# The effect of phosphate, fluorine, and soda content of the glass on the mechanical properties of the glass ionomer (polyalkenoate) cements

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## ARTICLE INFO

## ABSTRACT

The main objective was to study the effect of reducing the phosphate content of the glass structures and the mechanical properties of the resultant cements. The effect of fluorine and soda content on the fluoride release was also investigated.

A fluoro-aluminosilicate glass and its modified glass compositions were studied. The structures of the glasses were determined using X-ray diffraction (XRD), $^{27}Al$, $^{19}F$, and $^{31}P$ Magic Angle Spinning (MAS) NMR, and DSC. The mechanical properties and the fluoride release of the cements were also measured.

Phosphorous forms Al-O-P linkages in the glass. The formation of Al-O-P groups inhibits the degradation of the Si-O-Al bond in the Si-O-Al-O-$PO_3^{3-}$ group. Reducing the phosphate content decreases the proportion of Al-O-P bonds, with a concomitant change in the mechanical properties. The fluoride release kinetics was observed to be different, but there was no significant difference in the total amount of the fluoride released at 56 days.

The mechanical properties of the glass ionomer cements (GICs) increased by a simple reduction of the phosphate content. The compressive strengths of the cements were twice the ISO standard and were higher than the commercially available cements. Therefore, this study could be a basis to improve the properties of GICs.

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## 1. Introduction

The glass ionomer cements (GICs) or glass polyalkenoate were first introduced by Wilson and Kent in the 1970s. Since then, GICs have been widely used in dentistry as luting cements, anterior and posterior filling materials, as well as bone cements in medicine [1].

The GICs are formed by the acid-base reaction between aluminosilicate glass and a polymeric acid, usually poly(acrylic acid), PAA. When the acid attacks the Si-O-Al bond in the glass network, $Al^{3+}$ and $Ca^{2+}$ are released and ionically crosslink with the carboxylate groups in the PAA. One of the advantages with the GICs is fluoride release, especially for dental applications, as fluoride has anti-cariogenic effect. The fluoride ion is released from the cement to form fluoroapatite, which is among the most chemically and thermally stable of all apatite phases, formed by replacement of the hydroxyl group, by fluoride, in enamel and dentine hydroxyapatite [1]. Some of other advantages of the GICs are minimal exothermic reactions during setting, controlled setting properties, no shrinkage upon polymerisation, excellent, optical translucency, and very good surface adhesion. Radiopacity is also an advantage of GICs, but this property is highly dependent on the glass compositions. One of the disadvantages of the GICs, however, is that they are known to have inferior mechanical properties compared to composite resin materials.

There have been several studies which looked at the influence of glass compositions on the mechanical and the setting properties of the GICs [2–8]. The effect of the Si:Al ratio was investigated by Griffin and Hill [6] who found that this ratio played an insignificant role in determining the mechanical properties of the GICs. In contrast, they found that phosphorus has a more significant role in determining mechanical properties [5]. Phosphorus is known to charge-balance $AlO_4^-$ tetrahedral forming Al-O-P bonds [9,10]. This can maintain aluminium in tetrahedral coordination. They found that their cement containing the highest $P_2O_5$ content in the glass composition showed the lowest compressive strength. The reduction in the mechanical strength could have been caused by phosphate stabilizing the aluminium in the network through the formation of Al-O-P bonds, making the network hydrolysis and release of $Al^{3+}$ ions slower.

Therefore, in this paper, the phosphate content in the glass compositions is reduced, from the base glass composition known as LG26, to

study its effect on the glass structure and the mechanical properties of the cements. LG26 has been used in a commercially available cement for medical applications and has been extensively studied [4,5,11–13]. The rationale behind the reduction in phosphate content is that by decreasing the amount of phosphate, the glass network will become less stable with a smaller number of $Al^{3+}$ cations in the form of $AlO_4^-$ tetrahedral being locally charge-balanced by $P^{+5}$ cations. The reduction in phosphate content would be expected to lead to a more degradable glass in the presence of acid during the cement formation. In all the glasses studied here, the ratio of Al:P is ≥1 to reduce the possibility of the phase separation within glasses. It has been known that in the presence of an excess of phosphate, a double bond between oxygen and phosphorus forms which induces phase separation of a silicate glass into silicate and orthophosphate rich phases [14]. The effect of containing more fluorine and soda on fluoride release is also investigated in this paper.

## 2. Materials and methods

### 2.1. Materials

Four glasses were produced for this study including the base glass composition, LG26, $4.5SiO_2$-$1.5Al_2O_3$-$3AlPO_4$-$3CaO$-$2CaF_2$ (Table 1).

The appropriate amount of silica, $SiO_2$ (Tilcon Industrial Sands), alumina, $Al_2O_3$ (Johnson Matthey), aluminium phosphate, $AlPO_4$ (Lancaster), calcium fluoride, $CaF_2$ (Lancaster), calcium carbonate, $CaCO_3$ (Sigma-Aldrich), and sodium carbonate, $Na_2CO_3$ (Sigma-Aldrich) were mixed. The mixed powder was transferred to an alumina crucible, and the crucible was heated in an electric furnace at 1420 °C for LG26 and 1440 °C for all the lower phosphate content glasses for 1.5 h. The molten liquid was quickly quenched into water to produce a granular glass frit. 100 g of the frit glass was then ground and was sieved through <38 μm sieve.

Poly(acrylic) acid, PAA, used in this study, was supplied by Advanced Healthcare Limited (UK). It had a nominal molar mass of 90,000 Da. A typical powder:liquid ratio for dental cement was used with a PAA concentration of 35%wt.

### 2.2. Methods

The glass powder was first characterized using automated powder x-ray diffractometer, XRD, (Philips PW1700 series, Netherlands) with Cu K$_\alpha$ radiation at 40 kV/40 mA with a secondary graphite crystal monochromator. Each spectrum was taken in the 2θ range of 10° to 80° with a step size of 0.04°.

The magic angle spinning nuclear magnetic resonance spectrometry (MAS-NMR), was run on the $^{27}$Al, $^{19}$F, and $^{31}$P nuclei to determine the structural changes. The resonance frequencies were 156.3 MHz, 188.3 MHz, and 80.9 MHz, and the spinning rates were 15 kHz, 11–12 kHz, and 5 kHz for $^{27}$Al, $^{19}$F, and $^{31}$P respectively. $^{27}$Al nucleus was run on 600 MHz NMR spectrometer, and $^{19}$F and $^{31}$P on 200 MHz NMR spectrometer (Bruker, Germany), with the reference materials of 1 M aqueous solution of $AlCl_3$ and 85% $H_3PO_4$ acid for $^{27}$Al and $^{31}$P nuclei respectively. $^{19}$F was referenced against $CFCl_3$, and NaF powder was used as a secondary reference.

Differential scanning calorimetry (Labtherm Scientific, Main Packages V.4.30, UK), DSC, was used to determine the glass transition temperature, $T_g$, of each glass. Platinum-rhodium crucibles were used with alumina as a reference. The sample and the reference were heated up to 1050 °C with the heating rate of 10 °C min$^{-1}$. Experimental error were determined by repeat experiments.

Cement cylinders of 6.0 mm height and 4.0 mm diameter were used for the compressive strength measurements and were kept in at least 90% humidity at 37.0 °C ± 1.0 °C. The specimens were then stored in water for 1 day and 28 days for measurements. The measurement was done based on the ISO standard 'ISO9917-1: 2003 Dentistry - Water-based cements - Part 1: Powder/liquid acid-base cements' [15]. A Hounsfield machine (Tinius Olsen Ltd., UK), which displayed the maximum load, p, applied in Newtons was used for testing. The value was then converted to compressive strength, σ$_c$, using Eq. (1):

$$\sigma_c = (4p)/\left(\pi d^2\right) \tag{1}$$

where p is the maximum load in N, d is the diameter of the specimen in mm.

The flexural strengths were measured using a three-point bend test operated by the Hounsfield machine. Specimens measuring $2.0 \times 2.0 \times 25.0$ mm were prepared by placing the mixed cements in appropriate moulds for 1 h in 37.0 °C ± 1.0 °C oven with the relative humidity of 90%. Using the silicon carbide paper, the specimens were polished and were placed in distilled water in the oven for further 23 h prior to testing. For statistical analysis, the Student's t-test was performed with two tailed distribution at 5% significance level for both compressive strength and flexural strength measurements.

Fluoride release measurements were performed with one cement disc for each glass composition. The discs measuring 10 mm diameter and 1 mm thickness were prepared in moulds, and were stored in a 37.0 °C ± 1.0 °C oven with 90% humidity for 1 h. These specimens were then placed into 10 ml of distilled water and were placed back in the oven. The fluoride release measurements were performed at 1, 7, 21, and 56 days, with a fluoride ion selective electrode (Jenway 3045, Jenway, UK). A total ionic strength adjustment buffer (TISAB) was added.

## 3. Results

All the glasses studied here were optically clear, and the XRD measurement showed that all the glasses were amorphous (Fig. 1). However, there was a very small peak, with LPLG26 glass, on its amorphous halo at around 2θ = 32°. This crystalline region is very small and is <1% compared to the amorphous region.

The $^{27}$Al MAS NMR spectra are shown in Fig. 2. The LG26 glass exhibited a peak at 50.1 ppm. When the phosphate content was decreased, the chemical shift increased to 55.3 ppm, 54.6 ppm and 54.3 ppm for
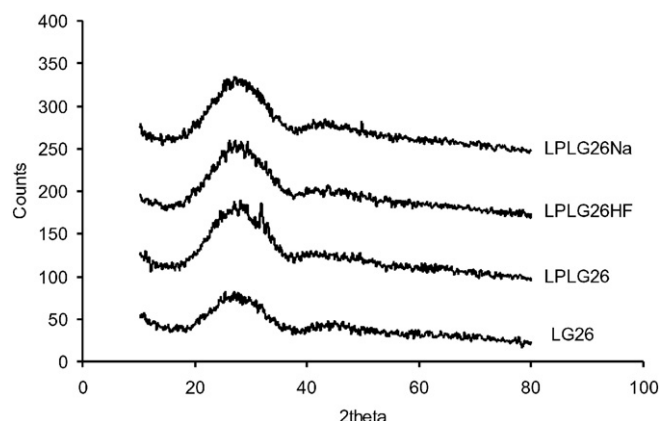
**Table 1**
Glass compositions in mol%.

| Glass | SiO$_2$ | Al$_2$O$_3$ | AlPO$_4$ | CaO | Na$_2$O | CaF$_2$ |
|---|---|---|---|---|---|---|
| LPLG26Na | 33.96 | 16.98 | 11.32 | 14.38 | 0.77 | 22.64 |
| LPLG26HF | 33.96 | 16.98 | 11.32 | 15.09 | 0.00 | 22.64 |
| LPLG26 | 33.96 | 16.98 | 11.32 | 22.64 | 0.00 | 15.09 |
| LG26 | 32.14 | 10.71 | 21.43 | 21.43 | 0.00 | 14.29 |



**Fig. 1.** The XRD pattern for LG26, LPLG26, LPLG26HF, and LPLG26Na glasses.