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Mechanical properties of New Calcium Based Cement Prepared From Egg Shell

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Abstract

Aims: The study was conducted to evaluate the microhardness and compressive strength of newly prepared calcium based cement.

Materials and methods: The cement was prepared from egg shell, for microhardness test 20 Samples 8mm diameter and 4mm thickness were prepared from plastic mold, 10 samples for experimental cement (calcium based cement) and 10 samples for polycarboxylate cement which is used as a control. The samples underwent a Vickers hardness test for microhardness, and for compressive strength 20 samples dimension according to ADA specification No.96 (6mm height and 4mm diameter) 10samples for experimental cement and 10 samples for control ; their extent of reaction was characterized using FTIR spectroscopy.

Results: Statistically significant differences were identified between the cements, the calcium based cement exhibited higher mean values of Vickers hardness numbers (VHN) and compressive strength than polycarboxylate cement(control group).

Conclusions: Within the limitation of this research it was concluded that the new calcium based cement has a better mechanical properties than poly carboxylate cement.

Keywords: calcium based cement, polycarboxylate cement , microhardness, compressive strength.

Introduction

Dental cements are widely used in dentistry, Cements can be used as base material, temporary filling material and luting. There are also different types of cements developed to be used in orthodontic and endodontic treatments. [(1)] Luting cements are used in adapting the tooth to indirect restorations prepared out of mouth. [(2)] It protects the pulp from thermal, electrical and chemical effects. [(2)] Cement may be permanent or temporary, depending on their physical properties and the planned longevity of the restoration.[(3)] It is still argued that there is no ideal cement answering all purposes yet, so different materials are required for the comprehensive patient treatment and it is not always that easy to make the best choice.[(4)] Dental cements are based on mixtures of an acid and a base. The base is a solid, typically powdered zinc oxide or a special ion-leachable glass, whereas as the liquid is acidic solution, either of phosphoric acid or polyacrylic acid. The cements set by a process of neutralization reaction to give a phosphate or polyacrylate salt matrix and leave some unreacted base to act as reinforcing filler.[(1)]

Calcium based cements are currently used in dentistry for direct or indirect pulp capping, apexification, apexogenesis and root canal filling. It presents certain advantages such as antimicrobial and anti-inflammatory activities, An important requirement for operative and preventive dentistry is the development of restorative materials able to induce the remineralization of hypomineralized carious dentin (demineralized/carious dentin). At present no restorative materials with proven capability to induce dentin remineralization are available on the market. [(6)] Surface hardness is one of the most important properties of restorative materials because the surface of the cement is considered to be directly affected by environmental conditions. [(7)] Compressive strength testing is the most commonly employed method to evaluate the strength of these materials. [(8)] Egg shells are waste materials from hatcheries, homes and fast food industries and can be readily collected in plenty.

The composition of the egg shell is approximately 98.2% calcium carbonate 0.9 % magnesium and 0.9% phosphate. [9,10] So egg shell is a rich source of mineral salts, mainly calcium carbonate. Eggshell calcium is probably the best natural source of calcium it is a much better source of calcium than limestone or coral sources. [9] Aim of the study was to prepare anew calcium based cement material prepared from the egg shell and evaluate its mechanical properties through hardness and compressive strength testes.

Materials and Methods

Preparation of the tested material:

The powder of the material consists of

1. Calcium oxide, which is prepared from chicken egg shell, the egg shell cleaned in tap water firstly, then remove of the internal protein layer from the shell after that the shell crashed and heated to 900°C (1173 K) for one hour by furnace (Manfredi / Italy), at this temperature the shell becomes porous, fragile and very white in color. It is concluded from this fact that the egg shell $CaCO_3$ decomposes (decarbonation process) and gave CaO and CO_2, according to the reaction:
   $CaCO_3 \rightarrow CaO + CO_2$ [11]
   (100grams of egg shell give us 64 grams of CaO).

2. Hydroxy appetite prepared from eggshell
   It was synthesized according to (Taqa and ALSandook 2002) [12] by the slow addition of 0.6M Phosphoric acid (H_2PO_4) to the aqueous (molar ratio) suspension of Calcium carbonate ($CaCO_3$) under constant stirring. The resultant was filtered and dried at 50°C for 3 hours then sintered in air atmosphere at 1100°C for 2 hours. To obtain principal hydroxyappettite, critical control of the pH of the reaction and concentration of the reactant is required. [11]

3. Magnisium oxide (BDH/ England).

4. Bismuth oxide (Alfa Aesar/Germany).

5. Calcium acetate (Alfa Aesar/Germany).

6. Liquid: polyacrylic acid (tg ,England).

The powder of the tested material composed mainly from calcium oxide (70%) magnesium oxide (25%), Hydroxy appetite (3%), calcium acetate (0.5%) and bismuth oxide (1.5%). The powder particle size was standard in size using 25µm sieve, the mixture was mixed using grinder.
The powder \liquid ratio were determined by trial 1p\1L, 2P\1L ,1P\2L and 1P\3L ratio by volume, were done and evaluate the setting time and the micro hardness test, the ratio of 1\1 by volume was the perfect ratio give acceptable working time and harder than the other so this ratio will be used in this study.

Mixing, Working, Setting Time

Mixing Time: That part of the working time required in order to obtain a satisfactory mix of the components.

Working Time: Period of time, measured from the start of mixing, during which it is possible to manipulate a dental material without an adverse effect of its properties.

Setting Time: Period of time measured from the end of mixing until the material has set.

Setting time of the material was measured under controlled temperature and humidity (37°c +-1 °c and 95 +- 5 % relative humidity), the materials were mixed and inserted in metallic ring molds (10mm diameter and 4mm thick)

According to ANSI/ADA Specification No. 96 for dental water-based cements. Three specimens were made, 90 seconds after end of mixing lower the indentor vertically onto the surface of the cement and allow it to remain there for 5 s. each

specimens was indented using standard gillmore needle (Maruto /japan),using 113.5 gram gillmore needle with tip diameter (2.12mm) for determining initial setting time.

While for final setting time it obtained using a 456.5 gram gillmore needle (tip diameter 1.06mm). carefully lowered the indentor vertically to the horizontal surface of the cement.

This will be repeated at half-minute intervals. The time of setting is the number of minutes elapsed from the starting of the mix to the time when the needle fails to make a perceptible circle on the surface of the specimen when viewed using x 2 magnification. Clean the needle, between indentations. The setting time will be reported to the nearest minute. [13]
Mixing time was: 40seconds.
Working time: 2miutes.
Setting time: 4.5minutes.

Formation of cement:

The formation of cement passes through the reaction between acid-base reaction the acid is poly acrylic acid figure (1) and the base is CaO to form calcium polyacrylate.

(a) (b)

n = number of repeated monomer

Figure (1): The structure of (a) mono and (b) poly acrylic acid.

The reaction forms a stable white complex of calcium polyacrylate as suggested structure in Figure (2).

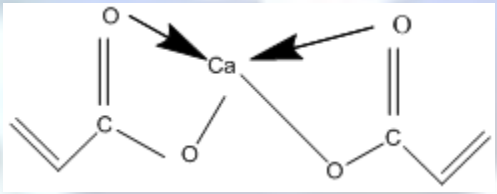

Figure (2): Calcium polyacrylate complex.

This structure was confirmed by FTIR spectra (Using alpha Bruker spectrophotometer,Germany), as shown below:

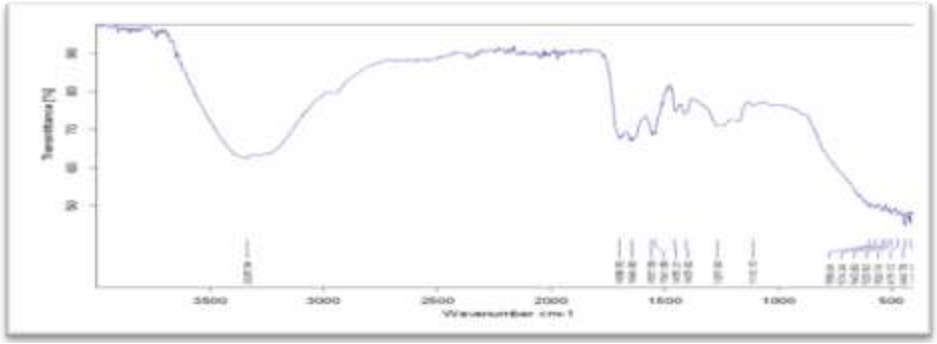

Figure (3): FTIR spectra of Liquid of experimental cement before reaction.

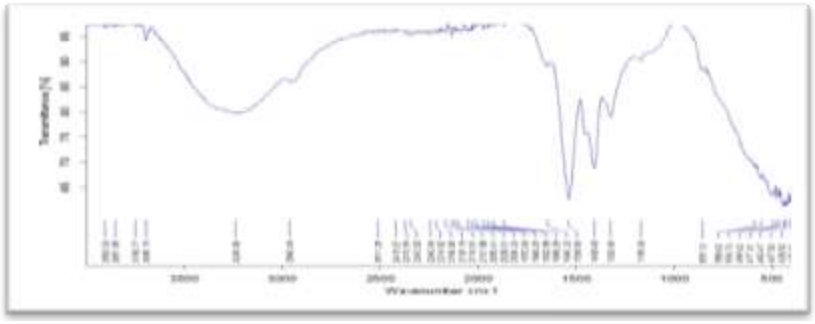

Figure (4): FTIR spectra of Powder of experimental cement before reaction.

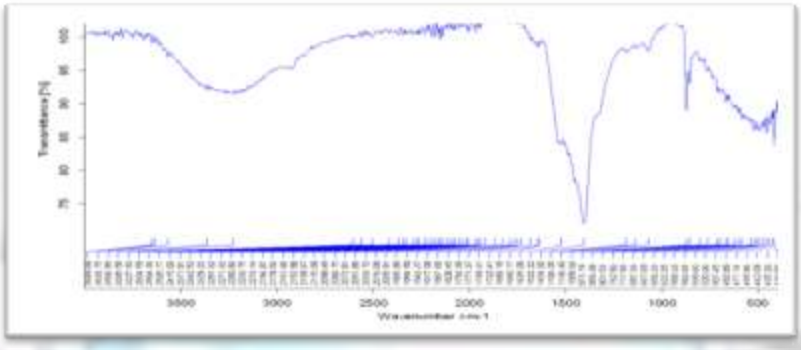

Figure (5): FTIR spectra of experimental cement after reaction of powder and liquid.

Microhardness Test:

Samples were 8mm diameter and 4mm thickness prepared from plastic mold the cement was mixed and poured inside the mold between 2 glass plates and the molds were stored in the 37^0C incubator for 1 h, and then the specimens were removed from the molds and immersed in distilled water at 37^oC for 23 hours. (The time lapse between the starting of the mixing and the test was 24 hours). Ten specimens were fabricated for each group, Group I (10 specimens for experimental group calcium based cement) and Group II (10 specimens for control group zinc polycarboxylate cement). in a total of 20 specimens.

After complete setting the specimens were polished with silicon carbide (SiC) papers (800-, 1000-, 1500- and 2000 grit paper).

Then each specimen positioned centrally beneath the Vickers microhardness tester (Wolpert/Germany) to calculate the Vickers hardness number (VHN).

A diamond indenter with a 9.8 N load and a dwell time of 45 seconds was used. Each of the 10 specimens was indented, the average of three indentations, made at least 100 μm apart on the surface of each specimen was determined, only specimens with indentations on their surfaces that were sufficiently sharp to obtain accurate diagonal lengths were included in the analysis of data.[14, 15]

The Vickers hardness number for each specimen was calculated according to the following equation:

$$VHN = \frac{1.8544xL}{D^2}$$

Where L = applied load (kg), and d = mean diagonal length (mm).
Where the Vickers hardness number (VHN) has units of kg/mm^2. (Figure 6).

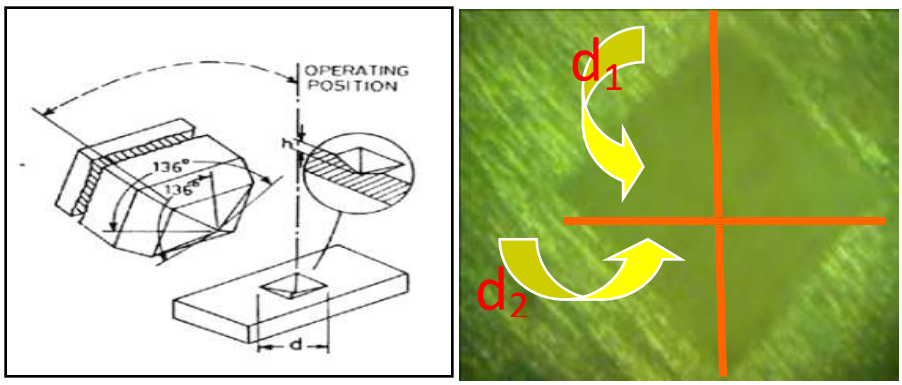

Figure (6): Vickers microhardness indentation on cement surface.

Compressive strength Test:

Compressive strength is the maximal stress required to fracture a structure, it's considered to be important in restorative dental materials, and this test is the most commonly employed method to evaluate the strength of these materials. Specimen dimensions: 6 mm x 4 mm, according to ANSI/ADA Specification No. 96 for dental water-based cements. [13](Figure 7).

Figure (7): Specimens dimension (6mm x 4mm) according to ADA NO.96.

A metallic mold was made (6 mm in height and 4 mm in diameter). Ten specimens were fabricated for each group, in a total of 20 specimens. Group I (10 specimens for experimental group calcium based cement) and group II (10 specimens for control group zinc polycarboxylate cement). The metallic mold was previously isolated with Vaseline and protected at the bottom surface using a mylar strip. The materials were slowly inserted through matrix then another mylar strip was placed on the upper surface followed by a 2mm thick glass slab manually pressured to obtain a regular material surface.
Three minutes after starting the mix, the specimens were transferred to an atmosphere of 100% relative humidity at 37^{o}C, and one hour later the specimens removed from the mold and immersed in distilled water at 37^{o}C for 23 hours. (The time lapse between the starting of the mixing and the crushing was 24 hours). A small piece of blotting paper (approximately 0.5mm thick) wet with water were inserted between the ends of the specimens and the platens of Universal Testing Machine (Imada ZP , japan). Each specimen was loaded at across head speed of 1mm /minute and strength values (in MPa) were calculated from the loads at failure (figure 8).

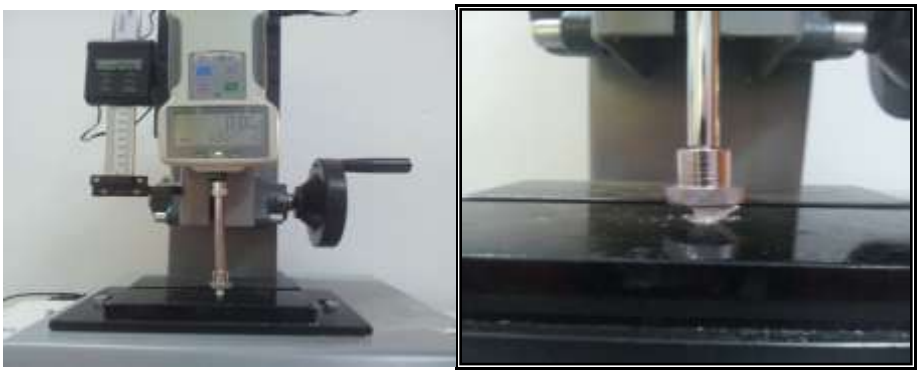

Figure (8): Imada universal testing machine used in the study

Statistical analysis:

Means and standard deviation were calculated. The student T-test was used to investigate statistical differences.

Results

The mean values of Vickers hardness numbers recorded for groups I and II were presented in (Table I). Group I (calcium based cement) exhibited higher mean values of Vickers hardness numbers (VHN) than Group II (polycarboxylate cement). Statistical analysis using student T-test revealed that there was a significant difference ($p \leq 0.05$) in the Vickers hardness number between group I and group II.(Table II).

Table (I): Descriptive show the Vickers hardness of calcium based cement and polycarboxylate cement.

Types of cement	N	Minimum	Maximum	Mean	SD
Calcium based cement	10	33	38	36.05	1.64
Polycarboxylate cement	10	23	29	26.80	2.30

SD: Standard Deviation

Table (II): Student t-test between two groups.

Types of cement	N	Mean±SD	t-value	p-value
Calcium based cement	10	36.05±1.64	8.71	<0.001*
Polycarboxylate cement	10	26.80±2.30		

* Significant at $p \leq 0.05$

For compressive strength the mean values and standard deviation recorded for groups I and II were presented in (Table III). Group I (calcium based cement) show higher mean values in compressive strength than Group II (polycarboxylate cement). Statistical analysis using student T-test revealed that there was a significant difference ($p \leq 0.05$) in the compressive strength between group I and group II. (Table IV).

Table (III): Descriptive show the compressive strength of calcium based cement and polycarboxylate cement.

Types of cement	N	Minimum	Maximum	Mean	SD
Calcium based cement	10	73	78	75.50	1.90
Polycarboxylate cement	10	53	60	56.80	2.86

SD: Standard Deviation

Table (IV): Student t-test between two groups.

Types of cement	N	Mean±SD	t-value	p-value
Calcium based cement	10	75.50±1.90	17.73	<0.001*
Polycarboxylate cement	10	56.80±2.86		

* Significant at $p \leq 0.05$

Discussion

The setting time of the experimental (calcium based cement) was 4.5 minutes which is accepted with ANSI/ADA Specification No. 96 for dental water-based cements.[13] Hardness is the ability of a material to resist a permanent indentation, hardness testing is widely used to determine the mechanical properties of materials, such hardness tests can be correlated with a number of mechanical properties like, indentation hardness has been used to study elastic modulus, creep and fracture of brittle materials. [15, 16] Surface hardness is one of the most important properties of restorative materials because the surface of the cement is considered to be directly affected by environmental conditions. [17] Strength properties of a material define as its ability to resist disintegration during function. Adequate compressive strength ensures integrity of the adhesive joint under vertical functional load, Strength properties of crystalline structures (like set cement) are related to the crystal lattice structure and resistance offered by it against forces of disintegration in a vertical (compressive).[18]

Based on the results of the present study a significant difference between the hardness and compressive strength of the experimental calcium based cement specimens and the control group (polycarboxylate cement) was observed. The improvements in mechanical properties of the experimental calcium based cement may indicate increased homogeneity and poly-salt bridge formation in the final set material. [19] Undoubtedly, stronger bonds between the organic and inorganic networks caused the increase in strength of the final set cement. By increasing the degree of crosslinking through increased poly-salt bridge formation, mechanical properties improve considerably. This in turn might make the material a better choice for posterior tooth restoration and as a bone grafting material in stress bearing areas. [20] This result suggested that the calcium ions reacted with the polyacrylic acid groups, these reactions were considered to form strong of the polyacid salt matrix. This result agrees with the result of Shiozawa et al., how concluded that the surface hardness of the GIC, after immersion in the $CaCl_2$ solution significantly increased with an increase in both the concentration of $CaCl_2$ solution and the immersion period. Immersion in a higher concentration of $CaCl_2$ solution showed a greater increase in the surface hardness. They concluded that the absorbed calcium had an effect on the increase in the surface hardness of GIC. [15]

Conclusions

Within the limitations of the experimental methods employed in the present study, the following conclusions can be drawn:

1- Calcium based cement prepared from egg shell show higher hardness and compressive strength values than polycarboxylate cement.

2- The reaction between calcium ions in calcium based cement and polyacrylic acid is considered to increase the surface hardness and compressive strength.

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