

A Preliminary Study on pH Changes of Storage Solution and Weight Changes of Ionomer Cements: Influence of Phosphate Content

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Abstract

This *in vitro* study was carried out to investigate the impact of varying phosphate fractions on pH changes of storage solution of artificial saliva and weight changes for four experimental ionomer cements at specific time intervals. Three disc-form specimens for each composition were prepared, weighed-out (initial weight = W_0) and then immersed individually in 10 ml of artificial saliva (initial pH = 6.5) for the experimental periods at 37°C. At 7, 14 and 28 days, the final pH values of artificial saliva solutions were measured using a pH electrode meter. The discs were immediately collected, dried and re-weighted (final weight = W_1) to calculate the weight changes by percentage. All tested cements were bringing the pH slightly down towards the acidity level after 7 days, and then the values became relatively stable when the time progressed further up to 28 days. As well, the data showed that the less phosphate was added to the basic ionomer glasses, the less influence on pH rate was evaluated. A linear relationship between the pH values as a function of phosphate content was obtained at all time points. In terms of weight changes, there was a moderate increase in the mass during the entire experimental period. The extent of the changes in pH values of artificial saliva and in specimens weights led to the conclusion that the ionomer glass components has a crucial role in controlling the material behaviour. Further studies have to be done.

Keywords: Ionomer Cements; Phosphate; pH Changes; Weight Changes; Artificial Saliva

Introduction

Various proton donor cements are used in modern clinical dentistry; such as zinc-phosphate, zinc-polycarboxylate and glass-ionomer cements (1). Their applications are including as liners and bases under the restorations, for luting crowns and bridges, for fixing orthodontic appliances, and also as fissure sealant and restorative filling for repairing damaged tooth surfaces in the case of glass-ionomers (2). Moreover, the use of ionomer cements is not limited to dentistry. Researchers have developed numerous applications that include bone cement for orthopaedic use, artificial ear ossicles and alveolar bone augmentation (3, 4).

All these cements have essentially similar structure after setting, despite of the differences in their chemical compositions (5). The final set cement is such a cored structure of continuous amorphous matrix phase consisting of the salt formed via the neutralization reaction (acid-base reaction), with filler particles of unreacted

base dispersed in it (6). The structure of glass-ionomers is more complex, since the matrix is also partly composed of an inorganic network formed of alumina (7). Basically, the calcium/strontium fluoro-aluminosilicate glasses are the most used system for production of ionomer cements with additions of phosphate in some cases; typically in form of aluminium phosphate (AlPO_4) (8). These glasses are made of highly cross-linked O-Si-O linkages that chemically stable in nature; contributing to hardening and maturation process of ionomer cements (9). The addition of alumina yields Si-O-Al linkages with negative charge sites which become later available to neutralise the polymeric acid and thus enabling cement formation (10).

On the other hand, the existence of phosphate as one of the glass networks former has been proven in many studies; evidently affecting the glass degradability and solubility (11, 12). Griffin and Hill (13) studied the influence of phosphate on

the properties of GICs. They reported that presence the phosphate in the polysalt matrix of ionomer cements are likely to compete with the carboxylate groups of poly-acrylic acid for crosslinking metal cations of calcium and aluminium. This causes disrupting in the crosslinking process, strongly influences the rheology of the setting cement paste and the mechanical properties of the hardened cement as well.

Well known that solution-uptake changes the physical, chemical and mechanical properties of the cements; as directly interfering with the maturation process of the material (14). The oral cavity is a complex environment that possibly will

Materials and Methods

Four experimental ionomer glasses based on $4.5\text{SiO}_2\text{-}3\text{Al}_2\text{O}_3\text{-}1.5\text{P}_2\text{O}_5\text{-}3\text{CaO-}2\text{CaF}_2$ system = (LG26), were designed and synthesised in the same manner (melt-quench route) that used previously by Hill and his colleagues (15). The compositions (P1, P2, P3, and P4) were produced with

influence the properties of dental materials. Currently, many *in vitro* studies use artificial saliva (AS) as a storage solution, to simulate the condition of the oral cavity. Subsequently, it is necessary to understand the influence of the storage solution on the ionomer cements properties, also to know the behaviour of these materials in the oral cavity and to predict their performance with time. Therefore, this preliminary research study was aimed at evaluating the pH changes of the storage solution of AS and the weight changes of the tested ionomer cements with studying effect of variation in the phosphate fractions; using four experimental ionomer cements.

varying in the phosphate fractions; as shown in Table 1.

1. Specimens Preparation

Three disc-shaped specimens were prepared for each material by mixing of fine glass powder, poly-acrylic acid in powder form and with addition of water at specific powder to liquid ratio (P:L = 5:1).

The components were mixed on a clean, dry glass slab with a stainless steel spatula for about 40-60 sec at room temperature. The paste was packed in a Teflon mould with internal dimensions of 10 ± 0.1 mm in diameter and 3 ± 0.1 mm in thickness. The mould was covered with acetate sheets from both sides and immediately clamped between two metal plates using G-clamp to remove excess material and to avoid air entrapment. Each assembly was left to set in an oven (Carbolite[®], USA) at 37°C for 1 hr.

2. Specimens Storage

Following 1 hr from the start of mixing, the specimens were removed from the mould and underwent visual examination in order to discard any non-standard discs. The specimen were weighed-out using an analytical balance (Denver Instrument, SI-403, UK) to an accuracy of ± 0.001 g; to obtain the initial weight (W0). Each disc was immersed separately in a polypropylene centrifuge tube filled with 10 ml of artificial saliva (AS) solution at

pH = 6.5 (initial pH); that made according to Ten Cate *et al.* modified recipe (16). The immersed cements were kept in a shaking incubator (IKA[®], KS 4000 i control, Staufen, Germany) at 37°C during the entire period of the experiment; to simulate the condition of oral environment.

3. Specimens Testing

3.1 Acidity (pH changes)

Measurements:

After the storage period, the pH of the storage solution was recorded using a pH electrode meter (Oakton[®], Eutech Instruments, pH 11 Series, Malaysia); at 7, 14 and 28 days (Final pH) after immersing. The used pH electrode consists of a glass probe that contains two electrodes inside, which one electrode is in contact with a fixed acidity liquid and the other one will be in contact with the storage solution of AS to measure the exact pH value. Calibration of pH electrode was done before measuring the actual solution using three standard buffer

solutions with pH of 4.0, 7.0 and 10.0 respectively.

3.2 Solution-uptake (weight changes)

Measurements:

The investigated specimens were taken-out of solutions, dried with a laboratory tissue to remove the excess water and then re-weighed to obtain the final weight (W1). Care has to be taken, thus the whole process should not take more than 30 sec; to avoid the specimen desiccation.

Percentage of solution-uptake (weight changes) for each specimen was calculated as follows:

$$\text{Weight Change (\%)} = \frac{W1 - W0}{W0} \times 100$$

Where W1 is the weight at the regular time intervals after specimen immersion; W0 is the original weight before specimen immersion.

Table 1: Composition of experimental ionomer glasses in mole proportion.

ID	Mole Proportion				
	SiO ₂	Al ₂ O ₃	P ₂ O ₅	CaO	CaF ₂
P1	4.50	3.00	0.75	3.00	2.00
P2	4.50	3.00	1.00	3.00	2.00
P3	4.50	3.00	1.25	3.00	2.00
P4	4.50	3.00	1.50	3.00	2.00

Results

Figure 1 shows the pH changes of AS solution after immersion of various cement discs, plotted against the square root time ($t^{1/2}$) at 7, 14 and 28 days respectively.. All experiments exhibited a significant

decrease in the pH values after 7 days of immersion. With increasing the exposure time of the cement specimens to storage solution, the pH values became relatively stable in all cases.

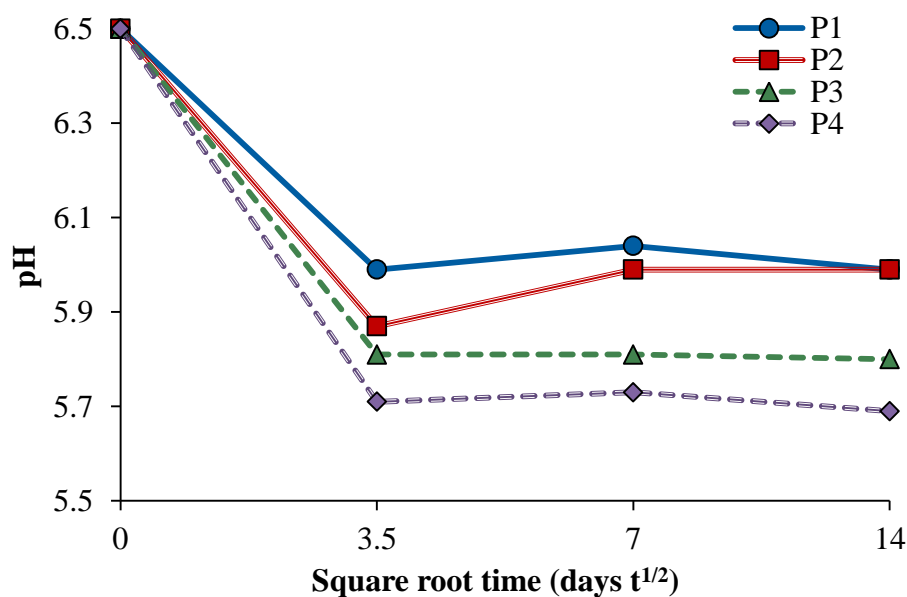


Figure 1: Changes in the pH values of storage solution of artificial saliva over time ($t^{1/2}$ days).

Further, the relationship between the pH values and the phosphate content in molar percentage were presented in Figure 2 (A-C). Generally, a substantial change in pH value of the surrounding media was clearly observed with increasing the phosphate amount in the parent glasses. P4-based ionomer cements (high phosphate content)

exhibited more reduction in the values compared to P1-based ionomer cements (low phosphate content). The obtained trend clearly displayed a strong linear relationship upon the compositions at all time points; R-squared values (R^2) were 0.9865 at 7 days, 0.9539 at 14 days and 0.8929 at 28 days.

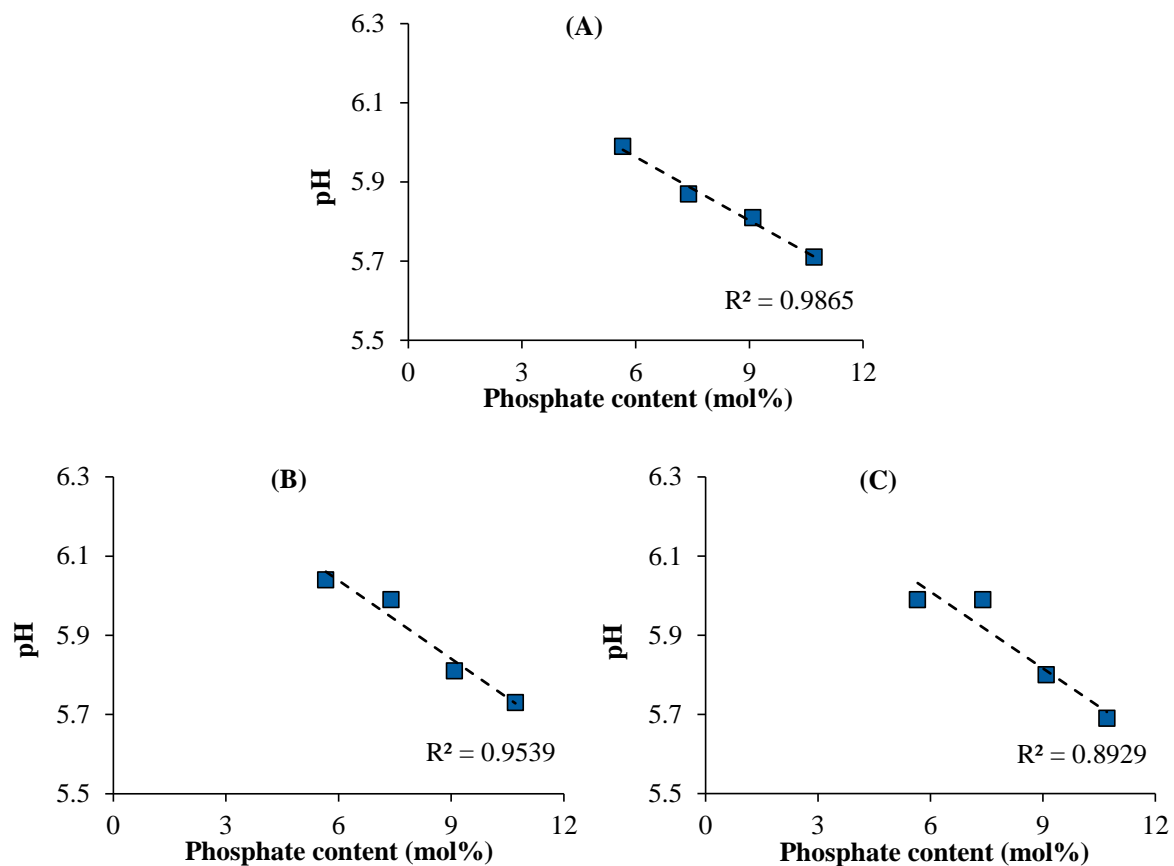


Figure 2: The relationship between the pH values and phosphate content at (A) 7 days, (B) 14 days and (C) 28 days.

The corresponding data of the weight change percentages for different cement compositions that resulting from solution-uptake trial are listed in Table 2. All cement specimens appeared to have increased positive numbers in relation to the weight changes with a slight variation

in the calculated proportions over the experiment period. Obviously, the cement discs revealed no apparent adverse effects regarding to the appearance of external surfaces following the exposure to AS solutions.

Table 2: Percentage of weight changes for tested ionomer cements at three time points ranged as 7, 14 and 28 days.

ID	7 Days		%	14 Days		%	28 Days		%
	W0	W1		W0	W1		W0	W1	
P1	0.350	0.354	1.14	0.308	0.317	2.92	0.285	0.292	2.46
P2	0.342	0.349	2.05	0.382	0.388	1.57	0.352	0.358	1.70
P3	0.349	0.354	1.43	0.331	0.339	2.42	0.362	0.365	0.83
P4	0.325	0.332	2.15	0.327	0.335	2.45	0.340	0.347	2.06

Discussion

The results of the current study have potential importance clinically on understanding the behaviour of ionomer cements and their ability on buffering the surrounding media. The pH data of the storage solution of AS showed a steadily decrease over all the experimental period, as ranged between 5.69 and 5.99 pH units from the initial value of 6.5; depending on the cement composition. This could be explained due to the fact that some of residual carboxylic groups (-COOH) of poly-acrylic acid on the specimen surfaces consume some elements; such as calcium from the saturated AS rather than using these elements from un-reacted glass particles within the cement matrix itself.

Calcium is known to be involved in the initial setting process of these cements to produce calcium polyacrylate via acid attacks (17, 18). Other possible reason might be due to that some AS elements precipitate on the outer surface of the cement specimen, leading to reduction in the pH values of the storage solution.

Previous studies have revealed that there are changes on the surfaces when the ionomer cements and other restorative materials were stored in salivas (19, 20). These changes can be expected to have an influence on the setting mechanism and the final properties of the cements. Further, Ngo *et al.* research (21) concluded that ionic exchange between the set cement and its environment occurs

continuously even after maturation of the cement. These observations go in good agreement with the outcomes of the present study.

The obtained findings further emphasised that none of the storage solution has a pH below the critical value. The critical pH is the pH at which saliva and plaque fluids being saturated in relation to enamel minerals (22). It is influenced by the concentration of the calcium and phosphate in the fluids of oral cavity, thus its value is not stable and varies with the oral health of individuals (22, 23). It has been known that the dental caries occurs when the mineral phase (hydroxyapatite) of the tooth attacks by acids that produce from the microorganisms (bacteria) as a by-product of their metabolism (24, 25). This mechanism activates when the pH of the released acids (lactic acid + acetic acid) below the critical value of 5.5 in correlation with the exposure time (26). Actually, the active caries has a pH of 4.9,

and becomes arrested when the pH is shifted to a value of 5.7 (27).

Understanding the role of phosphate is of great interest for controlling the behaviour of self-hardening ionomer cements and to predict its impact on the surrounding media; especially with the secondary setting continues in the long-term. Our observations exhibited that ionomer cements based on low phosphate content had less influence on decreasing the pH rate when compared to the other compositions with high proportions. Pervious researches stated that the incorporation of phosphate into the ionomer glass network could provide instable structure, as a result of one oxygen atom is begin double bonded to the central phosphorus atom, even though being hydrolysed at the neutral pH (13, 28). Accordingly, there is perhaps a certain degree of saturation on the phosphorus addition, which in turn provides the most of beneficial effects on material properties.

In this study, it typically determines that the weight changes correlated with solution-uptake gave a moderate positive rate for all ionomer cements types. Well known that the materials take-up water, their dimensions and structural integrity will be altered. Those self-hardening cements are recognised to absorb water from the surrounding media; causing an additional mass during the maturation process (29). Kanchanavasita *et al.* (30) claimed that the absorbed solutions may act as a plasticiser; leading to weakening the final set cements. Additionally, they expected that the obtained expansion could cause stresses at tooth-restoration interfaces. This fact suggests that the solution particles could be diffused through the cements invisible micro-voids. Human saliva is complex fluid secreted by major and minor salivary glands and varies from one individual to another (31). It is able to buffer the acids produced by oral bacteria and neutralizes other acids taken into the mouth as erosive beverages (32).

Studies using artificial saliva have relatively complicated outcomes as the tested materials continue contact with supersaturated saliva that contains a variety of inorganic and organic species (33). This will cause degradation of the dental restorations with time by reacting with it chemically. Further investigations have to be done considering the ability of self-hardening cements formulations on altering the storage solutions pH and the mechanism of solution-uptake during the maturation process.

Conclusion

Within the limitations of this study, it can be concluded that: (i) knowing the functions of original glass components and optimising the compositions of ionomer cements play a fundamental role on understanding the target material properties; (ii) the low phosphate-based ionomer cements showed less effect on decreasing the pH of AS in comparison with other high phosphate-based compositions; (iii) the reduction was

within the critical pH value; (iv) it found that the pH values and phosphate content had a clear linear relationship; (v) the solution-uptake rate for all tested cements was moderate at all time points. These materials may have the beneficial effect of inhibiting caries development *in vivo*.

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