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EFFECT OF WATER STORAGE ON THE MECHANICAL PROPERTIES OF ZINC POLYCARBOXYLATE CEMENTS

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This work was aimed to study the effect of water absorption on the mechanical properties of several zinc polycarboxylate cements by changing the samples' storage times. The water absorption of four commercial zinc polycarboxylate cements were measured using specimens immersed for 1 h to 840 h (35days) in distilled water. Hardness and compressive strength values were measured using specimens immersed for 1 day and 35 days in distilled water. All samples took up most of the water during the first 24 h. Poly-F Plus (PFP) and Durelon (D) cements absorbed less water than Adhesor Carbofine (AC) and Polycarboxylate WP (P) cements. Adhesor Carbofine (AC) is the most hydrophilic material among the polycarboxylate cements. Water altered the physical properties of polycarboxylate cements after 35 days of water storage. Water sorption also provoked an expansion in volume of the immersed specimens, ranging from 1.72% to 9.19%. PFP, AC and D cements were shown an important increase in the hardness for 1 day and 35 days in the water (PFP:32%, AC:22%, D:9%). However, P cement showed a decrease in the hardness (52%). The highest compressive strength was obtained with D (110 MPa), whereas the lowest value was observed with P (60 MPa). Water sorption (μg/mm^3), volume change (ΔV%), hardness (HV) and compressive strength (MPa) of zinc polycarboxylate cements were listed from high to low value: AC>P>PFP>D; AC>P>PFP>D; PFP>AC>P>D and D>PFP>AC>P.

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1. Introduction

A number of commercially available dental cements differ in chemical composition and therefore possess significantly different physical, mechanical and biological properties [1]. Although all these materials are used in small quantities, they are the most important materials in clinical dentistry because of their application as luting agents, orthodontic attachments, cavity linings and bases, and restorations for teeth. These multiple uses of dental cements require more than one type of cement, since no one material has yet been developed that can perform all the desirable requirements [2]. These different applications require different physical properties and appropriate clinical manipulative characteristics. During the last four decades, several new types of dental cements have been developed that have found significant clinical usage. These are the zinc phosphate, zinc polycarboxylate, glass ionomer and resin composite cements. Polycarboxylate cements have been on the market for more than thirty years. Many research has shown that the biological and adhesive properties of this cements are better than those of other luting or base materials but several mechanical properties (such as compressive hardness, compressive strength, tensile strength etc.) are inferior to those of the other luting materials [3]. Whereas, recent works on the polycarboxylate cements have shown several improvements of their mechanical properties [4,5]. The compressive and tensile strengths of zinc polycarboxylate cements were increased by adding approximately 54% with a 10% concentration of talc [4]. The developed a novel polycarboxylate cement system was shown 85%

higher in compressive strength (CS), 98 % higher in diametral tensile strength (DTS) and 183% higher in failure strength (FS), compared to Durelon [5].

The restorative materials used in dentistry are required to have long-term durability in the oral cavity [6]. Zinc polycarboxylate cement is a water-based material that hardens following an acid-base reaction between zinc-rich powder and an aqueous solution of polyacrylic acid [7,8]. Since its invention in 1968, zinc polycarboxylate cement has been widely used to cement inlays and crowns and to make bases [9]. The main advantage of this cement lies in its strong adhesion to dentin. However, its working time (~ 1–2 min) and compressive strength (40–70 MPa) are relatively low [7, 8], which allows the cement to be used only as base or cementing restorative. The above disadvantages are formed with two reasons. The first reason is attributed to the fast setting nature of the reaction between zinc cations and polyacrylic acid anions and the second is probably due to the high molecular weight of polyacid that has been used in the cement. The polyacrylic acid, is usually an aqueous solution with 40–50% solid content and a molecular weight of 40,000–50,000 Da, which leads to a high viscosity of the aqueous solution, difficulty in mixing, and thus lower compressive strength and adhesion due to the inclusion of air bubbles in the course of mixing [10]. Attempts have been made to overcome these disadvantages by modifying polycarboxylic acid using copolymers of acrylic acid [11] and adding polyvinyl phosphonic acid) [12] or by incorporating various fillers into the zinc-containing powder using aluminium compounds [3,13], silicon dioxide [14], magnesium oxide [15], etc.

Microhardness and compressive strength are the most important physical characteristics for a comparative study of dental materials. Although there are available studies comparing microhardness[15-22] and compressive strength[19,23-26] between different dental cements, however, little has been published on the alteration of the hardness and compressive strength of polycarboxylate cements when they have been placed in water for a varying times.

The present work was aimed to study the effect of water absorption on the mechanical properties of four commercially avaible carboxylate cements.

2. Materials and methods

Sample preparation

Four commercially available polycarboxylate cements were chosen according to their different powder-liquid combinations and were used in this study: Adhesor Carbofine (Spofa Dental, Germany), Poly-F Plus (Dentsply, Germany), Polycarboxylate (WP Dental, Germany), Durelon (3M ESPE, Germany). Their composition and description are shown in Table 1.

Table 1. The four commercial zinc polycarboxylate cements used in the present study.

Product Abbr.	Product Name	Manufacturer	Composition (Powder/Liquid)
AC	Adhesor Carbofine	Spofa Dental, Germany	Powder: Zinc oxide, magnesium oxide, aluminium trihydroxide, boric acid Liquid: Acrylic acid, maleic acid anhydrit, distilled water
PFP	Poly-F Plus	Dentsply, Germany	Powder: Zinc oxide, magnesium oxide, dried polyacrylic acid Liquid: Distilled water
P	Polycarboxylate	WP Dental, Germany	Powder: Zinc oxide, dried polyacrylic acid, stannous fluoride Liquid: Polyacrylic acid solution
D	Durelon	3M ESPE, Germany	Powder: Zinc oxide, zinc fluoride, dried polyacrylic acid, stannous fluoride Liquid: Polyacrylic acid solution

All materials were handled and prepared at the powder/liquid ratios recommended by the manufacturers in atmospheric conditions: Adhesor Carbofine 3.0 g powder to 1.0 g of liquid; Poly-F

Plus 5.0 g powder to 1.0 ml of distilled water; Polycarboxylate 1.8 g powder to 0.5 ml of liquid and Durelon 2.0 g powder to 1.0 g of liquid. All cements were mixed using by a glass mixing pad and stainless steel spatula. Six samples of each cement were moulded in a teflon ring (2 mm thickness and 7 mm diameter) and placed between two flat glass plates. The slight pressure was applied on the moulds and bulk of extruded excess cement was removed. The samples were obtained at atmospheric storage conditions and cylindirical cement disks were placed in an oven at 37°C and 100% humidity for 1 h to allow the setting reaction. Finally, the specimens were stored in distilled water for 1, 2, 3, 4 hours and 1, 2, 3, 6, 7,14, 28 and 35 days at 37°C.

Immersion test

Water sorption values were determined according to the ISO specification 4049, except for specimens' dimensions and period of water immersion that was extended up to 35 days. After setting, the specimens were placed in a dessicator and then transferred to an oven at 37°C. The specimens were repeatedly weighed after 24h intervals until a constant mass (m_0) was obtained. Thickness and diameter of the specimens were measured using a digital micrometer, rounded to the nearest 0.01 mm and these measurements were used to calculate the volume (V) of each specimen in mm^3. They were then individually placed in sealed glass vials containing 30 ml of distilled water (pH 6.9) at 37°C. After fixed time intervals of 1, 2, 3, 4 hours and 1, 2, 3, 6, 7,14, 28 and 35 days of storage, the glass vials were removed from the oven and left at room temperature for 30 min. The specimens were washed in running water, gently wiped with a soft absorbent paper, weighed in an anlytical balance (m_1) and returned to the vials containing 30 ml of fresh distilled water. Following the 35 days of storage, the specimens were dried inside an dessicator containing fresh silica gel and weighed daily until a constant mass (m_2) was obtained. The initial mass (m_0) was used to calculate the change in mass after each fixed time interval, during the 35 days of storage in water. Water sorption (WS) values over the 35 days of water storage were calculated using formulae (1) and plotted against to storage time (Fig.1):

$$WS = \frac{m_1 - m_2}{V} \tag{1}$$

The diameter (D, mm) and thickness (h, mm) of the specimen disks were measured using a digital micrometer (±0.001 sensitivity) before and after immersion in distilled water. Five specimens were prepared for each material and three measurements were taken in each quadrant, totaling fifteen measurements and calculated the average volumetric change as percentage (ΔV %) using formulae (2).

$$\Delta V\% = \frac{V_e - V_0}{V_0} \tag{2}$$

V_e= Expanded volume (mm^3)
V_o= Original volume (mm^3)

Mechanical tests

Vickers hardness was measured with a microhardness test machine (Zweick), using cylindirical samples of 7 mm in diameter and 2 mm in height. A load of 200 g for 20 s was applied and each sample was subjected to ten indentations at randomly selected areas. The measurements were taken for 1 and 35 days.

The specimens for compressive strength testing were produced in cylindirical molds measuring 6 mm in diameter and 20 mm in height. The compressive test was performed using a universal test machine (Instron 8511.20) at a cross-head speed of 0.5 mm/min. Specimens were stored at 37°C in the molds for 1h, then each specimen was then immersed in 50 ml of distilled water in containers kept at 37°C for 1 and 35 days.

The free and fractured surfaces of the cement disks before and after immersion were also examined under a scanning electron microscope (SEM; JEOL-5410LV) to assess shape, cracks, small voids and surface morphology.

3. Results

Table 2 present the mean values of water sorption (WS) and volumetric change (ΔV%) at 35 days of storage in the four zinc polycarboxylate cements analyzed. Durelon (D) absorbed more less water than the other commercial polycarboxylate cements. Adhesor Carbofine (AC) and PolyF Plus (PFP) cements were the most hydrophilic materials among the four polycarboxylate cements.

Adhesor Carbofine (AC) and Polycarboxylate WP (P) cements absorbed the large amounts of water (164 and 148 µg/mm^3) compared to Poly-F Plus(PFP) and Durelon (D) cements (56 and 24 µg/mm^3) during the first day as shown Fig.1. These increases continued up to 28 days but after 28 days water sorption values decreased and then fixed in 35th days. Water sorption also provoked an expansion in volume of the water immersed specimens, ranging from 1.72% to 9.19% after 35 days as shown Table 2.

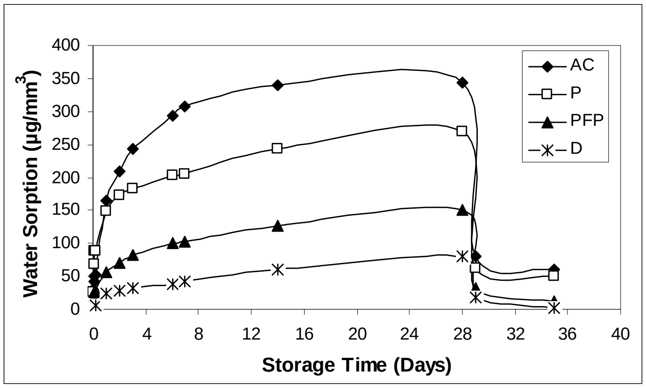

Fig.1.Water Sorption of commercial zinc polycarboxylate cements for 35 days of water storage.

Table 2. Water sorption and volumetric change of commercial zinc polycarboxylate cements after 1 day and 35 days of water storage.

Material	Water Sorption (µg/mm^3)				Volumetric Change (ΔV%)	
	1 Day		35 Days		35 Days	
	Mean	SD	Mean	SD	Mean	SD
AC	164.22	6.28	59.46	2.28	9.19	0.02
P	148.00	5.51	49.34	1.84	4.31	0.02
PFP	56.01	1.07	11.83	0.22	3.56	0.02
D	24.40	0.44	1.67	0.04	1.72	0.02

Water altered the mechanical properties of zinc polycarboxylate cements after 35 days of water storage. Fig. 2 and Fig. 3 present the mean hardness values and compressive strengths of four polycarboxylate cements immersed for 1 day and 35 days in distilled water, respectively. All cements except of P cement were shown an important incresae in the hardness for 1 day and 35 days of storage (PFP:32%, AC:22%, D:9%,). However, P cement showed a decrease in the hardness (52%). The highest compressive strength were obtained with Durelon (D) (110 MPa) and Poly F Plus (PFP) (109 MPa), whereas the lowest were observed with Polycarboxylate WP (P) (65 MPa) and Adhesor Carbofine (AC) (84 MPa).

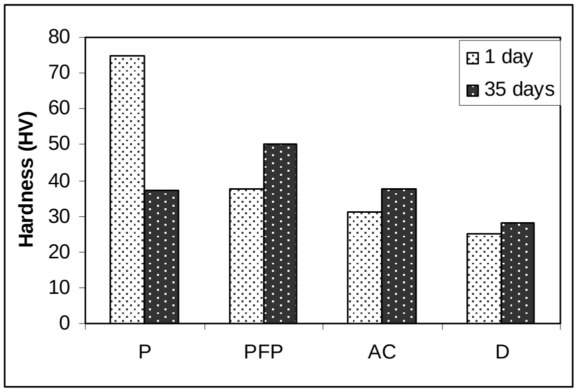

Fig. 2. Surface hardness values of commercial zinc polycarboxylate cements after 35 days of water storage.

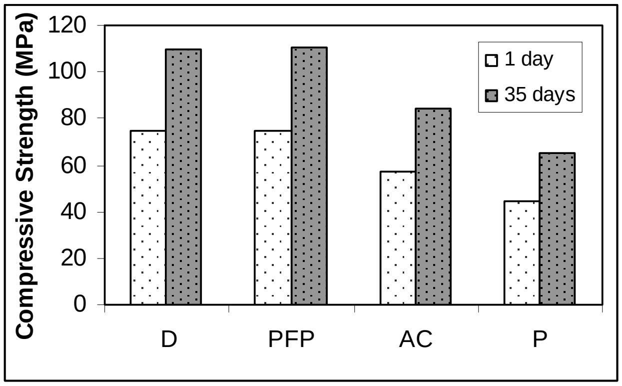

Fig.3. Compressive strength values of commercial zinc polycarboxylate cements after 35 days of water storage.

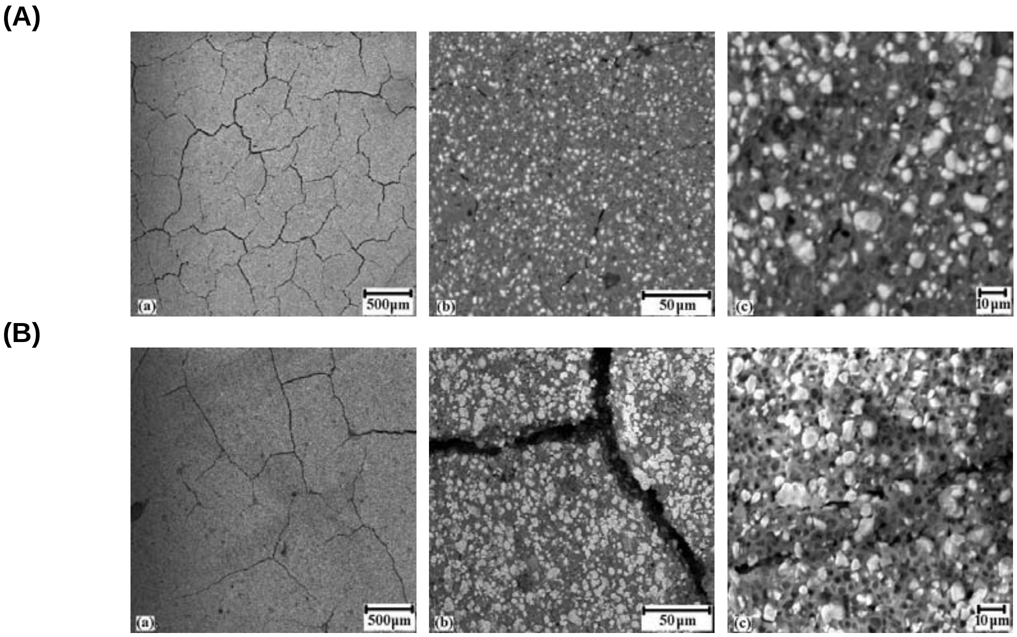

Fig.4. SEM images of Adhesor Carbofine (AC) cement (A) before water storage and (B) after 35 days of water storage: (a) surface (x35), (b) surface (x500), (c) fractured surface (x1000).

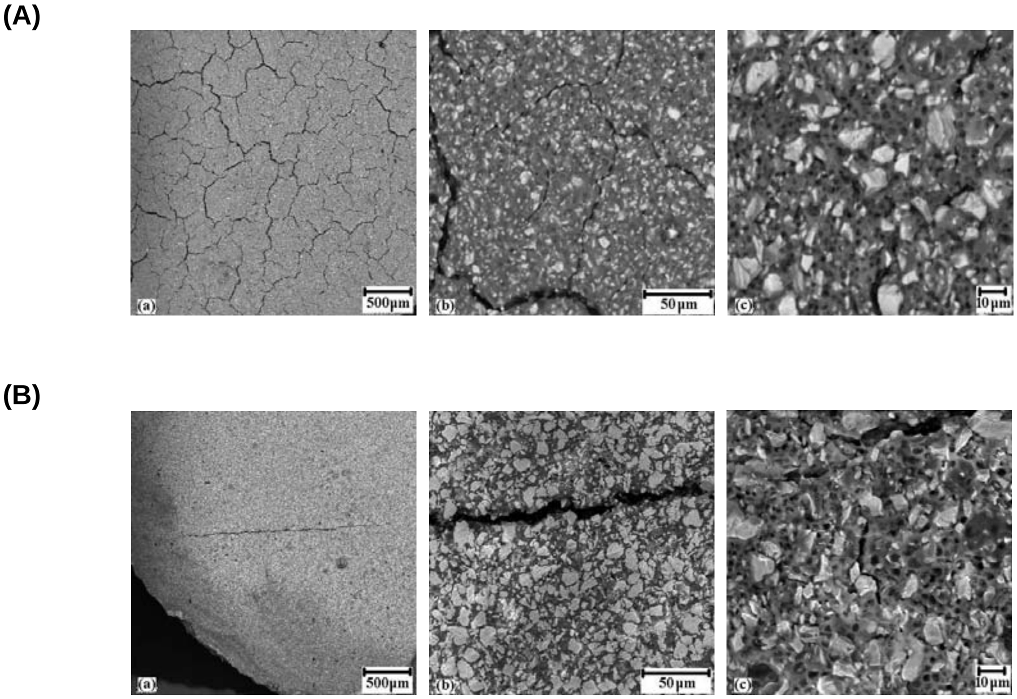

Fig.5. SEM images of Polycarboxylate WP (P) cement (A) before water storage and (B) after 35 days of water storage: (a) surface (x35), (b) surface (x500), (c) fractured surface (x1000).

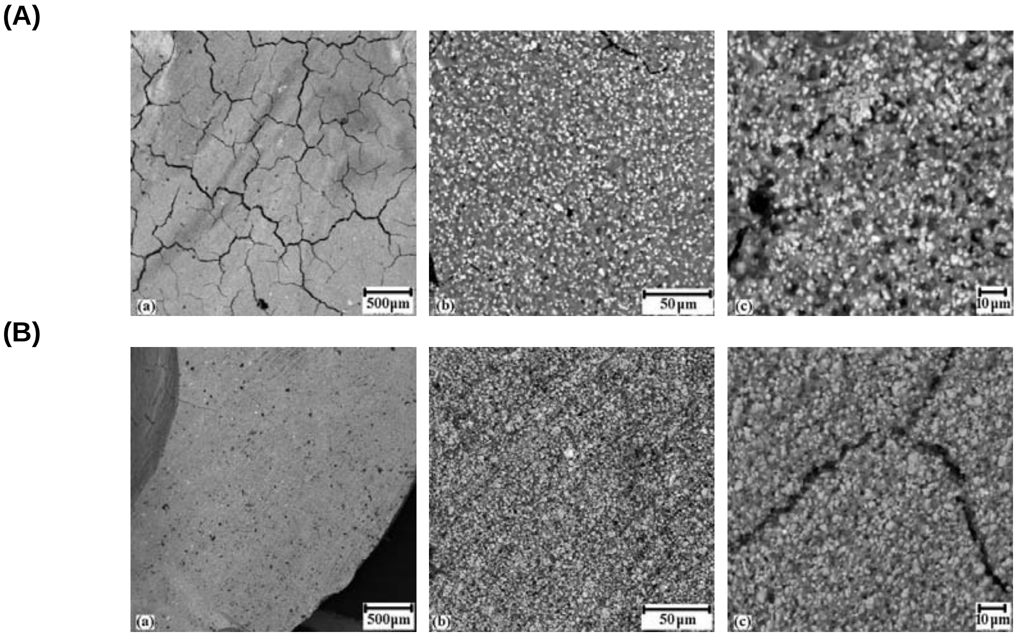

Fig.6 SEM images of Durelon (D) cement (A) before water storage and (B) after 35 days of water storage: (a) surface (x35), (b) surface (x500), (c) fractured surface (x1000).

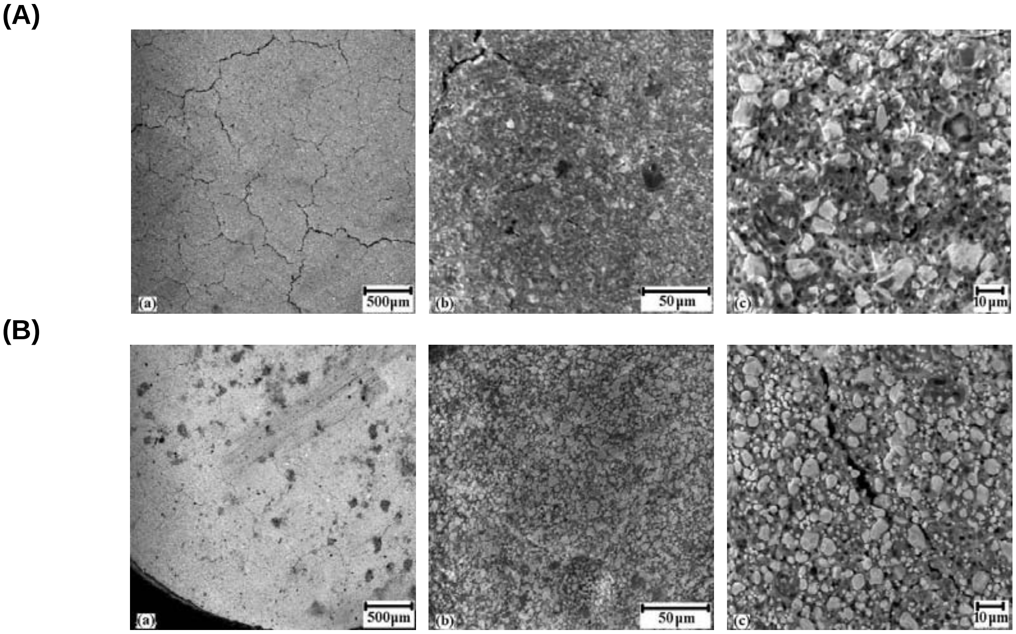

Fig.7. SEM images of Poly F Plus (PF) cement (A) before water storage and after 35 days of water storage: (a) surface (x35), (b) surface (x500), (c) fractured surface (x1000).

The results showed that P cement was significantly harder measured than the other materials tested after 1 day of storage but same cement showed significantly smaller values at 35th days of storage in distilled water. The D material displayed a significantly lower hardness than that shown by the other two cements values at 35 days of storage in water; nevertheless, its hardness values was close to AC material after 35 days in water. Within the four commercial zinc polycarboxylate cements, only PFP cement showed a significant increase after 35 days of storage in water. P cement was significantly harder at 1 day than others, but decreased significantly after 35 days of water storage.

The compressive strengths of all cements used in this study considerably increased in distilled water. Durelon (D) and Poly F Plus (PFP) cements showed the higher values than others, whereas Adhesor Carbofine (AC) and Polycarboxylate WP (P) showed lower values. The changes of compressive strengths were effectively the same (~46%).

The free and fractured surfaces of commercially polycarboxylate cement disks before and after immersion in distilled water for 35 days were shown in Figs. 4-7. The surfaces of the cements before immersion were relatively smooth, the cement having been hardened between two parallel glass plates. After immersion in distilled water, all of the cements except of PFP had rough surfaces, with many cement particles were not seen on the surface (Fig. 7b). There were cracks and many small voids on the surfaces of all cements. Many small voids were seen on the surfaces of D and PFP materials (Fig. 6 and Fig.7).

Water sorption (μg/mm^3), volume change (ΔV%), hardness (HV) and compressive strength (MPa) of zinc polycarboxylate cements were listed from high to low value: AC>P>PFP>D for water sorption; AC>P>PFP>D for volume change; PFP>AC>P>D for hardness and D=PFP>AC>P for compressive strength.

4. Discussion

The main purpose of this study was aim to investigate the effect of water absorption on the mechanical properties of four commercially available zinc polycarboxylate cements for 1 and 35 days of water storage. The polycarboxylate cements evaluated were chosen based on their different formulations and popularity.

The water sorption and mechanical properties of dental restorative materials are of considerable clinical importance. Most of the studies were compared among different dental cements about water absorption [6,23,24,27-29] and mechanical properties [3,5,14,15,17-26,29], but there is no comparison between different polycarboxylate cements up to now.

The present results showed that commercial dental polycarboxylate cements absorbed most of the water with in 1st day of water storage. They continued to absorb the water at a slower rate for 28 days until equilibrium was reached (Fig. 1). As shown in Table 2, the water sorption of D cement was rather less than that from AC, P and PFP cements. The same result was also observed for the values of volumetric change. The results of this investigation showed that the water absorption of the commercial dental polycarboxylate cements was significantly depend on material composition. The oxide particles in the polycarboxylate matrix considerably improves some of its properties. The water absorption of all cements were roughly the same against time (Fig. 1). AC absorbed a considerable amount of water compared to P, PFP and D cements. As shown in Table 1, the powder composition of AC cement is different from others and contains Al_2O_3 and B_2O_3 in addition to ZnO and MgO but it no contains dried poly(acrylic acid).

Zinc polycarboxylate cement is a water-based material that hardens following an acid-base reactions between zinc-rich powder and an aqueous solution of poly(acrylic acid) [5]. The hydrophilic nature of a polymer is a function of the chemistry of its monomers and polymerization linkages. The presence of hydroxyl, carboxyl and phosphate groups in monomers and their resultant polymer make them more hydrophilic and more prone to water sorption [28]. When zinc oxide and polyacrylic acid are mixed, hydrated proton formed from ionization of the acid attack the zinc and magnesium cations which form polycarboxylates that crosslink the polymer chains. The result is a zinc polycarboxylate crosslinked polymer matrix in which unreacted zinc oxide particles are embedded [7]. These cements include water in their formulation. The poly(acrylic acid) is typically used as a solution at a concentration of about 35%-45% by mass, though it may alternatively be employed as a dry powder, with the necessary amount of powder being added to the cement at the mixing stage. This water becomes fully incorporated into the cements as it sets, there being no phase seperation. In the solid state, this water can occupy various locations, for example co-ordination sites around Zn^{2+}, Mg^{2+} and Al^{3+} ions or hydration regions around the polyanion chain[23] .

The water sorption is certainly facilitated by the chemical composition of the materials. The basic constituents of polycarboxylate cements, polyacrylic acids and ion leachable powders, bond water molecules. This also the case of the salt products of the acid-base reaction. Moreover the crosslinked polymeric matrix formed by polymerization of monomers.

The microhardness measurements of zinc polycarboxylate cements showed that the PolyF Plus (PFP) and Adhesor Carbofine (AC) were harder than 3M Durelon (D) and Polycarboxylate WP (P) in distilled water at 37°C during 35 days. The powder composition of P cement is similar to D and they showed similar values after 35 days.

The intercrossing between the Zn^{2+} and Mg^{2+} ions with the polyacrylic acid reaches its maximum value at 1 day, therefore, a certain stability in some of the mechanical properties can be deduced after 1 day. The hardness measurements reflect an increase in the surface microhardness of the PFP, AC and D after 35 days of storage. These results are possibly related to the presence of a solid polycarboxylate phase around the non-reacting zinc oxide (or other metal oxides) responsible for the hardening throughout the time. P cement reached maximum hardness at 1 day but after 35 days of water storage, it exhibited a significant decrease. P cement showed a significantly greater microhardness at 1 day than at 35 days. If the cement matrix contain the large amounts of functional hydrophilic groups, the matrix will be absorbed a large quantity of water. In this case, the matrix will expand and produce a plasticizing effect resulting in a decrease in microhardness. Hardness measurements were denoted significant differences the initial and final values of PFP and AC. This increase was attributed to the different compositions and concentrations of the powder and liquid parts of these materials. The microhardness of PFP, AC and D cements increased significantly for 1 and 35 days.

Fig. 3 shows results for compressive strengths of the polycarboxylate cements. There are significantly differences between compressive strengths of materials. P cement was weaker than others when stored in water for 1 day and 35 days. D and PFP cements had aboutly the same compressive strengths. Average compressive strength of the AC cement was found between PFP and P cements.

Figs 4-7 show the free and fractured surfaces of AC, PFP, P and D cement disks before and after immersion in distilled water for 35 days. The free and fractured surface characteristics of disks for each cement are quite different in distilled water. The free surfaces of the cements before immersion were quite including the cracks (Fig. 4A-a, b - Fig. 7A-a,b), but after 35 days of immersion, except of AC and P, the surface cracks of the cement disks quite decreased (Fig. 4B-a - Fig. 7B-a). The AC, PFP and P cements had rough surfaces with many cement particles exposed (Fig. 4B-b - Fig. 7B-b). The surface of D cement was very smooth, although there were large cracks on the fractured surface (Fig. 6B-c). P and PFP cements showed same surface features as shown in Fig. 5B-c and Fig. 7B-c. Many small voids were seen on the fractured surfaces of AC and D cements (Fig. 4B-c and Fig. 6B-c).

The cement matrix and powder particles were simultaneously dissolved and the surface became rough. Many powder particles were exposed on the cement surfaces. The driving force of the dissolution is both H^+ ion attack and the complex formation of these cations in the cement. The extent of matrix erosion was determined by the differences of the crosslinking of carboxylate ions by Zn^{2+} and Mg^{2+} (or Al^{3+}) in the matrix and unreacted powder particles. The surfaces of polycarboxylate cements showed that the matrix areas of the cements were eroded through the unreacted oxide particles. The matrix of P and PFP seemed to be eroded more severely than those of AC and D. This fact explains the effect of the surface reaction to the dissolution. The matrix was highly stable compared to unreacted particles. The matrix of P seemed to be less stable than those of AC, PFP and D cements (Fig. 4B-c - Fig. 7B-c), probably because the composition of the liquid components were different each other.

5. Conclusions

This study showed that water sorption, microhardness and compressive strength of four polycarboxylate cements are depend on cements' composition and hydrophilicity. PFP and D cements are more resistance to degradation than AC and P. There was not significant difference between the PFP and D cements in regard of compressive strength. AC cement showed more water sorption than the other cements. Among polycarboxylate cements evaluated, D cement exhibited the least sorption than did PFP, P and AC cements. It was found that Durelon and Poly F Plus cements were the most stable materials for sorption and mechanical properties.

Water sorption ($\mu g/mm^3$), volume change ($\Delta V\%$), hardness (HV) and compressive strength (MPa) of zinc polycarboxylate cements were listed from high to low value as below: AC>P>PFP>D for water sorption; AC>P>PFP>D for volume change; PFP>AC>P>D for hardness and D>PFP>AC>P for compressive strength.

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References

[1] D. A. Milutinović-Nikolić, V. B. Medić, Z. M. Vuković, Dent. Mater., Article in press.
[2] D. C. Smith, Adv. Dent. Res. **2**(1), 134 (1988).
[3] G. Øilo, I. E. Ruyter, J. Dent. Res. **62**(28), 937 (1983).
[4] R. K. Bansal, U. S. Tewari, P. Sing, D.V.S. Murthy, J. Oral. Reh. **24**, 76 (1997).
[5] D Xie, M Faddah, J G Park, Dent. Mater. **21**, 739 (2005).
[6] H.M. Widchaya Kanchanavasita and J.P. Pearson, Biomaterials **18**(4), 343 (1997).
[7] https://decs.nhgl.med.navy.mil/DMNOTES/cements.pdf
[8] N. Ewoldsen, R. S. Demke, Am. J. Orthod. Dentofacial. Orthop. **120**, 45 (2001).
[9] R.G. Craig, Restorative dental materials, (Mosby-Year Book, St. Louis, 244 (1997).
[10] T.T. Kohmura and K. Ida, J. Dent. Res. **58**, 1461 (1979).
[11] Jurecic A. Water soluble acrylic acid copolymers for dental cement. German Patent **2**, 110, 665 (1971).
[12] J. Ellis and A.D. Wilson, Polym. Int. **24**, 224 (1991).
[13] R.K. Bansal, U.S. Tewari, P. Sing and D.V.S. Murthy, J. Prosth. Dent. **73** (2), 210 (1995).
[14] L.G. Lawrance, D.C. Smith, J. Can. Dent. Assoc. (Tor) 39 (6), 405 (1973).
[15] G. Willems, J.P. Celis, P. Lambrechts, M. Braem and G. Vanherle, J. Biomed. Mater. Res. **27**, 747 (1993).
[16] A.M. Diaz-Arnold, D.W. Wistrom and E.J. Swift, Jr, Am. J. Dent. **8**, 134 (1995).
[17] Gladys, B. Van Meerbeek, M. Braem, P. Lambrechts and G. Vanherle, J. Dent. Res. **16**, 883 (1997) .
[18] Y. Z. Bayındır, M. Yıldız, The J. Contem. Dent. Prac. **5**(4), 42 (2004).
[19] S. O. Hondrum, J. Prost. Dent. **81**(4), 464 (1999).
[20] A. U. J. Yap, J. Mater. Sci.: Mater. Med. **8**, 413 (1997).

[21] J. E. McKinney, J.M. Antonucci, N.W. Rupp, J. Dent. Res. **67**, 831 (1988).
[22] H. Forss, L. Seppä and R. Lappalain, Dent. Mater. **7**, 36 (1991).
[23] J. W. Nicholson and A.D. Wilson, J. Mater. Sci: Mater. Med. **11**, 357 (2000).
[24] J. W. Nicholson, M.A. Mckenzie, R. Goodridge, A. D. Wilson, J. Mater. Sci: Mater. Med. **12**, 647 (2001).
[25] J. W. Nicholson and F. Abiden, J. Mater. Sci.: Mater. Med. **9**, 269 (1998).
[26] J. L. Drummond, J. W. Lenke and R.G. Randolf, Dent. Mater. **4**, 739 (2005).
[27] J. B. Moser, D. B. Brown, D. B. Dowling, E. H. Greener, J. Dent. Res. **54** (2), 280 (1975).
[28] J. Malacarne, R. M. Carvalho, M. F. de Goes, N. Svizero, D. H. Pashley, F. R. Tay, C. K. Yiu, M. Rocha de Oliveira Carrilho, Dent. Mater. **22**(10), 973 (2006).
[29] J.F. McCabe, S. Rusby, Biomaterials **25**, 4001 (2004).