main spectral changes and assignments are listed in Table I. Comparison of the ATR and transmission spectra indicated that the reactions occurring at the surface and in the bulk cement were similar.

Model systems were examined by extracting the disalicylate with chloroform and mixing it at a powder–liquid ratio of 1:1 (g ml^{-1}). Fig 5 shows the spectrum of this set cement. A similar system was prepared, using zinc oxide instead of calcium hydroxide, but no cement formation occurred, and no changes were observed in the infra-red spectra to indicate a chemical reaction.

Interpretation of the spectra was simplified by comparison with the spectrum of the disalicylate

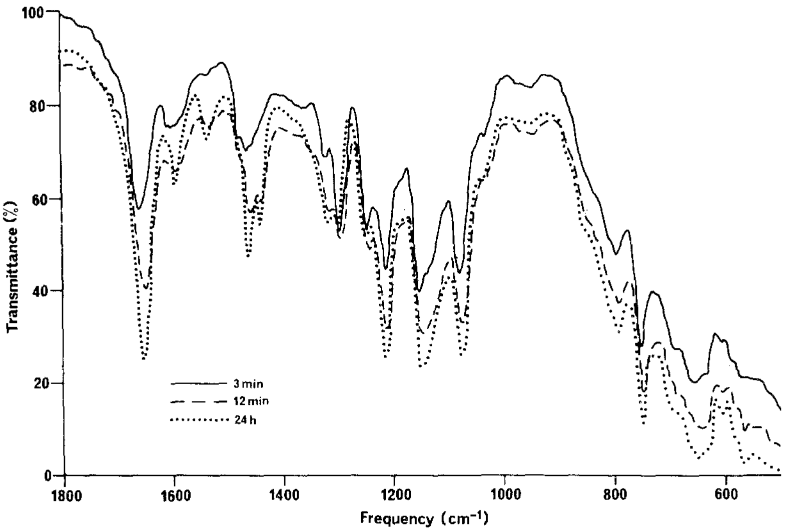

Figure 4 Infra-red ATR spectra of the setting Dycal cement ——— at 2 to 7 min, – – – – at 8 to 13 min, ... at 6 h.

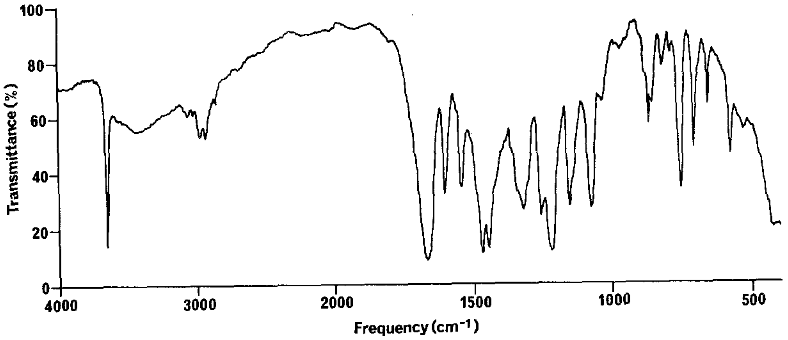

Figure 5 Infra-red transmission spectrum of a set model cement formed between calcium hydroxide and 1-methyl trimethylene disalicylate.

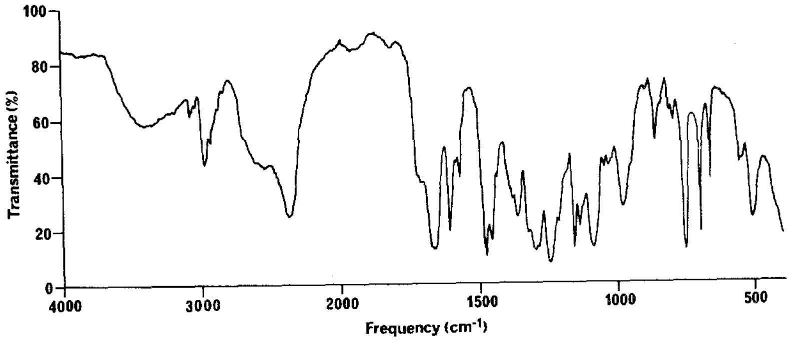

Figure 6 Infra-red spectrum of 1-methyl trimethylene disalicylate after deuteration.

TABLE II Main spectral differences between 1-methyltrimethylene disalicylate and the cement

Disalicyclate (cm^{-1})	Deuterated disalicylate (cm^{-1})	Cement (cm^{-1})	Assignments
	–	3655 s	O–H stretch in Ca(OH)$_2$
3440 w	2560 w	3440 m	O–H stretch, intermolecular hydrogen-bonded
3190 m	2380 s	3200 w	O–H stretch, intramolecular hydrogen-bonded
1725 sh	1725 sh	1725 w	C=O stretch of ester, intermolecular hydrogen-bonded
1675 s	1670 s	1670 s	C=O stretch of ester, intramolecular hydrogen-bonded
1615 s	1610 m	1600 m	Aromatic C–H bend
1585 m	1575 w		
–	–	1545 m	Asymmetric C–O stretch of chelate
1485 s	1480 s	1470 s	Aromatic C–H bend
1470 m	1460 m	1450 s	C–CH$_2$–C bend and C–CH$_3$ bend
1400 sh	–	–	Ring stretch mode coupled with O–H in plane deformation
1370 w	1370 w	1385 sh	C–CH$_3$ bend and symmetric C–O stretch of chelate
1325 m	1330 sh	1325 m	Ring stretch mode
1300 s	(1300 s 1290 sh)	1300 sh	C.CO.O skeletal mode of ester
1250 s	1250 s	1260 sh	C–O stretch of ester
1215 s	(1215 sh 985 m)	1225 s	O–H in plane deformation and C–O stretch of chelate
1140 m	1140 m	1145 sh	C.CO.O skeletal mode of ester
725 w	550 w	720 vw	O–H out of plane deformation

s = strong, m = medium, w = weak, sh = shoulder.

after deuteration (Fig. 6). Table II summarizes the main differences between the spectra of the ester, deuterated ester and the model calcium hydroxide cement.

4. Discussion

4.1. Structure of 1-methyl trimethylene disalicylate

The infra-red spectrum of the disalicylate shows that the O–H stretch band (3190 cm^{-1}) and the C–O stretch band (1675 cm^{-1}) are displaced from the normal frequencies of these groups because of very strong intramolecular hydrogen bonding referred to as conjugate chelation [8]. Evidence of this effect comes from a study of *n*-butyl salicylate [9] where the carbonyl band moves from 1675 cm^{-1} to 1723 cm^{-1} on acetylation of the hydroxyl group, and hence, removal of the intramolecular hydrogen bonding. The conjugate chelation arises from resonance between the ester and its enolised form (Fig. 7) and is favoured sterically by the close proximity of the phenolic proton to the carbonyl group. The appearance of a shoulder at 1725 cm^{-1} and a peak at 3440 cm^{-1} indicates that intermolecular hydrogen bonding also occurs. The predominance of intramolecular hydrogen bonding in salicylates is indicated by the low melting point of methyl salicylates (–8.6° C) compared with that of methyl 3-hydroxybenzoate (69° C), where only intermolecular hydrogen bonding can occur.

4.2. Chemistry of the setting reaction.

The essential cement-forming reaction in the Dycal cement is between calcium hydroxide and the disalicylate. This was demonstrated in model systems; thus, infra-red spectroscopy indicated that a simple calcium hydroxide powder, reacted chemically with the disalicylate liquid and formed a cement, whereas zinc oxide neither reacted with the ester nor formed a cement. Hence, the only role of zinc oxide in this cement system is that of an inert filler, although with other chelating agents, notably guaiacol and eugenol, cements are formed [10].

The infra-red spectrum of the setting Dycal

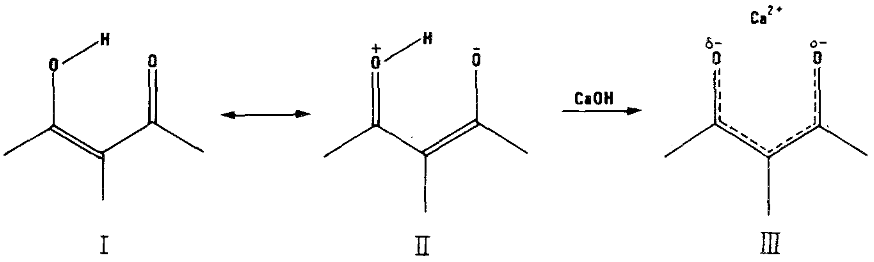

Figure 7 Structure of 1-methyl trimethylene disalicylate (I, II) and the cement formed with calcium hydroxide (III).

cement (Fig. 4) developed new bands at 1530–40 cm^{-1} and 1380 cm^{-1} which became prominent at the time of set (8 min). These bands were also found in the model calcium hydroxide–disalicylate cement (Fig. 5) and can be assigned respectively to the asymmetric and symmetric stretching frequences of the carbonyl group. Bands in these positions are found in metal-β-diketone complexes [11] and in metal polyacrylates [12].

Together with the development of the carbonyl bands at 1540 cm^{-1} and 1380 cm^{-1}, the transmission spectra of the setting cement also showed the diminution of the band at 3190 cm^{-1} because of the loss of hydroxyl groups, when the cement set. The development of chelate formation which was monitored from the optical density at 1540 cm^{-1}, was related to the development of hardness after the cement had set. Fig. 2 shows that both chelate formation and hardness develop rapidly in the first day following cement preparation. Thereafter, both continue to increase but more slowly. This correlation, together with the results of the study of the model systems provide ample evidence that the setting and hardening of this cement results from the formation of a calcium chelate.

4.3. Infra-red spectroscopic changes on cement formation

The decrease in intensity of the hydroxyl band at 3190 cm^{-1} and the appearance of asymmetric and symmetric carbonyl bands indicates that both groups participate in the chelation of calcium ions (Fig. 7). Further evidence of the role of the phenolic hydroxyl groups in chelation is more difficult to elucidate because of overlapping peaks, especially in the region 1200 to 1400 cm^{-1}. In the spectrum of eugenol [10] the O–H in-plane deformation occurs at 1210 to 1215 cm^{-1} but the infra-red spectrum of the 1-methyl trimethylene disalicylate shows several bands at 1200 to 1300 cm^{-1}. Nevertheless, the spectrum of the deuterated ester does indicate that the band at 1215 cm^{-1} becomes very weak in intensity and a new band at 985 cm^{-1} is observable consistent with its assignment as the O–H in-plane deformation band. On cement formation this band does not increase in intensity but, instead, broadens. A possible explanation is that the band arises from the C–O stretching mode in the cement and is displaced from 1250 cm^{-1} where it occurs in the ester. Thus, although cement formation results in a reduction of intensity at 1210 to 1215 cm^{-1} because of the removal of hydroxyl groups, this reduction may be compensated by the displacement of the C–O mode.

The weak band observed at 725 to 720 cm^{-1} in the spectrum of the ester has been assigned previously in a study of salicylates to the O–H out-of-plane deformation [13]. Evidence for this assignment arises from the displacement of the peak to 550 cm^{-1} in the spectrum of the deuterated disalicylate. The decreased intensity of the peak at 720 cm^{-1} on cement formation confirms the role of the hydroxyl groups in chelation of calcium ions.

Other changes in the infra-red spectra of the setting cement are not clearly related to the chelation by the hydroxyl and carboxyl groups of the ester. In phenols, a band observed at 1370 cm^{-1} has been assigned to a ring-stretching mode which couples with the O–H in-plane deformation mode [14], but on deuteration, coupling no longer occurs and the ring-stretching mode is displaced to 1320 to 1330 cm^{-1}. The spectrum of the disalicylate did show a broad band at 1400 cm^{-1} which was removed on deuteration, but since a strong band is already present at 1325 cm^{-1}, it is not clear if the band had moved. However, the ATR spectra of the setting cement does clearly indicate the increased intensity of a band at 1320 cm^{-1}, possibly because of the removal of the coupling effect. Comparison of the transmission spectra of the ester and set cement shows that cement formation is accompanied by a decrease in the intensity of the band at 1300 cm^{-1}. Katritsky *et al.* [15] have assigned this peak together with a peak at 1250 cm^{-1} to skeletal modes of the C.CO.O group in salicylates. A third skeletal mode is observed at 1173 cm^{-1} in ethyl salicylate, but, in the spectrum of 1-methyl trimethylene disalicylate, this band is observed at 1140 to 1145 cm^{-1}. There is evidence of a shoulder at 1260 cm^{-1} in the spectrum of the set cement, possibly because of the displacement of this mode from 1300 cm^{-1}, on formation of the calcium chelate.

4.4. Cement structure

Although calcium hydroxide may be consumed in the cement-forming reaction, the occurrence of the sharp O–H peak at 3655 cm^{-1} in the spectrum of the cement, shows that unreacted calcium hydroxide remains. The X-ray diffraction pattern of the simple calcium hydroxide–disalicylate cement confirms the presence of unreacted calcium hydroxide. The absence of any new lines in the diffraction pattern of the cement indicates that amorphous material is formed in the reaction.

In the set cement, the divalent calcium ions are likely to be chelated by two disalicylate molecules and hence act as bridging units between the difunctional ester molecules, to form a chain structure. Unlike the zinc oxide–eugenol cements, where water may be necessary to link zinc eugenolate molecules [1], the role of the water produced in these cements is unclear. It is probable that water hydrates the calcium ions and may be important in forming the three-dimensional cement structure. Other calcium hydroxide cements based on salicylate esters are now being investigated to ascertain the importance of the ester structure on cement formation.

5. Conclusions

Analysis of the calcium hydroxide cement, Dycal, confirmed that calcium hydroxide and 1-methyl trimethylene disalicylate are the main components of the cement. Very strong intramolecular hydrogen bonding occurs between the phenolic hydroxyl group and the carbonyl group of the ester. Cement formation occurs as calcium ions replace the acidic phenolic protons to yield a chelate structure with the bidentate ester ligand. The calcium ions can cross-link the difunctional ester molecules to form a chain structure, which can be regarded as a type of ionic polymer [16]. The reaction continues after set and hardness develops as chelate formation continues. The set cement contains amorphous calcium-disalicylate salt, together with unreacted calcium hydroxide which is available to sterilize dentine and effect remineralization.

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