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Characterisation of a remineralising Glass Carbomer[®] ionomer cement by MAS-NMR Spectroscopy

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ABSTRACT

Objectives. The purpose of this study was to characterize commercial glass polyalkenoate cement (GPC) or glass ionomer cement (GIC), Glass Carbomer[®], which is designed to promote remineralization to fluorapatite (FAP) in the mouth. The setting reaction of the cement was followed using magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. **Methods.** Glass Carbomer[®] initial glass powder and cements were subjected to ²⁷Al, ³¹P, ¹⁹F and ²⁹Si MAS-NMR analysis. X-ray powder diffraction (XRD) was employed to determine the presence of crystalline phases.

Results. ²⁷Al MAS-NMR showed the Al to be predominantly four coordinate, Al(IV), and the presence of Al–O–P species in the glass. The proportion of Al(IV) was reduced with setting reaction of the cement and significant amount of six coordinate Al, Al(VI), was found in the cement. The ³¹P MAS-NMR spectra showed clearly a decrease of the orthophosphate peak of apatite on initial setting. ¹⁹F MAS-NMR showed only a small fraction of FAP. ²⁹Si MAS-NMR demonstrated the presence of largely Q⁴(2Al) in the glass which changed only little in the aged cement.

Significance. This study also demonstrated how the setting reaction in Glass Carbomer[®] cement and other GICs can be followed by ²⁷Al MAS-NMR examining the conversion of Al(IV) to Al(VI). Our data revealed that the apatite in this cement was not FAP but largely hydroxyapatite, which was partially consumed during the cement formation.

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1. Introduction

The perfect restorative filling material would be the one that can degrade in the mouth and be replaced by natural tooth enamel and dentin. Such an ideal material does not yet exist, however two previous studies indicate that some commercial glass polyalkenoate or ionomer cements (GPCs/GICs) made headway toward this goal and are capable of remineralizing

in the mouth to apatite [1,2]. It is worth noting that the two commercial cements, Fuji IX and Ketac Molar, that have been shown to promote remineralization in the mouth are based on glasses that can either have orthophosphate phases that are similar to hydroxyapatite (HAP) or crystallize to fluorapatite (FAP) [3,4]. Previous studies showed that glasses containing phosphate crystallize to apatite [5–10]. In the case of Fuji IX, it crystallizes to strontium FAP. The remineralization process in the mouth may be aided, not only by the presence of fluoride,

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but also by the presence of strontium in the glass. Strontium has a known synergistic effect in the conjunction with fluoride on the apatite mineralization [11]. The Sr^{2+} cation has a very similar ionic size to Ca^{2+} and exhibits complete solid solution phase behavior with calcium in apatite crystal lattices [12,13].

Glass Carbomer[®] is a relatively new commercially available GIC used as a restorative filling material and fissure sealant that is designed to deliberately remineralize in the mouth. Glass Carbomer[®] is claimed to contain nanocrystals of calcium FAp, which can act as nuclei for the remineralization process and initiate the formation of FAp. The glass has a much finer particle size compared to conventional GICs [2,14] which is thought to aid its dissolution and ultimate conversion to FAp.

Addition of HAp and FAp are also reported to enhance the mechanical properties of the GICs [14,15]. However, the influence of FAp on the mechanical properties is not fully understood.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy is a powerful technique that probes coordination states and gives information on chemical bonding and next nearest neighbors. It is particularly suitable for investigating the structure of the amorphous glasses and cements. One of the earliest study was done by Matsuya et al. [16,17] where they used ^{29}Si , ^{31}P and ^{27}Al MAS-NMR to follow and characterize the setting reaction of GIC. They observed the conversion of Al with tetrahedral or four-fold coordination in the glass, Al(IV), to the Al ions with six-fold coordination, Al(VI), the species that crosslinks the cement matrix. Repolymerization of silicate network during glass degradation and cement formation was also observed by ^{29}Si MAS-NMR. More recent work by Pires et al. [18,19] and Stamboulis et al. [3,20] also used the same technique to investigate the setting chemistry of the GICs. Recently, we [21,22] have carried out ^{27}Al MAS-NMR at much higher magnetic field (14.1 T) than used in previous studies, which has enabled quantitative measurements and the ability to study the kinetics of the setting reaction of the cements by following the ratio of Al(IV) to Al(VI).

In the present study, the Glass Carbomer[®] glass is characterized and the setting reaction of Glass Carbomer[®] cements aged from 5 min to 10 months is followed by using ^{29}Si , ^{31}P , ^{19}F and ^{27}Al MAS-NMR spectroscopy.

2. Materials and methods

2.1. Cement preparation

Commercial Glass Carbomer[®] capsules for filling applications were provided by GCP Dental, Netherlands. The untreated glass in granular form and FAp in powder form were additionally provided by the First Scientific (GmbH Germany). The chemical composition of the commercial glass powder was analyzed at the Ceram Research Limited (Stoke-on-Trent, England) using the X-ray fluorescence spectroscopy. The cement capsules were activated and mixed in a mixer for 10–15 s. No heating via the light gun was applied to accelerate the setting. The cement was placed into a disc mold, clamped and allowed to set for 1 h at 37 °C. The termination of setting reaction was done by the method described by Matsuya et al.

[17]. The samples of the cement with aging time less than 1 h were quenched into liquid nitrogen and then dehydrated with ethanol. Cement specimens with aging time greater than 1 h were demoulded and placed into deionized water at 37 °C for the appropriate time prior to termination of the reaction by using the above method. This was done to prevent dehydration at longer setting times. The cements were then ground to a fine powder in an agate pestle and mortar prior to MAS-NMR spectroscopy.

2.2. X-ray diffraction

X-ray diffraction (XRD) was performed on Philips Powder Diffractometer with a copper ($\text{Cu K}\alpha$) X-ray source (Philips PW 1700 series diffractometer, Leiden, Netherlands). The powder samples (<45 μm particle size) were scanned between $2\theta = 10\text{--}80^\circ$ with a step size of $2\theta = 0.04^\circ$.

2.3. MAS-NMR spectroscopy

The sample powders were packed in 4 mm zirconia rotor and sealed with Kel-F cap. MAS-NMR analyses were conducted on ^{29}Si , ^{31}P and ^{19}F nuclei at resonance frequencies of 39.8, 81.0 and 188.3 MHz, respectively, using FT-NMR spectrometer (AM-200, Bruker, Germany). Spinning rates of the samples at the magic angle were 5 kHz for ^{29}Si , ^{31}P and 10–12 kHz for ^{19}F MAS-NMR. Recycle times were 2–10 s for ^{29}Si , ^{31}P and 1–120 s for ^{19}F MAS-NMR depending on the nature of the sample. Background subtraction was performed on the ^{19}F MAS-NMR. Reference materials for chemical shift (in ppm) were polydimethylsilane for ^{29}Si , 85% H_3PO_4 for ^{31}P and CaF_2 for ^{19}F .

^{27}Al MAS-NMR spectroscopy measurements were conducted at resonance frequency of 156.3 MHz using a higher magnetic field (14.1 T) on a 600 MHz Bruker FT-NMR spectrometer. The recycle time was 1 second with spinning rate of 10–15 kHz. The short rf pulse of 0.3 μs corresponding to the $\pi/12$ magnetization tip angle has been used. The spectra were referenced to 0 ppm of 1 M AlCl_3 solution. In order to follow the setting reaction of the cements, the deconvolution of the ^{27}Al MAS-NMR spectra was conducted using *dmfit* software [23]. This was carried out assuming a Gaussian curve to model the peak shape.

3. Results

The chemical composition of the initial Glass Carbomer[®] glass was determined by X-ray fluorescence technique and is given in Table 1. The analysis showed that the Glass Carbomer[®] glass has higher amount of silica and fluorine and is lower in alkali oxides and phosphorus than many experimental ionomer glasses studied to date [3,17–21].

Fig. 1 shows the XRD pattern for Glass Carbomer[®] glass and FAp. The glass had a broad halo which is indicative of the amorphous nature of the glass phase and the FAp showed sharp lines characteristic of a crystalline phase. The diffraction pattern of the FAp sample matched both calcium HAp and calcium FAp. It is impossible to distinguish these two apatites by XRD because of their almost identical lattice parameters.

Table 1 – The composition of Glass Carbomer® glass (initial glass powder) in Mol%.

| Components | SiO ₂ | Al ₂ O ₃ | P ₂ O ₅ | SrF ₂ | CaF ₂ | NaF | ZnO | BaO |
|------------|------------------|--------------------------------|-------------------------------|------------------|------------------|-----|-----|-----|
| Mol% | 54.6 | 20.0 | 3.2 | 11.9 | 4.1 | 5.4 | 0.7 | 0.2 |

Fig. 2(a) shows the ²⁹Si MAS-NMR spectra for Glass Carbomer® cements at different aging times together with the original glass. There was one major peak at –97.0 ppm in the original glass, which was attributed to Q⁴(2Al) species. As the setting reaction proceeded to 3 months, the chemical shift of the peak moved slightly to a more negative value at –100.8 ppm. This peak can be assigned as a mixture of Q⁴(2Al) and Q⁴(1Al) species.

The ³¹P MAS-NMR spectra for Glass Carbomer® cements, its original glass and FAp are shown in Fig. 2(b) for comparison purposes. The original glass had a single broad peak at around –10.7 ppm, which was assigned to a mixture of pyrophosphate species Q¹ and phosphate species connected to Al with Al–O–P linkages. In this moiety the Al is connected to phosphorus via the bridging oxygen and therefore is still a Q¹ species. For the Glass Carbomer® capsules, which contained a non-reacted mixture of the glass and FAp, the ³¹P signal shifted to a more negative chemical shift at –16.0 ppm. There was an additional sharp peak at 3.1 ppm that was assigned to a crystalline calcium orthophosphate environment or apatite. During the setting reaction, the center of gravity of the signal moved from –16.0 ppm in the glass to a more positive value at –11.0 ppm after 10 months aging time in the cement with the simultaneous decrease in the linewidth. It was also found that the intensity of apatite signal decreased with time.

Fig. 3(a) illustrates the ¹⁹F MAS-NMR for Glass Carbomer® cements, its original glass and FAp. The glass had a peak at –142.7 ppm which can be assigned Al–F–Ca/Sr(n). However, the peak shifted to a more negative value at –150.0 ppm for

the mixture of glass and FAp in the Glass Carbomer® capsules. Both glasses had two other peaks at around –90.0 to –100.0 ppm which can be assigned as F–Ca(n) or F–Sr(n) sites and at –187.0 ppm for Al–F–Na(n). There is no significant sharp peak of the F–Ca(3) in FAp at around –103.0 ppm even before the mixture in the capsule being activated.

The ²⁷Al MAS-NMR spectra of Glass Carbomer® cements from 5 min to 10 months aging time and its original glass are shown in Fig. 3(b). The original glass showed one major peak at 50.0 ppm which was assigned as Al(IV). Two other peaks at –0.4 ppm and a broad shoulder at around 30.0 ppm which were assigned as Al(VI) and Al(V), respectively. For glass with FAp in the capsule, an additional peak appeared at 15.0 ppm which was assigned as ‘unknown species’. The ²⁷Al MAS-NMR spectra and their assignment are similar to the reported previously in [18,22] for the commercial glass ionomer cements. In these reports the identification of the several aluminum species has been confirmed by two-dimensional ²⁷Al 3QMAS NMR data. The intensity of Al(VI) increased with increasing aging time and became more intense than Al(IV) after 1–6 h aging time. There were two sites of Al(VI) in most of the aged cements and the shift for Al(IV) moved to a more positive value at around 54.0 ppm in the cement at 10 months aging time.

The setting reaction was followed by taking the ratio of Al(VI)/(Al(IV)+Al(V)). Fig. 4 shows the ratio of Al(VI)/Al(IV)+Al(V) estimated from the deconvolution data for Glass Carbomer® cements and the original glass. The deconvolution was done using Gaussian lineshapes assuming that the quadrupolar coupling constant for the individual

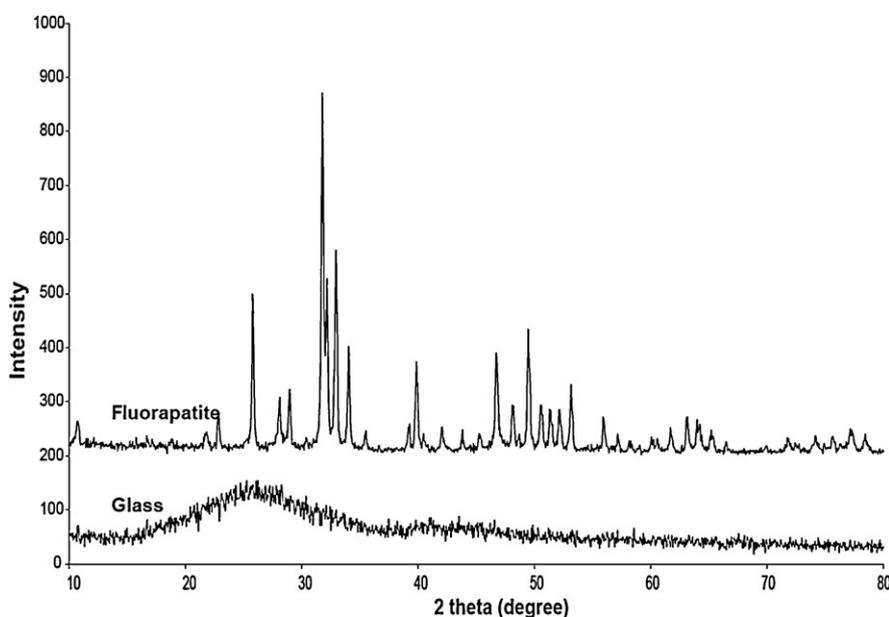


Fig. 1 – XRD patterns for Glass Carbomer® glass and FAp. The lines for FAp sample match with HAp (reference code: 01-086-1199) and FAp (reference code: 01-073-1727).

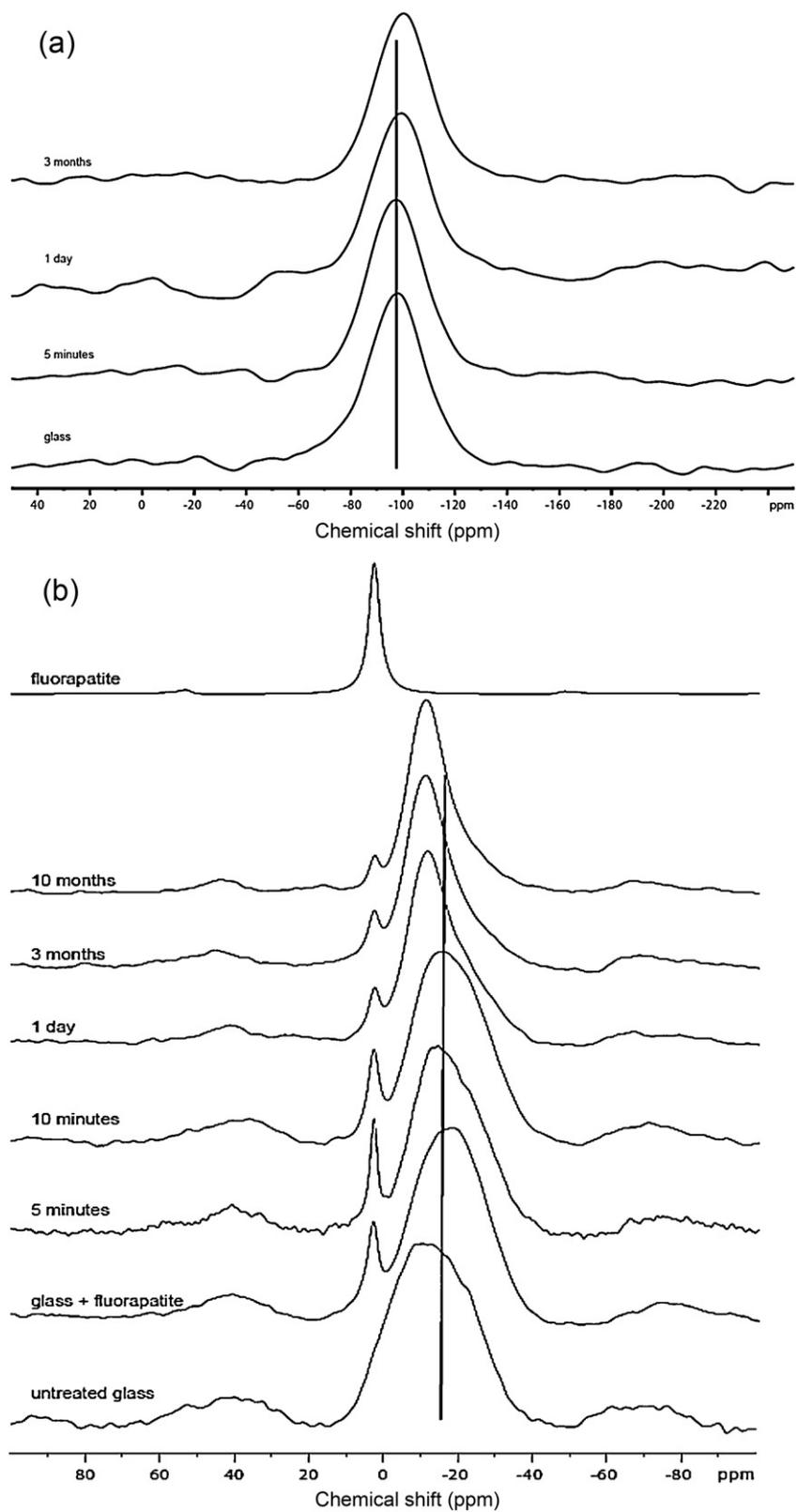


Fig. 2 – (a) ^{29}Si MAS-NMR spectra for Glass Carbomer[®] cements from 5 min to 3 months setting time and untreated glass. (b) ^{31}P MAS-NMR spectra for Glass Carbomer[®] cements from 5 min to 10 months setting time, untreated glass and FAp. The vertical lines are a guide to eye only.

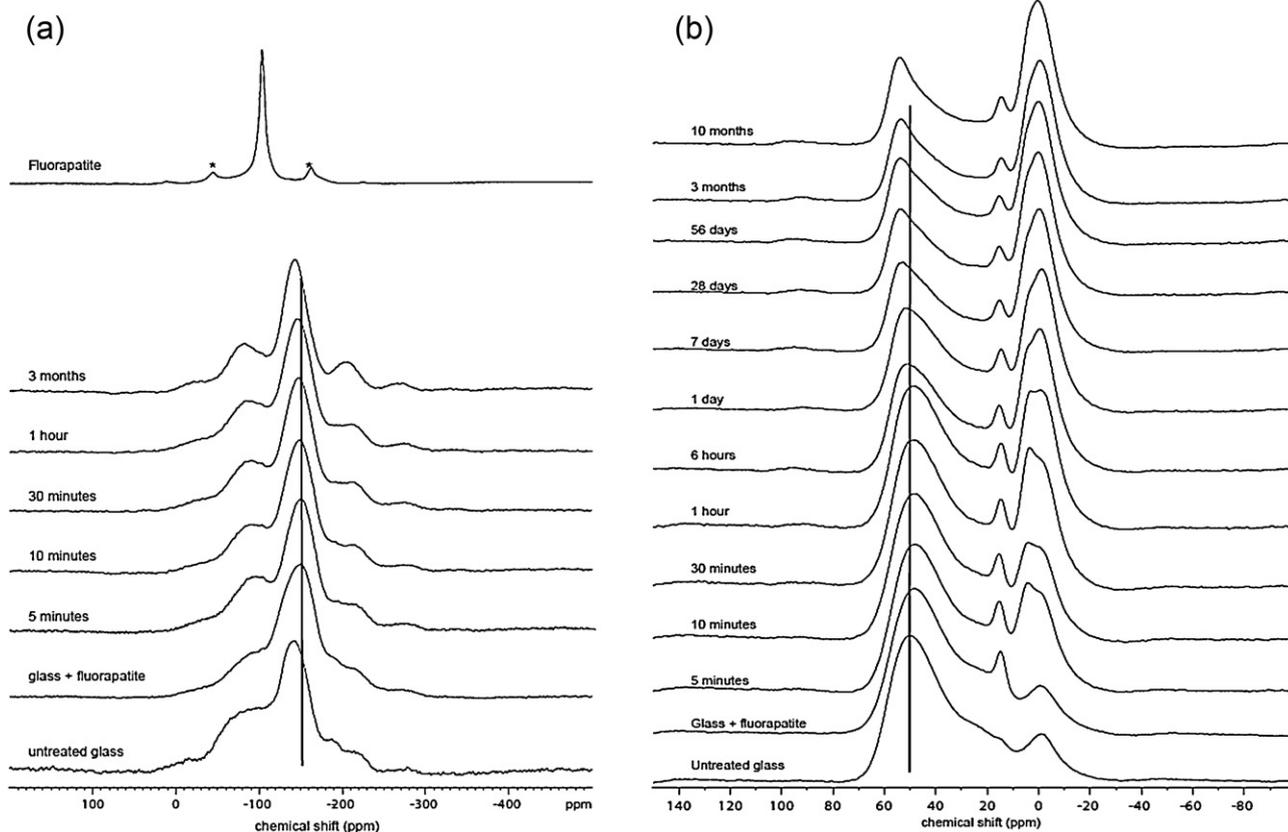


Fig. 3 – (a) ^{19}F MAS-NMR spectroscopy for Glass Carbomer[®] cements at 5 min to 3 months setting time, its untreated glass and FAp. (b) ^{27}Al MAS-NMR spectra for Glass Carbomer[®] cements from 5 min to 10 months setting time, glass in capsule and untreated glass. The spinning sidebands are indicated by asterisks and the vertical lines are a guide to eye only.

aluminum sites does not exceed 5 MHz and the integral intensities from the ^{27}Al MAS-NMR spectra taken at this relatively high medium field could be quantified.

4. Discussion

In this study, the setting reaction of the Glass Carbomer[®] was followed by using MAS-NMR spectroscopy. During the formation of GIC, the polyacrylic acid (PAA) attacks the glass, causing partial dissolution and ions such as Al^{3+} , Ca^{2+} and F^- are released [24]. In the glass, the Al^{3+} ions predominantly exist as Al(IV) which accommodate the tetrahedral silicate network of the glass. However, during the formation of the cement, these Al^{3+} cations switch the coordination from Al(IV) to Al(VI) [25] as they become co-ordinated to the carboxylate groups of the polymer, PAA. The silicate network of a residual glass undergoes repolymerization as the number of Al(IV) around Si decreases during the setting reaction [16,17,19].

The ^{29}Si MAS-NMR spectrum for the Glass Carbomer[®] glass showed a single broad peak of $\text{Q}^4(2\text{Al})$ species. This represents four bridging oxygens and two Al atoms connected to a SiO_4 tetrahedron. From the chemical composition of the glass, it showed that the glass has relatively small amount of network modifying oxides and thus there are no non-bridging oxygens (NBOs) in the Si network. The transformation of $\text{Q}^4(2\text{Al})$ species in the glass to a mixture of $\text{Q}^4(2\text{Al})$ and $\text{Q}^4(1\text{Al})$ in the

cements showed that during the setting reaction, the Al ions are released from the aluminosilicate network in the glass and hence decreased the number of Al ions in the glass network. In addition, the ^{29}Si MAS-NMR for Glass Carbomer[®] cements demonstrated a slightly different trend compared to the previously studied experimental and commercial GICs [3,17–20]. Glass Carbomer[®] gave a sharper, more symmetric ^{29}Si NMR peak whereas previously studied cements showed

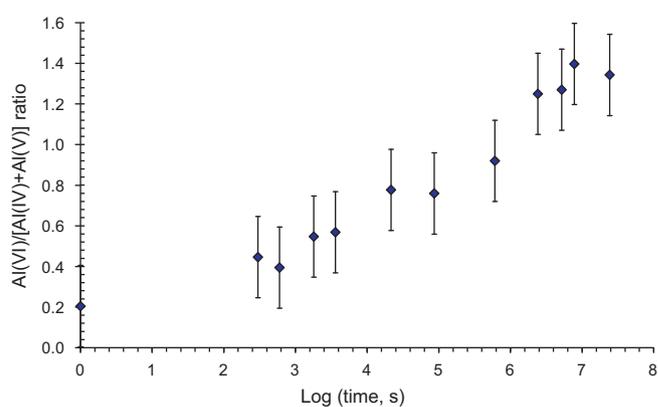


Fig. 4 – Ratio of $\text{Al(VI)}/[\text{Al(IV)} + \text{Al(V)}]$ plotted against logarithm of the aging time for Glass Carbomer[®] cements and original glass. The setting reaction continues up to 10 months.

an asymmetric peak even at early times of setting reaction. This could be due to the lower amount of Al and lack of NBOs in Glass Carbomer® glass.

The ^{31}P MAS-NMR for Glass Carbomer® glass showed broad peak in the pyrophosphate region (Fig. 2(b)). The chemical shift was more negative and broader compared to the previously studied glasses [20,26]. This suggests that the peak contains more than one species. The chemical composition of Glass Carbomer® (Table 1) shows that apart from Na^+ , Sr^{2+} and Ca^{2+} cations, there are also small amount of Zn^{2+} and Ba^{2+} in the glass. Consequently, there is possibility of mixed cations charge balancing the pyrophosphate environments in the Glass Carbomer® glass. There is also possibility of having a small amount of Q^2 phosphorus sites (metaphosphate species) because of the low concentration of alkali cations available to promote the formation of orthophosphate, PO_4^{3-} .

In commercial GPCs, a surface of initial glass powder is often pretreated by acid, i.e. undergoes acid washing, to decrease the surface reactivity of the glass and control the setting characteristics [27]. This could explain the shift in the untreated glass mixed with FAp to a more negative chemical shift at -16.0 ppm in the Glass Carbomer® capsule compared to the original glass. A possible explanation for this is that the pre-treatment of the glass decreases the amount of cations available to charge balance the Al-O-PO_3^{3-} . This will cause the polymerization of the PO_4 groups with Al to form $\text{Al-O-PO}_2^{2-}\text{-O-Al}$ species. Dollase et al. [28] reported that the chemical shift of ^{31}P MAS-NMR for solid solution of $\text{Na}_3\text{PO}_4\text{-AlPO}_4$ moved to a more negative value with increasing number of Al around the PO_4 tetrahedron.

The pyrophosphate peak moved to a more positive value with increasing aging time and reached -11.0 ppm after 10 months aging time. This trend is similar to previous studies [20,26], which showed a peak between -8.0 and -9.0 ppm after setting. It is unclear what type of the phosphorus environment is in the final cement due to severe overlapping of non-resolved signals. Some of the Al-O-P and P-O-P bonds in the glass could be consumed during the acid attack. Moreover, the ^{31}P signal also became narrower with increasing the aging time, which suggests that the cement has a more ordered environment. This peak is slightly asymmetric on the right side, which suggests that the Q^2 phosphate may not be involved in the setting reaction.

The ^{19}F MAS-NMR of the original and pre-treated glasses revealed the existence of $\text{Al-F-Ca/Sr}(n)$ species which represent the AlO_3F^- species locally charge balanced either by Ca^{2+} or Sr^{2+} . There is also a peak at -187.0 ppm which assigned to $\text{Al-F-Na}(n)$. The formation of $\text{Al-F-Na}(n)$ species has been observed previously in commercial GICs [3]. The ^{19}F MAS-NMR spectra for Glass Carbomer® cements showed that the intensity of $\text{F-Ca/Sr}(n)$ species decreased and $\text{Al-F-Na}(n)$ species disappeared with increasing aging time.

According to the manufacturer, there is approximately 20% of FAp added to the glass powder [29], which would be expected to give a sharp peak at -103 ppm in ^{19}F MAS-NMR. However, there is only a very small peak of FAp in the Glass Carbomer® capsule observed in this study. Compared to the ^{19}F MAS-NMR of the FAp obtained from the manufacturer, there was a very sharp peak of $\text{F-Ca}(3)$ of FAp at -103.0 ppm.

A combination data of XRD, ^{31}P and ^{19}F MAS-NMR would give a better explanation why the FAp in the Glass Carbomer® capsule has a distinct orthophosphate peak in the ^{31}P MAS-NMR but not a well-defined peak in the ^{19}F MAS-NMR. It is because either the FAp added is a solid solution of FAp and HAp, or it is physical mixture of FAp and HAp. However, the FAp sample in this study gave a sharp peak of $\text{F-Ca}(3)$ in ^{19}F MAS-NMR spectrum. This sharp peak suggested that the FAp added to Glass Carbomer® glass is in fact a mixture of FAp and HAp. If this was a solid solution of FAp and HAp, the ^{19}F MAS-NMR will be broadened because of the disordered fluorine environment.

The fact that Glass Carbomer® contains a mixture of FAp and HAp can explain the decrease in the intensity of the orthophosphate peak in ^{31}P MAS-NMR. HAp is basic and can react with PAA to form calcium salt of polyacrylic acid. In contrast, FAp is more resistant to acid and would react to a smaller extent with PAA. A study by Moshaverinia et al. [15] reported that the incorporation of HAp and FAp to GPCs enhanced the mechanical properties of the cements. They suggested that during the setting reaction the HAp and FAp involved in the acid-base reaction via their phosphate and calcium ions. The results here support the view that HAp participates in the setting reaction.

As the setting reaction proceeds, the surface of the glass will be modified as the Al(IV) released to the cement matrix to form Al(VI) . In addition to these peaks there is a small peak at around 15.0 ppm (Fig. 3(b)), which is assigned as 'unknown species' in the untreated glass. Interestingly, this 'unknown species' becomes significantly sharper in the glass with FAp in the capsule, which is believed to be due to the acid pre-treatment of the glass. The 'unknown species' is also present in a large number of the GICs investigated previously [3,21,22].

The intensity of Al(VI) peak increased and became higher than the Al(IV) peak with increasing aging time. Two sites of Al(VI) were observed from the ^{27}Al MAS-NMR in the Glass Carbomer® cement (Fig. 3(b)). Similarly, two sites of Al(VI) have been observed in cements containing (+) tartaric acid [19]. The intensities of these two Al(VI) sites grow at different rates. The one with more positive chemical shift grows more rapidly at early aging times while the other site with more negative chemical shift starts growing at longer aging times. The Al(VI) with more positive chemical shift may correspond to an Al(VI) tartarate/polyacrylate species, which is thought to form earlier in the cement reaction whereas the Al(VI) with more negative chemical shift may correspond to the formation of Al(VI) polyacrylate.

The chemical shift of Al(IV) moved to a more positive value at around 54.0 ppm in the 10 months cement. There are two factors that can influence the chemical shift of Al, the Al:Si [30] and the Al:P [31] ratios. Decreasing the Al:Si ratios causes shift of the Al(IV) resonance toward 0 ppm (less positive). However, the movement of Al(IV) peak to a more positive chemical shift may be due to decrease in Al-O-P linkages with time. The Al(IV) peak became narrower with aging time, which suggests the existence of a second Al(IV) site in the degraded glass. Similar finding has been reported by Pires et al. [19] where they described the presence of second sites of Al(IV) as a result of modification of the surface layer during the acid attack.

The conversion of Al(IV) to Al(VI) continues linearly with the logarithm aging time period studied (Fig. 4). This suggests that the reaction in terms of ratio between different aluminum species is still taking place up to 10 months of the aging time.

5. Conclusions

The setting reaction in Glass Carbomer® cement was followed by multinuclear ^{27}Al , ^{31}P , ^{19}F and ^{29}Si MAS-NMR. The conversion of the Al(IV) into Al(VI) is well approximated by a linear function of logarithm of aging time. At least two different Al(VI) species formed as a result of the cement formation. The data showed that secondary setting reaction still continues up to 10 months. Combination of the ^{27}Al and ^{31}P MAS-NMR data indicates presence of the Al–O–P linkages in the initial glass. The acid pre-washing of the glass powder is thought to affect the formation of the surface species and also alter the amount of Al–O–P linkages per phosphorus. Presence of the apatite was monitored during the acid–base reaction. This study suggested that the apatite in Glass Carbomer® is a mixture of HAp and FAp. Although the ^{31}P MAS-NMR showed a significant amount of apatite, the ^{19}F MAS-NMR revealed that only a small amount of F–Ca(3) in Glass Carbomer®. This is also supported by looking at the decrease in intensity of apatite peak in ^{31}P MAS-NMR. The HAp was partially consumed during the setting reaction. Consequently, smaller amount of apatite is available for remineralization process. The absence of sharp peak of F–Ca(3) of FAp after 10 months aging time in ^{19}F MAS-NMR suggested that FAp did not promote the nucleation of apatite. However, the presence of some fraction of apatite after 10 months aging time in the cement from ^{31}P MAS-NMR data showed that it may be available for nucleating the remineralization process at longer aging time.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dental.2012.06.011.

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Introduction

What is Glass Carbomer® ?

A glass-ionomer filling and sealing material that sets chemically, by an acid base reaction, that is designed to remineralise in the mouth and is also optimised for heat curing using an high energy LED (halogen) lamp.

The cement is claimed to contain nano crystals of calcium fluorapatite (CaFAP), which act as nuclei for the remineralisation process. The glass is thought to have a much finer particle size than in conventional glass ionomer cements [1].

What is MAS-NMR spectroscopy?

Solid state nuclear magnetic resonance (SS-NMR) spectroscopy is capable of probing the local environment and coordination states of the various atoms present in these materials. In solid state NMR the dipolar and chemical shielding interactions can be removed by magic angle spinning (MAS) by introducing an artificial motion on the solid [2].

What is the advantage of MAS-NMR in this study?

MAS-NMR can be used to study the local structure and setting reaction of glass polyalkenoate cement.

Objectives

To study the structure of Carbomer® using the ¹⁹F and ³¹P MAS-NMR technique

Experimental

Cement Preparation

1. Activate capsule in the Caps Activator
2. Put capsule in capsule mixer, 15-20 seconds
3. Ageing time 5 minutes to 90 days

XRD Analysis

1. The glass and FAP were analysed using Phillips Powder Diffractometer with a copper (Cu Kα) x-ray source (Phillips PW 1700 series diffractometer, Philips, Eindhoven, NL)

2. The powder samples (<45µm particle size) were scanned between 2θ = 5-80° with a step size of 2θ = 0.04

MAS-NMR Analysis

¹⁹F
Spinning rate: 10 kHz, recycle time: 10s

³¹P
Spinning rate: 3 kHz, recycle time: 20s

Spectrometer: Bruker, 200MHz

Results

XRD Analysis

The XRD pattern for the glass shows no diffraction lines and is therefore completely amorphous (Figure 1).

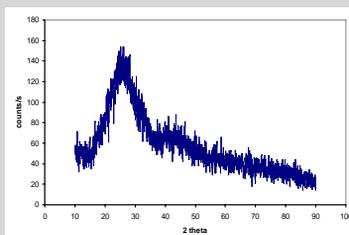


Figure 1. XRD pattern for the glass

For CaFAP, it shows characteristic crystalline lines pattern. From the Xpert software, we found that this pattern is matched closely with FAP (Figure 2) and HAP (Figure 3) crystals. Therefore, we suggest the crystals are a mixture of FAP and HAP.

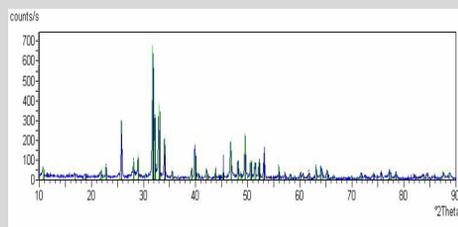


Figure 2. XRD pattern of CaFAP matches with FAP

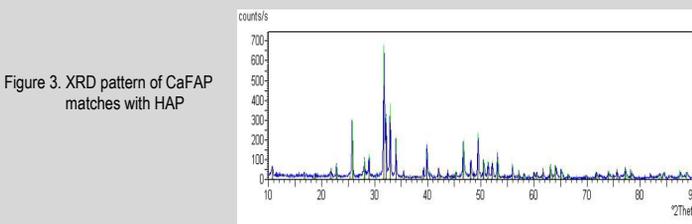


Figure 3. XRD pattern of CaFAP matches with HAP

MAS-NMR Spectroscopy

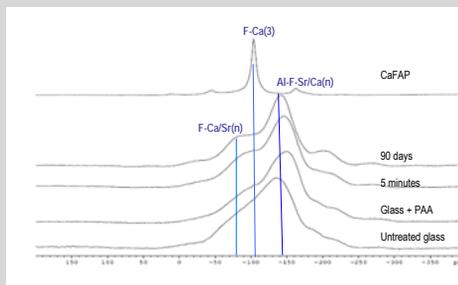


Figure 4. ¹⁹F MAS-NMR for glass Carbomer

¹⁹F MAS-NMR shows that in presence of CaFAP, there is a small peak at -103 ppm which is assigned as F-Ca(3) from the CaFAP. There are two major peaks at -135 ppm and -75 ppm which we assigned as Al-F-Sr/Ca(n) and F-Ca/Sr(n) sites respectively.

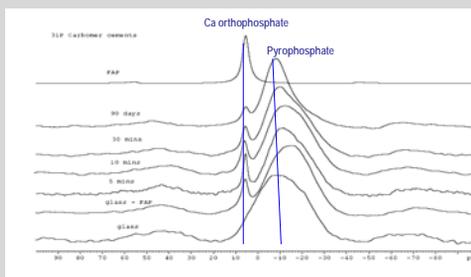


Figure 4. ³¹P MAS-NMR for glass Carbomer

³¹P MAS-NMR shows two peaks in the cements which are assigned as Ca orthophosphate in the crystalline phase of CaFAP at 3-4 ppm and pyrophosphate in the glass phase at -10 to -20 ppm.

Discussion

XRD Analysis

The XRD patterns show that the glass is amorphous and the CaFAP is a mixture of HAP and FAP and not a mixed solid solution phase. This point will be discussed further in the MAS-NMR spectroscopy.

MAS-NMR Spectroscopy

Figure 4 shows a sharp peak of F-Ca(3) in CaFAP and we found that this peak is very small in the cements mixture even before the setting reaction.

However, from the ³¹P MAS-NMR we found a significant orthophosphate peak from Ca FAP (3-4 ppm) in the cements as well as the pyrophosphate from the glass.

From the XRD and MAS-NMR analyses we suggest that the reason why we could not detect a significant peak of F-Ca(3) in the cements is because of the CaFAP that has been used in this glass Carbomer® is not only consists of FAP but also HAP. However, because the ¹⁹F MAS-NMR spectrum for CaFAP shows a very sharp peak of the F-Ca(3) site, we suggest that the apatite consists of a mixture of FAP and HAP. If these are a mixture of FAP/HAP in the crystal lattice, the ¹⁹F MAS-NMR will be broadening out because of the disordered environment.

During the setting reaction, the fluorine and phosphorus environment change with the ageing time. The decrease of orthophosphate peak in CaFAP (3-4 ppm) suggests that CaFAP is being consumed during the setting reaction.

Conclusions

- Apatite presents as a mixture of FAP and HAP crystalline phases.

- The fluorine and phosphorus environment change with the ageing time suggest the involvement of FAP in the setting reaction.

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