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Calcium hydroxide-modified zinc polycarboxylate dental cements

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Abstract

In this research, the effects of calcium hydroxide addition to zinc polycarboxylate cements have been studied on microstructural properties, setting time, pH changes and compressive strength. The results indicated that the setting time of the resultant cements increased with increase in the calcium hydroxide content to the cement matrix. Moreover, the compressive strength of the set cement optimally increased with addition of 5 wt% calcium hydroxide and then decreased by addition of 10 and 15 wt% calcium hydroxide. The effect of calcium hydroxide content on the properties of the set cements however was somewhat more complex, and a variable correlation was observed between the initial setting time and compressive strength. The prepared cements could be useful in surgical sites that are not freely accessible when using minimally invasive techniques. This is a preliminary study and more detailed work is required to evaluate other properties of this class of material.

Keywords: Zinc polycarboxylate; Calcium hydroxide; Dental cement

1. Introduction

The development of tissue engineering and regenerative medicine has led to the production of a wide range of biomaterials [1–7]. The association of these biomaterials, cells and growth factors has yielded the development of new treatment opportunities in dentistry [8–11]. Among different biomaterials, dental cements are highly promising for wide clinical uses due to their self-setting ability, resistance to marginal leakage, adhesion to enamel and dentin, moisture resistance, low pulpal irritation, and easy manipulation [12–14].

Polyelectrolyte cements are used in both restorative and luting applications in dentistry [15]. In fact, the clinical success of fixed prostheses is dependent on the cementation procedure. Dental cements must be used to act as a barrier against microleakage, sealing the interface between the tooth and restoration and holding them together through durable bond between tooth and restoration materials [16,17]. In addition, ideal dental luting cements should provide favorable mechanical strengths and demonstrate adequate working and setting times [17]. Zinc polycarboxylate and glass polyalkenoate (glass ionomer) cements are two types of polyelectrolyte cements, which are widely used as adhesives in dentistry. They are the only materials currently available that are capable of chemically bonding to dentine and enamel. Due to their hydrophobicity, they can wet dentine and enamel surfaces, which is an important requirement of any adhesive or dental material [18]. Not only adhesion is important for the mechanical integrity of a joint or restoration but also adhesion to the tooth material ensures an enclosed seal. This helps prevent percolation of bacteria and fluids beneath a filling and thereby reduces the likelihood of secondary caries and pulp irritation. Among polyelectrolyte cements, zinc polycarboxylate cement has been widely used clinically, including cavity liners, as adhesive for placement of crowns and for the adhesion of orthodontic application. The adhesive bond can be formed primarily due to enamel. Although, a weaker bond to dentin may be also formed. This is due to the fact that bonding

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appears to be the result of a reaction between the carboxyl groups of the cement and calcium in the tooth structure. Therefore, the more highly mineralized the tooth structure, the stronger the bond [19,20]. When zinc oxide and poly(acrylic acid) are mixed, hydrated protons formed from ionization of the acid attack the zinc and magnesium powder particles. This causes the release of zinc and magnesium cations which form polycarboxylates that cross-link the polymer chains. The result is a zinc polycarboxylate cross-linked polymer matrix in which unreacted zinc oxide particles are embedded [19,21]. The chemical reaction between poly(acrylic acid) and ZnO was explained this phenomena

$$ZnO+2(–CH_2–CHCOOH–)\rightarrow(–CH_2–CHCOO–)_2Zn+2H_2O \quad (1)$$

Cross-linking was reported to take place via a sort of "salt-bridge" between the divalent zinc cations and the hydrophilic functional groups on the polymeric chains. Neutralization in the zinc polycarboxylate cements was found to occur more rapidly than that which occurred in the glass polyalkenoate as it depends on the diffusion of the metal ions [22]. In fact, the part of zinc carboxylate drawbacks is attributed to the fast nature of the reaction between zinc cations and poly(acrylic acid) anions [15]. These drawbacks include its working time (less than 1–2 min) and compressive strength (40–70 MPa) which are relatively low [23–25].

Many attempts have been made to overcome these drawbacks by modifying the formulation of polycarboxylate cement by incorporating various fillers into the component [24,26–28]. Furthermore, the effect of ionic additives on these cements has been studied extensively [29,30]. Monovalent salts, such as NaCl, KCl, or KBr, have been shown to accelerate the setting of zinc polycarboxylates but the compressive strength of zinc polycarboxylates was unaffected [31]. Divalent salts, such as $CaCl_2$ or $ZnCl_2$, had similar effects on setting, though, they reduced the compressive strength [32]. These results are related to changes in conformation and ionization of poly (acrylic acid) caused by the salts. Nicholson et al. [33] had studied the effect of two trivalent nitrates, $Al(NO_3)_3$ and $Fe(NO_3)_3$, in these cements. In contrast to results for mono- and divalent metal salts, the zinc polycarboxylate was more affected by trivalent salts. Addition of either $Al(NO_3)_3$ or $Fe(NO_3)_3$ to zinc polycarboxylate dental cements has been shown to cause an acceleration to their setting reactions.

There are number of possible mechanisms by which additives seem able to modify the setting reactions in zinc polycarboxylate cements. In this way, calcium hydroxide is expected to affect the neutralization reaction. Calcium hydroxide is one of the provisional luting materials, which is currently widely used owing to their proven properties of stimulating mineralization, protecting the pulp against thermoelectric stimuli, and favoring antimicrobial action [34]. According to Tronstad et al. [35], the mechanism of action of calcium hydroxide is attributed directly to its capacity of dissociating into Ca^{2+} and OH^- ions resulting in increased pH locally. In one hand, with the polymeric acid based cements it is reported [15] that di- and tri-valent ions such as calcium and aluminum are able to react with carboxyl groups to form ionic cross-links between the polymer chains.

On the other hand, Beech et al. [36] suggested three criteria about the characteristics of mineralizing solutions for enhancing the bond strength of all polycarboxylic acid cements to dentine. First, the solution must contain calcium or related ions which are compatible with the hydroxyapatite crystal lattice. Second, the solution must have a pH of 7 or above. A low pH may inhibit the receptivity of newly deposited mineral to ionic interaction with cement or may prevent the mineral itself from being laid down. Finally, the deposited mineral needs to react with the cement. The formation of highly insoluble phosphates (e.g., barium phosphate), or insoluble calcium salts (e.g., calcium fluoride), can greatly reduce bonding.

Hitherto, however, there have been no reports of studies of zinc polycarboxylate cements interaction with calcium hydroxide. The current article describes experimental work designed to determine calcium hydroxide addition affect on the setting time, mechanical strength and pH of zinc polycarboxylate cements.

2. Materials and methods

2.1. Preparation of cements

A commercially available zinc polycarboxylate dental cement, Hoffmann (Iso 9917), was mixed at the ratio recommended for use as a liner for pulp protection, 2.9 g powder to 1 g liquid. The cement samples were modified by adding calcium hydroxide powder ($Ca(OH)_2$), Merck (no. 2047, Germany), in the weight ratios in the range of 5, 10 and 15 wt% of the powder part of the cement. By increasing calcium hydroxide quantities of 0, 5, 10 and 15 wt%, the prepared cements were coded as S_1, S_2, S_3 and S_4, respectively.

According to the manufacturer's instruction, the powder and liquid phases were mixed at 23 ± 1 °C and a relative humidity of $50 \pm 10\%$. The samples were prepared by placing the freshly mixed cements in cylindrical molds with dimensions of 12 mm in height and 6 mm in diameter. The samples were stored in the molds for 24 h at 37 °C and 28% relative humidity.

2.2. Sample characterization

The setting time of the samples was measured in accordance with ASTM C266-89 standard using a Gillmore needle test with a needle weight of 113.5 g and a tip diameter of 2.1 mm.

The X-ray powder diffraction (XRD) studies of the set cement disks were carried out using a X-ray automated diffractometer.

The fractured set cements, 24 h after mixing, were ground and weighed to obtain 1 g of each sample, and then mixed with a measured amount of potassium bromide in an agate mortar. After pressing the mixed materials into rigid pellets, FTIR analysis was performed using a (Perkin Elmer FTIR spectrometer, Model 1403, USA) at a wavelength range between 400 and 4000 cm^{-1} [37,38].

For analysis of the morphology and microstructure of the prepared cement disks, the fractured surfaces were coated with gold and then monitored with a scanning electron microscope (SEM-Philips XL30) that operated at the acceleration voltage of 15 kV.

The specific surface area was obtained by fitting the Brunauer–Emmett–Teller (BET) equation to the N_2 adsorption isotherms measured at 77 K using a BELSORP mini (BEL Japan).

Compressive strength testing was performed, according to a modified form of BS ISO 9917 (2003) [39], specified for the testing of dental cements. The mixed cements were compacted in brass molds 6 mm in diameter and 16 mm height with 2 mm caps at both ends. These molds produced disks 6 mm in diameter and 12 mm height with plane ends. A vibrator device was used to avoid entrapped air. The disks were stored in an incubator at 37 °C and 100% humidity for 24 h, and compressive strength testing was then performed. The disks were compressed using a universal testing machine (Instron 1195, High Wycombe, UK) with a cross-head speed of 1 mm/min. The compressive strength was calculated from the following equation:

$$\text{Compressive strength} = \frac{4F}{\pi d^2} \quad (2)$$

where, F is the maximum load until fracture (N) and d is the diameter (mm) of the samples [40].

The pH was measured using a pH meter (Jenway Scientific, Felsted, UK) supplied with epoxy combination pH electrode. For this purpose the disks were placed in sealed containers filled with 6 ml of distilled water. The containers were kept in the incubator. The pH was monitored during the first 120 min.

All the data were presented as mean value ± standard deviation (SD) of each group.

3. Results and discussion

3.1. TEM observation

Fig. 1 shows the typical TEM micrograph of the calcium hydroxide powder. As can be seen here, the particles show uniformity in shape and size and the particle size is around 100 nm.

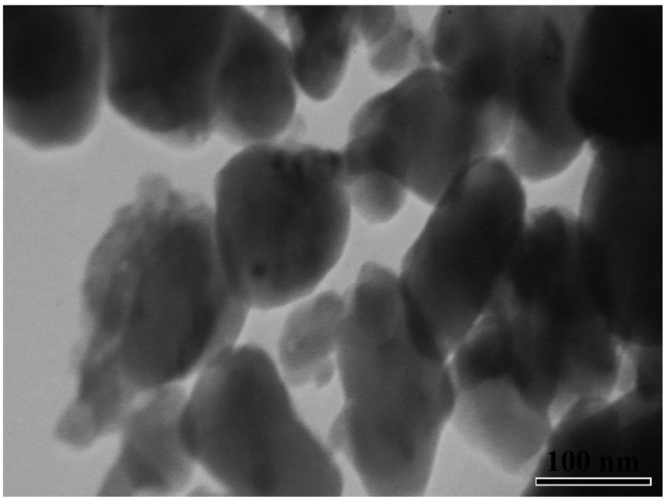

Fig. 1. Typical TEM micrograph of the calcium hydroxide powder.

3.2. XRD analysis

The XRD analysis of zinc polycarboxylate cements identified two crystalline phases ZnO and MgO. The presence of additives like SnO_2, SnF_2, SiO_2, iron or titanium depends on the cement type, which are usually small quantities (less than 1 wt%). Here, the presence of additives was not detected in the XRD patterns of all the samples, shown in Fig. 2. The cements should be composites of amorphous zinc polycarboxylate cross-linked polymer matrixes in which unreacted oxides ZnO (mainly) and MgO particles are embedded. These results are in accordance with the same structures proposed for such cements [41]. According to this figure, adding 5 and 10 wt% calcium hydroxide did not affect the XRD pattern significantly. It seems that calcium hydroxide totally participated during the acid–base setting reaction. In addition, the formed calcium polycarboxylate was not reflected in the XRD pattern since it probably formed an amorphous matrix. By increasing the calcium hydroxide to higher contents, unreacted $Ca(OH)_2$ particles might be detected. Studies of the reaction between the calcium hydroxide powder and partially neutralized

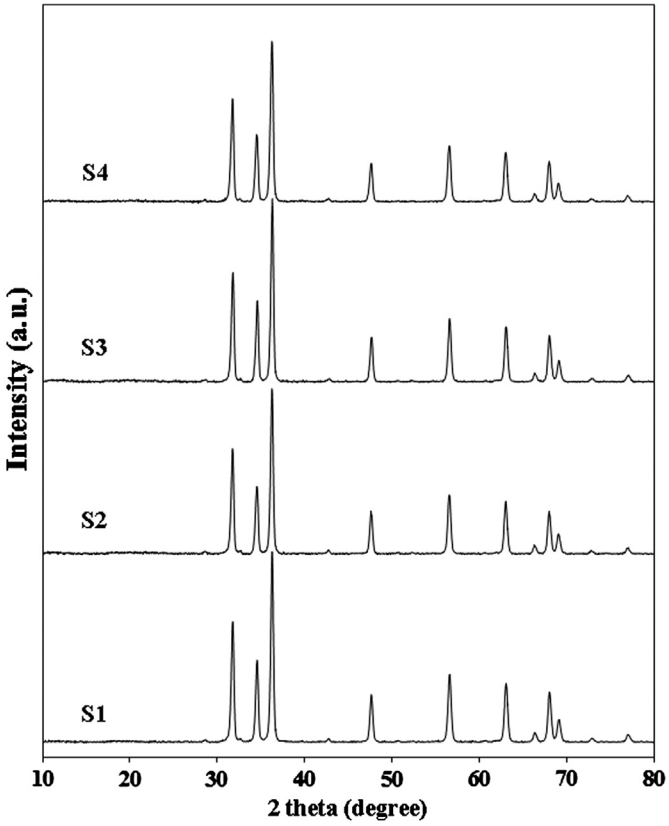

Fig. 2. The XRD patterns of the set cements.

polyacid solutions suggest that calcium hydroxide may partially participate in the form of calcium polycarboxylates [42].

3.3. FTIR analysis

As shown in Fig. 3, the infrared spectra of the set cements showed two absorption bands at 1518 and 1474 cm^{-1}, representing carboxylic acid salts (–COO) [43]. In addition, a stretching band was observed at 1605 cm^{-1}, representing the (–C═O) antisymmetric stretching band of the carboxylate groups in the poly(acrylic acid). The peak at 1640 cm^{-1} was attributed to non-structural OH peak. Further addition of calcium hydroxide showed a slight decrement of the stretching band at 1605 cm^{-1} and increment of the two other stretching bands at 1518 and 1474 cm^{-1}, indicating carboxylate salt formation. It is suggested that calcium hydroxide content may reduce the amount of remaining unsubstituted carboxylate groups but fail to completely substitute carboxylate groups. The presence of the peak around 3500 cm^{-1} in the samples containing higher amounts of calcium hydroxide suggested that small amounts of calcium hydroxide may remain unreacted [44].

3.4. SEM observation

The SEM micrographs of the surface topography of the samples are shown in Fig. 4. As can be seen, a relatively smooth surface with linear micro- and nano-cracks and many small voids were created on the surfaces of the samples by further addition of the calcium hydroxide content to the cement matrix. According to Bertenshaw et al. [45], the larger pores might be due to the entrapment of air during mixing and the additional finer porosity results from loss of excess water. Here, the surfaces of S3 and S4, as shown in Fig. 4(c) and (d), were less integrated and had more voids which was attributed to the disturbed setting reaction by adding more calcium hydroxide content. As shown in high magnification micrographs, a large number of pores were clearly observed.

To have a better understanding on the effect of calcium hydroxide on the cement structure, the textural properties of the basic cement was compared typically with sample S3. The N_2 adsorption isotherm of S1 and S3 samples are shown in Fig. 5(a) and (b), respectively. The textural properties of S1 sample including BET surface area and pore volume were 0.94 (m^2 g^{-1}) and 1.05 (cm^3 g^{-1}), respectively. Moreover, it can be seen that after the addition of 10 wt% of calcium hydroxide to the cement structure a significant enhancement in the textural properties of this sample (S3) was observed. For S3 sample BET surface area and pore volume were 1.24 (m^2 g^{-1}) and 1.43 (cm^3 g^{-1}), respectively, with a mean pore size of around 50.00 (nm). From these results one can also infer that the pores are specifically in nano-range.

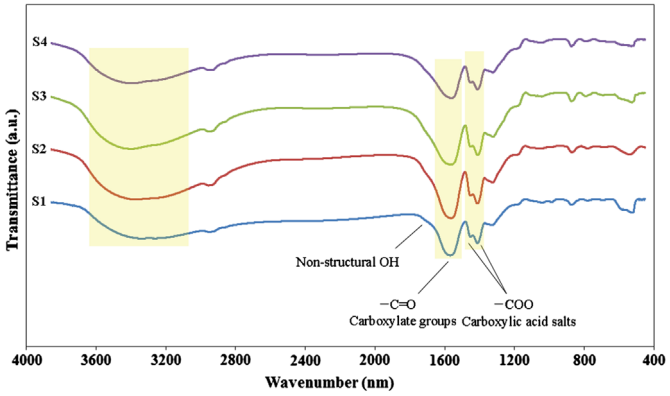

Fig. 3. The FTIR spectra of the set cements.

It is know that the release of drugs, such as antibiotics, from cements is largely influenced by the penetration of dissolution fluids into the pores [46,47]. The porosity of the cement depends on the air entrapment during the wetting and stirring of the cement powder, and depends on the effects of the components [48]. Moreover, penetration of dissolution fluids into the pores also depends on the wettability of the cement surface, which makes it essentially a surface phenomenon. Recently, Belt et al. [49] measured the release of gentamicin as a function of time for a series of gentamicin-loaded cements and related with porosity and roughness of the cements. They found that the initial release rates could be increased with surface roughness, although the correlation coefficient was low, while the total amounts of release increased linearly with the bulk porosity of the cements. They concluded that the release kinetics of drug from the cements was controlled by porosity. It seems that by even addition of small amounts of calcium hydroxide into the cement matrix and creation of small pores, the cements can be more efficient for drug delivery purposes. Total understanding of the effect of calcium hydroxide on the morphology and drug release of the samples is a daunting challenge which needs further investigation.

3.5. Setting time

The influence of the calcium hydroxide content on the setting time of different samples is shown in Fig. 6. It can be suggested that by further addition of calcium hydroxide to the cement matrixes the setting time increased from 5 to 16 min. The obtained results also indicated that adding 5 and 10 wt% calcium hydroxide showed a clinically acceptable setting time which was mainly attributed to the acid–base reaction and subsequent formation of carboxylate salts. Furthermore, a significant increase, around 16 min, was observed with adding 15 wt% calcium hydroxide for S4 sample.

Generally speaking, the setting reaction of polyelectrolyte cements consists of ionic salt-bridge formation and covalent cross-linking. Zn^{2+} and Ca^{2+} ions are able to form salt-bridges between these cations and carboxyl anions but there is a difference in size (Zn^{2+}: 0.74 Å and Ca^{2+}: 0.99 Å) and electronegativity (Zn^{2+}: 1.65 and Ca^{2+}: 1.00) between the Zn^{2+} and Ca^{2+} ions, which causes a two-step setting mechanism in these cements. Kenny et al. [27] suggested that it is not only the charge of cations that affects the neutralization reaction but the size of the ions can also have a major influence. It seems that the chemical bonding between the zinc ions and the poly(acrylic acid) can be more stable than the

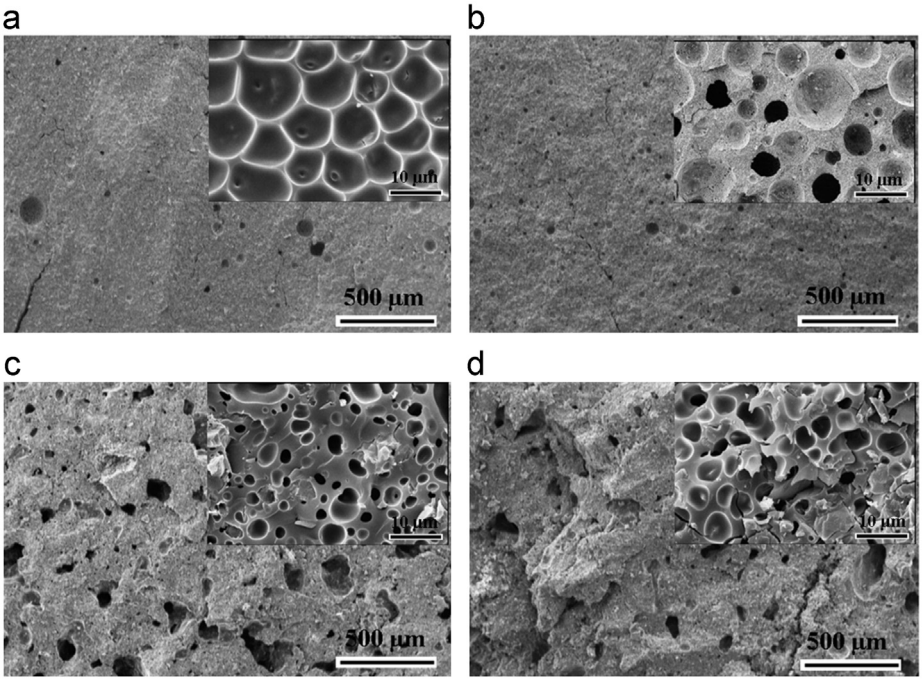

Fig. 4. The SEM micrographs of the surface morphology of the set cements, (a) S1, (b) S2, (c) S3 and (d) S4, (the images in the corners are high magnification images).

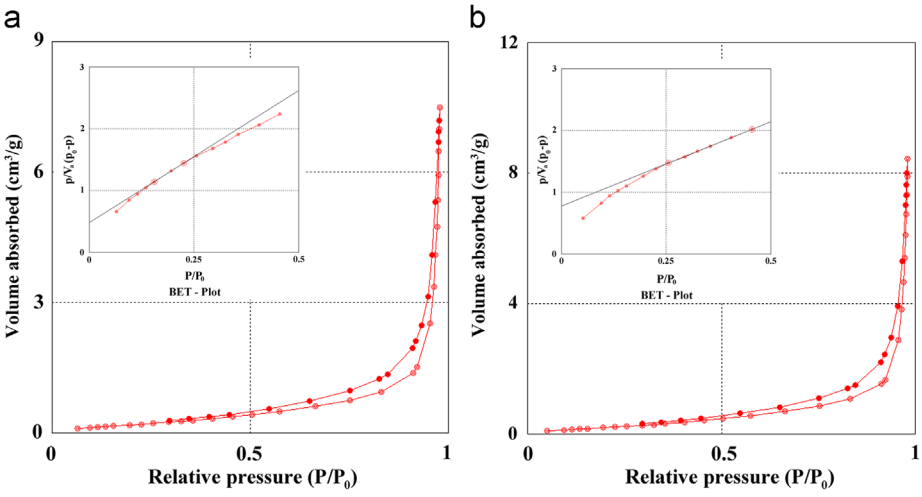

Fig. 5. N_2 adsorption isotherms and BET plots of (a) S1 and (b) S3.

chemical bonding between the calcium ions and the poly (acrylic acid), which is due to the smaller radius and greater electronegativity of zinc ions. The zinc polyacrylate species causes primary hardening of the cement, and later the formation of calcium polyacrylate leads to a second post-hardening step. In fact, calcium ions are released from the calcium hydroxide via neutralization of the hydrogen ions released from poly(acrylice acid), these are then cross-linked by poly(acrylic acid) molecules leading to setting via the formation of a calcium polyacrylate networks (see Fig. 7). A similar mechanism is believed to occur with glass polyalkenoate cements [31]. According to Fig. 4, addition of 15 wt% calcium hydroxide dramatically prolongs the setting times of these polycarboxylate cements. The presence of residual nonfunctional carboxylic groups and unreacted calcium hydroxide in the set cements could disrupt the setting reaction of the samples containing the higher amounts of calcium hydroxide.

3.6. Compressive strength

The calcium hydroxide contents effect on the compressive strength of the zinc carboxylate cements after 24 h of setting reaction is shown in Fig. 8. An increase in compressive strength could be achieved by addition of calcium hydroxide content from 0% to 5%. This enhancement was followed subsequently by gradual decrease of the strength to about 50 MPa for 10 wt% calcium hydroxide. The compressive strength dramatically decrease by adding 15 wt% calcium hydroxide. In fact, the zinc polycarboxylate cement reacts much more rapidly

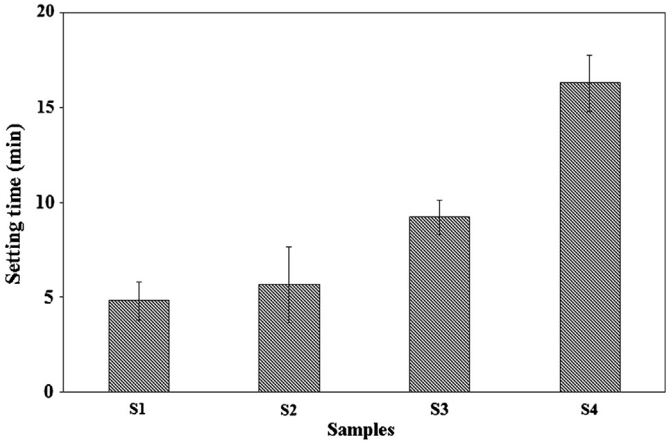

Fig. 6. The influence of the calcium hydroxide content on the setting time of different samples.

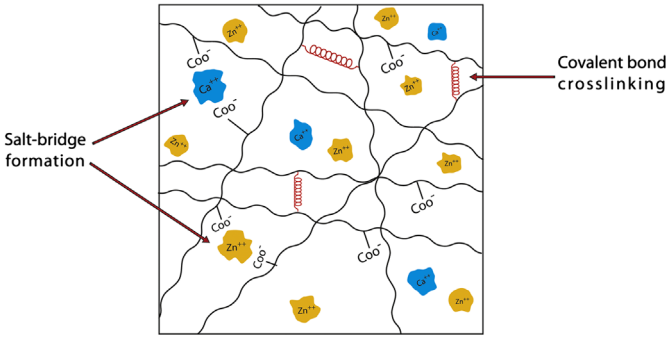

Fig. 7. The schematic of deposition of calcium hydroxide into the cement matrix.

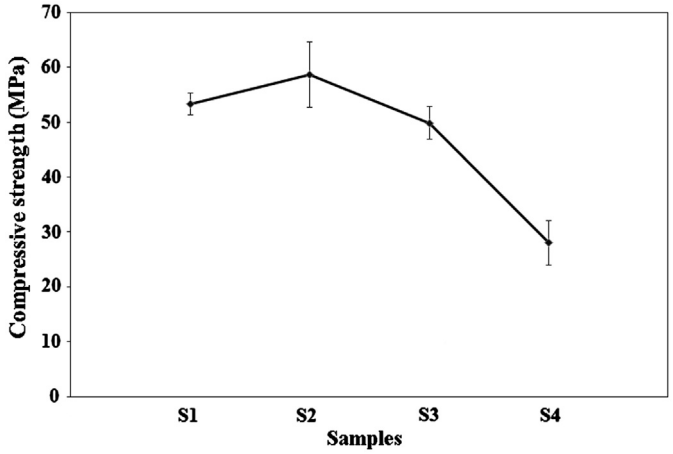

Fig. 8. The calcium hydroxide contents effect on the compressive strength of the zinc carboxylate cements after 24 h of setting reaction.

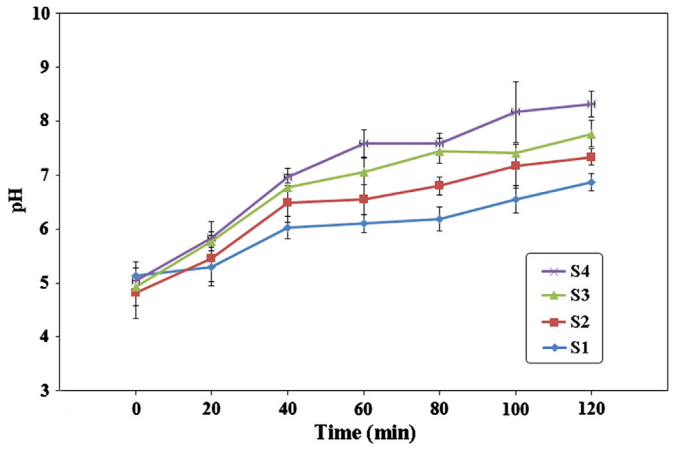

Fig. 9. The time-dependent pH variation of the samples in distilled water.

than the glass ionomers. This implies that the reaction of the glass ionomer cements is less developed at the "setting time", and may be partly responsible for the higher compressive strength of glass ionomer cements [50,51]. One of the reasons why calcium hydroxide was added is that it can delay the salt-bridge formation between zinc and carboxyl group by introducing two-step setting mechanism. By less developed setting reaction at the "setting time" more ionic salt-bridge and covalent cross-linking will form which is expected to improve mechanical properties [51]. Although, by adding more than 10 wt% calcium hydroxide setting reaction is disrupted and unreacted particles reduce compressive strength dramatically. The findings on the setting reactions and the analysis of the parameters determining the setting time correlates very well with the result of compressive strength.

3.7. pH value

Fig. 9 shows the time-dependent pH variation of the samples in distilled water. The pH changes over the time course showed that there was no statistically significant difference between the mean pH values for all samples. The initial pH readings were approximately the same for S1, S2, S3 and S4. However, there were slight increases in the pH value for all the samples at the same time points. Moreover, the gradual slope of the curves for S2 and S3 cements indicated that a relatively neutral pH is maintained during 40–120 min. It seems that adding 5 and 10 wt% calcium hydroxide were incapable of alkalinizing the cements. This is thought to be a result of setting reaction. It seems that calcium hydroxide is totally participating in setting reaction and unreacted calcium hydroxide particle is negligible. In addition, polycarboxcilic might be considered as a non-water soluble vehicle which could not release calcium and hydroxyl ions easily [52]. As can be seen, S4 sample presented higher pH values and the greatest variation ranging from 5 to 8 which is significantly different from other samples. According to FTIR and setting time results, this pattern might be attributed to the ionization of unreacted calcium hydroxide. From a biologic point of view, calcium hydroxide-contained cements permit the formation of mineralization when applied to dentin as capping materials, and evidence of pulp repair has been reported when they are applied to accidental pulp exposures [53,54]. However, to exert their antibacterial action these calcium hydroxide-contained materials must provide the release of hydroxide and calcium ions which raise the pH value of the surrounding environment to the higher levels after dissolution [55]. The

alkaline pH maintained at the injured/treated region creates favorable conditions for dentine formation [56].

4. Conclusion

In conclusion, adding calcium hydroxide to the cement matrix has a meaningful effect on setting time, compressive strength and pH value. The obtained results indicated that adding 5 wt% calcium hydroxide (S2 sample) presented a reasonable setting time, and significantly higher compressive strength when compared to zinc polycarboxylate cement (S1: control sample). By less developed setting reaction at the "setting time", more ionic salt-bridge and covalent cross-linking are predicted to form which was expected to enhance mechanical properties for S2 sample. The experiments provided data to support the use of the composite cements in dental applications.

References

[1] S.A. Poursamar, M. Azami, M. Mozafari, Controllable synthesis and characterization of porous polyvinyl alcohol/hydroxyapatite nanocomposite scaffolds via an in situ colloidal technique, Colloids and Surfaces B: Biointerfaces 84 (2011) 310–316.

[2] M. Jafarkhani, A. Fazlali, F. Moztarzadeh, M. Mozafari, Mechanical and structural properties of polylactide/chitosan scaffolds reinforced with nano calcium phosphate, Iranian Polymer Journal 10 (2012) 713–720.

[3] M. Jafarkhani, A. Fazlali, F. Moztarzadeh, Z. Moztarzadeh, M. Mozafari, Fabrication and characterization of PLLA/chitosan/nano calcium phosphate scaffolds by freeze casting technique, Industrial & Engineering Chemistry Research 51 (2012) 9241–9249.

[4] F. Baghbani, F. Moztarzadeh, A.Gafari Nazari, A.H.Razavi Kamran, F. Tondnevis, N. Nezafati, M. Gholipourmalekabadi, M. Mozafari, Biological response of biphasic hydroxyapatite/tricalcium phosphate scaffolds intended for low load-bearing orthopaedic applications, Advanced Composites Letters 21 (2012) 16–24.

[5] S.M. Naghib, M. Ansari, A. Pedram, F. Moztarzadeh, A. Feizpour, M. Mozafari, Bioactivation of 304 stainless steel surface through 45S5 bioglass coating for biomedical applications, International Journal of Electrochemical Science 7 (2012) 2890–2903.

[6] A. Hamlehkhan, M. Mozafari, N. Nezafati, M. Azami, A. Samadikuchaksaraei, Novel bioactive poly(ε-caprolactone)-gelatin–hydroxyapatite nanocomposite scaffolds for bone regeneration, Key Engineering Materials 493–494 (2012) 909–915.

[7] A. Razavi, F. Moztarzadeh, M. Mozafari, M. Azami, F. Baghbani, Synthesis and characterization of high-pure nanocrystalline forsterite and its potential for soft tissue applications, Advanced Composites Letters 20 (2011) 41–47.

[8] M. Azami, S. Jalilifiroozinezhad, M. Mozafari, Calcium fluoride/hydroxyfluorapatite nanocrystals as novel biphasic solid solution for tooth tissue engineering and regenerative dentistry, Key Engineering Materials 493–494 (2012) 626–631.

[9] M. Mozafari, E. Salahinejad, D.D. Macdonald, V. Shabafrooz, M. YazdiMamaghani, D. Vashaee, L. Tayebi, Multilayer bioactive glass/zirconium titanate thin films for bone tissue engineering and regenerative dentistry, International Journal of Nanomedicine 8 (2013) 1665–1672.

[10] M. Azami, S. Jalilifiroozinezhad, M. Mozafari, Synthesis and solubility of calcium fluoride/hydroxy-fluorapatite nanocrystals for dental applications, Ceramics International 37 (2011) 2007–2014.

[11] N. Nezafati, F. Moztarzadeh, S. Hesaraki, M. Mozafari, A. Samadikuchaksaraei, L. Hajibaki, M. Gholipour, Effect of silver concentration on bioactivity and antibacterial properties of SiO_2–CaO–P_2O_5–Ag_2O sol–gel derived bioactive glass, Key Engineering Materials 493–494 (2012) 74–79.

[12] N. Nezafati, F. Moztarzadeh, S. Hesaraki, Z. Moztarzadeh, M. Mozafari, Biological response of a recently developed nanocomposite based on calcium phosphate cement and sol–gel derived bioactive glass fibers as substitution of bone tissues, Ceramics International 39 (2013) 289–297.

[13] N. Nezafati, F. Moztarzadeh, M. Mozafari, In vitro evaluations of a mechanically optimized calcium phosphate cement as a filler for bone repair, Key Engineering Materials 493–494 (2012) 209–214.

[14] N. Nezafati, F. Moztarzadeh, S. Hesaraki, M. Mozafari, Synergistically reinforcement of a self-setting calcium phosphate cement with bioactive glass fibers, Ceramics International 37 (2010) 927–934.

[15] A.D. Wilson, J.W. Nicholson, Acid–Base Cements: Their Biomedical and Industrial Applications, Cambridge University Press, Cambridge, England, 2005.

[16] Serkan Nohut, Chunsheng Lu, Fracture statistics of dental ceramics: Discrimination of strength distributions, Ceramics International 38 (2012) 4979–4990.

[17] C.H. Pameijer, A review of luting agents, International Journal of Dentistry 2012 (2012) 1–7.

[18] A. Wilson, H. Prosser, D. Powis, Mechanism of adhesion of polyelectrolyte cements to hydroxyapatite, Journal of Dental Research 62 (1983) 590–592.

[19] A. Petrich, C.J. VanDercreek, C.K. Kenny, Dental luting cements, Clinical Update (National Naval Dental Center) 26 (2004) 31–32.

[20] A.P. Luz, V.C. Pandolfelli, $CaCO_3$ addition effect on the hydration and mechanical strength evolution of calcium aluminate cement for endodontic applications, Ceramics International 38 (2012) 1417–1425.

[21] J.W. Nicholson, P.J. Brookman, O.M. Lacy, G.S. Sayers, A.D. Wilson, A study of the nature and formation of zinc polyacrylate cement using Fourier transform infrared spectroscopy, Journal of Biomedical Materials Research 22 (1988) 623–631.

[22] S. Kenny, R.G. Hill, M. Towler, The influence of poly (acrylic acid) molar mass on the properties of polyalkenoate cements formed from zinc oxide/apatite mixtures, Journal of Materials Science: Materials in Medicine 11 (2000) 847–853.

[23] R.G. Craig, Restorative Dental Materials, in: Robert G. Craig, Marcus L. Ward (Eds.), Mosby, Maryland Heights, Missouri, USA, 1997.

[24] R.K. Bansal, U.S. Tewari, P. Singh, D.V.S. Murthy, Influence of talc on the properties of polycarboxylate cement, Journal of Oral Rehabilitation 24 (1997) 76–79.

[25] Z.C. Lia, S.N. White, Mechanical properties of dental luting cements, Journal of Prosthetic Dentistry 81 (1999) 597–609.

[26] D. Xie, D. Feng, Il-D. Chung, A.W. Eberhardt, A hybrid zinc–calcium–silicate polyalkenoate bone cement, Biomaterials 24 (16) (2003) 2749–2757.

[27] S. Kenny, M. Buggy, R.G. Hill, The influence of hydroxyapatite: zinc oxide ratio on the setting behavior and mechanical properties of polyalkenoate cements, Journal of Materials Science: Materials in Medicine 12 (2001) 901–904.

[28] R.D. Bagnall, A.M. Martin, J.F. McCord, J.M. Thompson, Observations on the introduction of calcium hydroxyapatite into dental zinc polyalkenoate cements, Clinical Materials 3 (1988) 285–289.

[29] M.A. Moharram, F.A. Saadalah, N. Abdel-Hakeem, O.M. Ibrahim, Effect of certain additives on the physical properties of a polycarboxylate cement, Materials Research Bulletin 27 (1992) 67–73.

[30] D. Xie, M. Faddah, J.G. Park, Novel amino acid modified zinc polycarboxylates for improved dental cements, Dental Materials 21 (2005) 739–748.

[31] J. Nicholson, F. Abiden, Studies on the setting of polyelectrolyte cements: Part VI the effect of halide salts on the mechanical properties and water balance of zinc polycarboxylate and glass-ionomer dental cements, Journal of Materials Science: Materials in Medicine 9 (1998) 269–272.

[32] J. Nicholson, Studies in the setting of polyelectrolyte cements: Part VII the effect of divalent metal chlorides on the properties of zinc polycarboxylate and glass-ionomer dental cements, Journal of Materials Science: Materials in Medicine 9 (1998) 273–277.

[33] J.W. Nicholson, The effect of trivalent metal nitrates on the properties of dental cements made from poly (acrylic acid), Journal of Applied Polymer Science 70 (1998) 2353–2359.
[34] S. Desai, N. Chandler, Calcium hydroxide-based root canal sealers: a review, Journal of Endodontics 35 (2009) 475–480.
[35] L. Tronstad, J.O. Andreasen, G. Hasselgren, L. Kristerson, I. Riis, pH changes in dental tissues after root canal filling with calcium hydroxide, Journal of Endodontics 7 (1981) 17–21.
[36] D. Beech, A. Solomon, R. Bernier, Bond strength of polycarboxylic acid cements to treated dentine, Dental Materials 1 (1985) 154–157.
[37] Y. Matsuya, J.M. Antonucci, S. Matsuya, S. Takagi, L.C. Chow, Polymeric calcium phosphate cements derived from poly (methyl vinyl ether-maleic acid), Dental Materials 12 (1997) 2–7.
[38] S.H. Dickens-Venz, S. Takagi, L.C. Chow, R.L. Bowen, A.D. Johnston, B. Dickens, Physical and chemical properties of resin-reinforced calcium phosphate cements, Dental Materials 10 (1994) 100–106.
[39] British Standards Institution: Specification For Dentalwater-Based Cements: Dentistry: Water-based cements. Part 1: Powder/liquid Acid–Base Cements, BS EN ISO 9917-1, 2003.
[40] S. Channasanon, W. Soodsawang, N. Monmaturapoj, S. Tanodekaew, Factors influencing compressive strength of glass ionomer cement, Journal of Metals, Materials and Minerals 20 (2010) 91–94.
[41] M. John, Powers, L. Ronald, Sakaguchi, Craig's Restorative Dental Materials, Mosby, Maryland Heights, Missouri, USA, 2006 ISBN: 0323036066, 9780323036061.
[42] R.M. Khashaba, M. Moussa, C. Koch, A.R. Jurgensen, D.M. Missimer, R.L. Rutherford, N.B. Chutkan, J.L. Borke, Preparation, physical–chemical characterization, and cytocompatibility of polymeric calcium phosphate cements, International Journal of Biomaterials 2011 (2011) 1–13.
[43] K. Miyazaki, T. Horibe, J.M. Antonucci, S. Takagi, L.C. Chow, Polymeric calcium phosphate cements: setting reaction modifiers, Dental Materials 9 (1993) 46–50.
[44] A. Akashi, Y. Matsuya, H. Nagasawa, Erosion process of calcium hydroxide cements in water, Biomaterials 12 (1991) 795–800.
[45] B. Bertenshaw, V. Piddock, Porosity in water-based dental luting cements, Journal of Materials Science: Materials in Medicine 4 (1993) 415–417.
[46] A.S. Baker, L.W. Greenham, Release of gentamicin from acrylic bone cement, Journal of Bone and Joint Surgery —America Volume 70 (1988) 1551–1557.
[47] D.K. Kuechle, G.C. Landon, D.M. Musher, P.C. Noble, Elution of vancomycin, daptomycin and amikacin from acrylic bone cement, Clinical Orthopaedics 264 (1991) 302–308.
[48] R.L. Wixson, E.P. Lautenschlager, M.A. Novak, Vacuum mixing of acrylic bone cement, Journal of Arthroplasty 2 (1987) 141–149.
[49] H. van de Belt, D. Neut, D.R.A. Uges, W. Schenk, J.R. van Horn, H.C. van der Mei, H.J. Busscher, Surface roughness, porosity and wettability of gentamicin-loaded bone cements and their antibiotic release, Biomaterials 21 (2000) 1981–1987.
[50] C.K.Y Yiu, F.R Tay, N.M King, D.H Pashley, R.M Carvalho, M.R.O Carrilho, Interaction of resin-modified glass-ionomer cements with moist dentine, Journal of Dentistry 32 (2004) 521–530.
[51] S.N. White, Z. Yu, Compressive and diametral tensile strengths of current adhesive luting agents, Journal of Prosthetic Dentistry 69 (1993) 568–572.
[52] F.B. de Andrade Ferreira, P. de A. Silva, E. Souza, M.S. do Vale, I.G. de Moraes, J.M. Granjeiro, Evaluation of pH levels and calcium ion release in various calcium hydroxide endodontic dressings, Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology, and Endodontology 97 (2004) 388–392.
[53] T. Takita, M. Hayashi, O. Takeichi, B. Ogiso, N. Suzuki, K. Otsuka, K. Ito, Effect of mineral trioxide aggregate on proliferation of cultured human dental pulp cells, International Endodontic Journal 39 (2006) 415–422.
[54] S. Mickenautsch, V. Yengopal, A. Banerjee, Pulp response to resin-modified glass ionomer and Calcium hydroxide cements in deep cavities: a quantitative systematic review, Dental Materials 26 (2010) 761–770.
[55] J. Siqueira, H. Lopes, Mechanisms of antimicrobial activity of calcium hydroxide: a critical review, International Endodontic Journal 32 (2001) 361–369.
[56] J. Javelet, M. Torabinejad, L.K. Bakland, Comparison of two pH levels for the induction of apical barriers in immature teeth of monkeys, Journal of Endodontics 11 (1985) 375–378.