Surface Durability of Newly Glass Ionomer Cement Modified with Chitosan

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Abstract: Aim of the study: The evaluation of Surface Durability of newly developed conventional glass ionomer cement modified by chitosan. **Materials and Methods:** A total of 380 cement disks were prepared to represent 4 groups; 90 disks for each. Conventional Glass Ionomercement disks; control group, (Group 1) and other groups' disks were modified by adding chitosan solution to poly carboxylic acid liquid of GIC (v/v) in ratio of 0.25, 0.5 and 0.75/1 to represent Groups 2, 3 and 4 respectively. The disks of each group were subdivided into 9 subgroups; n=10. Working and setting time of different groups were measured. Then, water sorption and solubility were calculated after storage in distilled water (37ºC) at time intervals 72 and 168 hrs. As well, micro-hardness and surface roughness changes after different storage time intervals 24, 72 and 168 hrs for each investigated groups were measured. Surface chemistry was analyzed by XRD. **Results**: Despite the highest significant prolonged working time and setting time was recorded by Group 1 (4.76±0.41,10.79±.43min), it was insignificantly decreased in the other investigated groups. The highest water sorption was recorded by Group4 after 72 and 168 hrs (105±7.9, 41.1±29.4 µg/mm^3), but the least values were recorded by Group 1 (61.8±11.5, µg/mm3). Also, the highest water solubility was recorded by Group 4 after168hrs (196.27±58.6µg/mm^3) whereas Group 2recorded the least one (150.7±38.3 µg/mm^3). Regarding the micro-hardness, Groups 2,3 & 4 revealed lower hardness value than Group 1 after 24 hrs (50.8±2, 45.3±5.38,37.1±8.76 and 54.9±2.9VHN). Meanwhile, Groups2 and 4 recorded the highest significant surface roughness (3.2±0.99 and 2.9±0.94 µm). The XRD chemical analysisreleaved that the surface of the samples composed mainly of aluminum silicon and sodium silicon fluoride. **Conclusions**:1) Increasing chitosan amount decreased both working and setting time of conventional GIC. 2) Increasing percentage of chitosan was adversely affect water sorption and water solubility; in addition to, surface hardness. 3) Durability of GIC was adversely affected by chitosan addition.

1. Introduction

Glass ionomer cement (GIC) is one of the smart esthetic restorative materials due to its adhesiveness, anti-cariogenicity, antibacterial and aesthetic properties.[1]Unfortunately, the conventional glass ionomer (CGIC) cement had many drawbacks with moisture sensitivity during the initial setting, long setting time, water sorption, and solubility.[2-3]Water sorption and solubility of cement lead to dimensional changes, loss of retention, staining and breaking of marginal contours.[4] Water sorption and solubility of the restoration have been adversely affect the surface hardness of restoration; consequently, surface durability and longevity of restoration.[5]

Many attempts are still being made to create glass-ionomer restoration fulfill the dentist and patients demands. Some of them based on adding constituents that change the setting mechanism, decrease setting time of glass ionomer and improve strength; accordingly, serviceability of restoration. Metal-reinforced glass ionomer cement was introduced by the addition of silver-amalgam alloy powder and pure silver to conventional materials resulting in increased strength and surface hardness.[6,7]However, the adhesiveness and fluoride releasing efficiency of GIC were decreased in addition to loss of esthetic.[4]To overcome these disadvantages, resin-modified glass ionomer cements (RMGICs) were developed. Adding polymerization reaction of resin to the initial acid-base reaction decreased setting time and strengthen the cement without adverse effect on the esthetic.[8,9] On another hand, the antibacterial effect that was derived from fluoride releasing was adversely affected.[1011]

Many trials to maintain the antibacterial action of GIC restorations like addition of chitosan which acts as catalyst for more release of Fluoride ions. Chitosan is a natural linear bio-polyaminosaccharide formed by

alkaline deacetylation of chitin, which occurs naturally in the shells of crabs and shrimps. Chitosanis considered to be one of the most widely disseminated biopolymers which is biocompatible, non-toxic, biodegradable, and is inherently antibacterial in nature. [12,13]

Recently, chitosan can be used in the form of powder or dissolved liquid in acetic acid.[14] Their properties differ according to molecular weight, and number of deacylated groups [11] The null hypothesis of this investigation is that modifying GIC with chitosan liquid would improve properties such as setting time, water sorption and solubility, surface roughness and surface hardness. Thus, the current study was designed to explore the effect of using chitosan liquid to modify polyacrylic acid on the surface durability of glass-ionomer restoration.

2. Material and Methods
1.1   Samples preparation and grouping:
The materials used in this study, are Conventional Glass ionomer (CGIC) (Medicem-Promedica, Germany - PRO2438), and medium molecular weight chitosan (Sigma Aldrich, Germany-242142) prepared in form of solution. A 0.7gchitosan powder was stirred in 100 ml of 1% aqueous acetic acid by magnetic stirrer at room temperature for 24 hrs. The pH value was adjusted at pH=3.7 by Tris-buffer hydroxyl amino-methane-HCL. Then, the chitosan solution was properly sealed and stored in a refrigerator until usage.

According to manufacturer instructions, 0.12 mg powder:0.5mlpolycarboxylic liquid (1/1V) was manually mixed to prepare the CGIC cement disks; **Control group (Group 1)**. One volume of polycarboxylic acid liquid was modified by adding chitosan volumes solution (0.75:0.25, 0.5:0.5 and 0.25:0.75 v/v). Finally, one volume CGIC powder was mixed with one volume of the modified liquid representing the different investigated groups as follow:

• **Group 1**: CGIC (control group), in P/L (PCA) ratio 1:1 by v/v.

• **Group 2**: CH modified CGIC, P: L (PCA +CH); [1: (0.75:0.25)] by v/v.

• **Group 3**: CH modified CGIC, P: L PCA +CH; [1: (0.5:0.5)] by v/v.

• **Group 4**: CH modified CGIC, P: L [PCA +CH; [1: (0.25:0.75)]by v/v.

1.2   Working and Setting Time:
The working time and setting time of newly developed modified CGIC by CH solution were conducted according to ANSI/ADA specification No. 66 for dental glass ionomer cements.[15]A total 80 specimens from different investigated cement groups were prepared; 40 for working time and setting time

(n=10). The specimens of each group were mixed and placed in split Teflon mold of 20mm diameter and 1.5±0.3mm thickness. The working time measurement was carried out using an indenter of 28±0.25 g mass with a flat end of 2±0.05 mm diameter. The flat ended needle tip was cylindrical for a distance approximately 5 mm and perpendicular to the long axis of needle. Two minutes after the start of mixing the indenter was carefully applied onto the surface of the mixed cement to mark circular indention. The indention was repeated after10 seconds and with equal time intervals, until needle failed to make a complete circular indentation. Indentation area was examined by using a hand lens of magnification (X10). The time elapsing between the start of mixing to the time when needle failed to make complete circular indentation was recorded as the working time.[15]

The setting time measurements was carried out using an indenter of 400 ±5g mass having a flat end of 1.0±0.01 mm diameter applied vertically onto the surface of the mix. Two and half minutes after the start of mixing the indenter was allowed to remain there for 5 seconds. The indentions were repeated at equal time interval, each 30 seconds, until the needle failed to make complete circular indention. Indentation area was examined by using a hand lens of magnification (x10). The time elapsed until failure of indentation or to penetrate was recorded as setting time,[15]

1.3   Surface characterization by XRD:
XRD was performed in order to identify the crystalline constituents' phases and their percentage in the surfaces of cement disks. Thin film X-Ray diffractometer with a copper target (Cu k α = 1.54060) and Nickel filter (PAN analytical, X'Pert Pro, Holand) was used. The mathematical procedures were facilitated by computer software (PSI-Plot, poly software international, salt lake, UT). The data of XRD were based on Bragg's equation.[16]

1.4   Water Sorption and Solubility:
80 cement disks were prepared for water sorption and solubility testing, 20 for each group and 10 for each storing time interval; (n=10). The standard cement disks were prepared with 15 mm diameter and 1mm thickness according to ISO 4049 (1998).[17] The prepared cements surfaces were flattened and pressed with another glass slab to get rid of excess material. The set cement samples were taken off the mold. The original disks were weighed by using digital sensitive balance (M1). The disks were stored into distilled water in pre-numbered plastic tubes in an incubator at 37±1 °C for different time intervals 72hrs, 186hrs. At each selected time interval the disks were removed and dried with dry soft tissue to be free from moisture and re-weighed to record (M2). The value for water sorption was calculated for each disk by Equation 1.

Water sorption = M2-M1/v----------- Equation 1

Then, the cement disks were dehydrated in incubator at 37°C for 24 hrs, and re- weighted to record dry constant weight (M3). The value for solubility for each disk was calculated as mass lost in relation to original desiccated weight (M1). Solubility was calculated according to the Equation 2:

Solubility=(M3-M1)/v ----------- Equation 2

Where:

M1: Represented the initial mass after complete setting (3times the setting time).

M2: Represented weight after storage time intervals as dry blotted by soft tissue.

M3: Represented dehydrated weight after each storage time intervals.

V: Represented the volume of standard disk (mm^3).

1.5　　Micro Hardness Test:

All cement disks for different investigated groups were subjected to micro hardness test by using Vicker's Hardness Tester (Shimadzu, HMV-2E-Japan) after storage in distilled water at different time intervals; 24, 72 and 168 hrs.120cement disks were prepared, 30 disks for each group which subdivided into three subgroup representing each time intervals; n=10. A Teflon mold with a central hole 8 mm in diameter and 2 mm height was placed on a Mylar strip bottomed by glass slab was used in preparation of samples of hardness Cement disks were prepared, according to[7]. The mix of each group was packed in the mold then covered with another Mylar strip and pressed for 30s under another glass slab to extrude the excess material and obtain a uniform smooth specimen surface. The surfaces were coated immediately by petroleum gel varnish. The set varnished cement disks were stored in distilled water at 37ºC for 24, 72 and 168 hrs. The specimens were tested for micro-hardness under applied load300g for 15s duration.

1.6　　Surface roughness

The different cement tested groups were surveyed by mechanical contact surface profilometery. The ten disks from each group were prepared by using standard Teflon mold have 8 mm diameter and 2 mm depth, according to [7]. The mold was first mounted on top of a glass plate and a Mylar strip then a second glass plate was placed on top of the filled mold with slight pressure application. The extruded excess cement amount was removed. The prepared disks were stored in distilled water at 37 °C for 24 h. The investigated disks were properly fixed by epoxy resin, traversed by a diamond tip of stylus (with average radius 2-10 μm). The tip of stylus attached to a cantilever was drawing across the surface in the horizontal X-direction and vertical Z-direction. Profile of the surface was recorded. The average arithmetic mean (Ra) of the departures of roughness profile from the mean line was measured in μm.

1.7　　Statistical analysis

All data were collected and were statistically analyzed using one way analysis of variance and the comparison of means was conducted using Tukey's post-hoc test at P-value≤0.05. The statistical analysis was performed using Predictive Analytics Software Statistics18.0 (SPSS; IBM Company, Chicago, Illinois, USA).

3. Results:
1.8　　Working Time:

The statistical analysis of the working time of the different investigated groups is presented in tables (3-1) and figure (3-1). **Group 1** showed the highest significant working time (4.76±0.41min.), whereas **Group3** recorded the least significant one (3.59±1.2min.). On another hand, there was no significant difference recorded in working time between **Groups 2,3** and **4** (3.59±.52, 3.59±1.2, 3.60±.44min.), respectively.

Table 3-1: Descriptive statistics and test of significance of working time (min) of the different investigated groups

Groups	Mean ±S.D.	P-value
Group 1	4.76±0.41^a	
Group 2	3.59±0.52^{be}	0.02*
Group 3	3.59±1.2^{de}	
Group 4	3.60±0.44^{ce}	

Means with the same letter within each column are not significantly different at P ≤0.05.
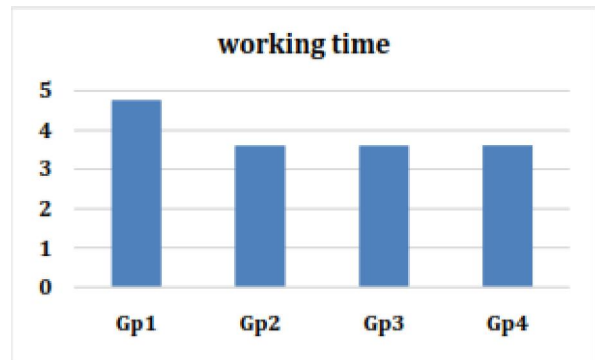

Figure3-1: Histogram for working time of the different investigated groups

1.9　　Setting Time:

The statistical analysis of the setting time among the different investigated groups is presented in tables (3-2) and figure (3-2). **Group 1** showed the highest significant setting time (**10.79±.43** min.), whereas **Group 2** was the least significant one (8.62±.86 min.). **Group 3**and **Group4** recorded values of non signficant difference in between (9.94±.55 and 9.97±.57min.) respectively.

1.10   Water Sorption:

Table 3-2: Descriptive statistics and test of significance of the setting time the different investigated groups

Groups	Mean ±S. D.	P-value
Group1	4.76±0.41[a]	
Group2	3.59±.52[be]	0.02*
Group3	3.59±1.2[de]	
Group4	3.60±.44[ce]	

Means with the same letter within each column are not significantly different at p=0.05.

The statistical analysis of the water sorption of the different investigated groups at different storage time intervals (72 hrs and168 hrs) are presented in Table 3-3 and Figure 3-3. After 72hrs storage, the water sorption of Group 1, Group 2, Group 3 and Group 4 recorded (61.8±11.5, 89.3±8.9, 82.7±9.7and 105±7.9μg/mm^3) respectively. They were significantly decreased after 168hrs, storage into (29.7±5.6

29.4±13.2 and 41.1±29. 4μg/mm3) respectively. After 72hrs and 168hrs the highest water sorption was group 4 (105±7.9, 41.1±29.4μg/mm3). On another hand, the group 1 showed the least water sorption after 72, 168 hrs (61.8±11.5, 28.7±13.2μg/mm^3).
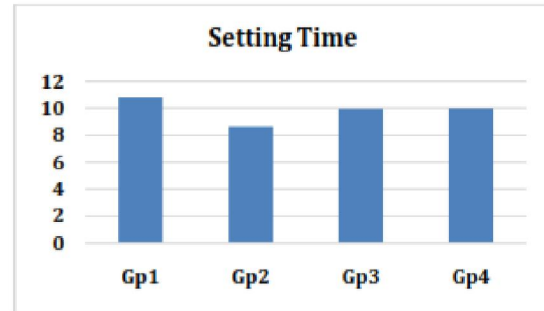

Figure 3.2: A histogram of the setting time of the different investigated groups

Table3.3: Descriptive statistics and test of significance of water sorption (μg/mm3) of the different investigated groups at different storage time intevals (72, 168hrs)

Groups	Storage Time s for water sorption				P-value among each raw
	1stinterval Mean ±S.D.		2ndinterval Mean ±S. D.		
Group 1	61.8±11.5*	a	28.7±13.2*	a	0.02
Group 2	89.3±8.9*	bd	29.7±5.6*	a	0.000
Group 3	82.7±9.7*	ada	29.4±13.2*	a	0.003
Group 4	105±7.9*	cea	41.1±29.4*	a	0.05
P-value	0.01		0.6		

Means with the same letter within each column and treatment are not significantly different at p=0.05
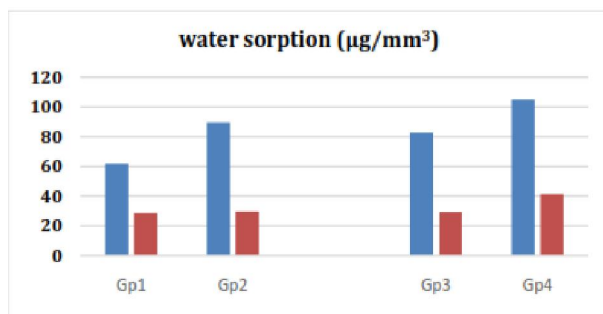

Figure 3-3: A histogram of water sorption of the different investigated groups at different storage time intevals (72, 168hrs)

1.11   Water Solubility:

The statistical analysis of the water solubility of the different investigated groups at different storage time intervals (72 hrs and168 hrs) are presented in Table 3-4 and Figure 3-4. After 72hrs storage, the water solubility of Group 1, Group 2, Group 3 and Group4; recorded (479.1±12.6, 442.9±88.9, 404.5±61.8 and 451.6±124.4(μg/mm^3) respectively.

They were significantly decreased after 168hrs storage into (159.4±39.1, 150.7±38.3,161.7±36.7and 196.27±58.6 μg/mm^3) respectively. After 72hrs, the highest water solubility was recorded by group 1(479.1±12.6 μg/mm^3) while the least one was recorded by Group 3(404.5±61.8 μg/mm^3). Whereas, the highest water solubility was recorded after 168 hrs for Group 4(196.27±58.6 μg/mm^3) and the least one was recorded by Group 2(150.7±38.3 μg/mm^3).
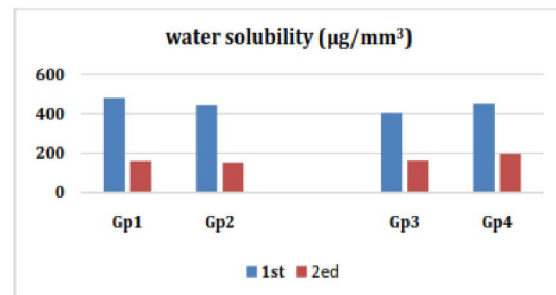

Figure 3.4: A histogram of the water solubility of the different investigated groups at different storage time intevals (72, 168hrs)

Table 3.4: Descriptive statistics and test of significance of the water solubility ($\mu g/mm^3$) of the different investigated groupsat different storage time intevals (72, 168hrs)

Groups	Storage Time intervals for water solubility				P-value
	1st interval Mean ±SD		2nd interval Mean ±SD		
Group1	479.1±12.6*	a	159.4±39.1*	a	0.000
Group2	442.9±88.9*	bd	150.7±38.3*	ac	0.000
Group3	404.5±61.8*	Cd	161.7±36.7*	a	0.001
Group4	451.6±12.4*	ad	196.27±58.6*	ab	0.01
P-value	0.05				

S.d.= Standard deviation, P= Probability level, NS= Insignificant (p>0.05), *= Significant at ≤ 0.05. ph= Post Hoc Tests Tukey HSD for the effect of storage time intervals on water sorption Means with the same letter within each column and treatment are not significantly different at p=0.05

1.12   Surface Characterization:

Table 3.5: % Surface area of crystalline phase constituents for different investigated cements groups.

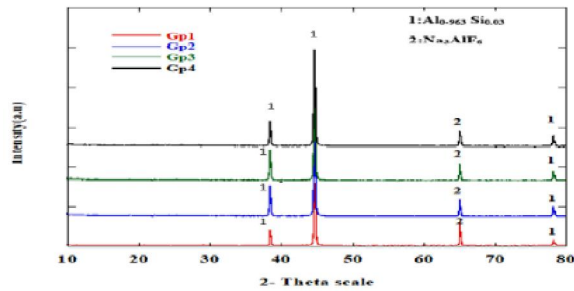| Phase	Intensity %			
	Group 1	Group 2	Group 3	Group 4
$Al_{0.963}\,Si_{0.037}$	54.39	86.06	86.06	77.81
Na_3AlF_6	45.61	13.94	13.94	22.19

Figure3-5: XRD pattern of different investigated groups 1.2,3 and 4

The constituting phases and their percent intensities of different investigated groups were characterized by XRD that are shown in figure (3-5) and table (3-5). The data were compared with International Centre for Diffraction Data (ICDD) card 04-003-7126, and 00-038-0684 for Aluminum Silicon (Al0.963 Si0.037) and Sodium Silicon Fluoride (Na2 Si F6), respectively. The maximum peak intensity 100% was found at 2θ=44.73 for Aluminum Silicon (Al0.963 Si0.037). Whereas Na3AlF6, was captured at 2 θ= 65.06844. The XRD pattern obtained for all investigated groups revealed the same crystalline structure but with different intensities of the two constituent's phases. The highest intensity value for Sodium Silicon Fluoride (Na2 Si F6) was recorded for group 1; 45.61%. Whereas the least intensity value was recorded for group 2 and 3; 13.94%.

1.13   Micro Hardness results:

The statistical analyses for the of hardness test data of different investigated groups after different storage time intervals; 24hrs, 72 hrs and168 hrs are presented in tables 3-6 and figure 3-6. The statistical analyses for the of hardness test data of Group 1 revealed increasing in the hardness number but with non-significant different throughout the different time intervals 24, 72 and168 hrs; (54.9±2.9, 55.0±3.5, 56.8±3.6 Vicker's Hardness no.) respectively. Meanwhile, Group 2 recorded a significant increase of hardness value throughout the different time intervals; (50.8±2.3, 53.6±3.6 and 54.3±4.2 VHN), respectively. On contrary, statistical analyses for the hardness test data of Group3 recorded significantly decreased hardness number after168 hrs than 24hrs; (44.8±6.7 and 45.3±5.38) VHN, respectively. Meanwhile, Group 4 showed a significant decrease in hardness number from 24 hrs to 72hrs storage (39.1±4.8, and 32.0±4.9), respectively. That was significantly increased after 168hrs storage into (40.4±8.3) VHN, respectively.

The statistical analyses of the hardness test data among different investigated groups showed that; Group 1 was the highest significant hardness number at all-time intervals 24, 72, 168 hrs. Group 2 and 3 showed lower significant hardness number than group 1 along the different time interval. On another hand, Groups 4 was the least significant one all investigated time intervals.
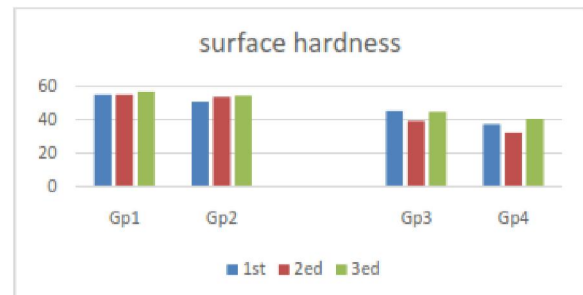

Figure 3-6: **A histogram of the effect of different storage time intervals on the surface hardness**

Table 3.6; Descriptive statistics and test of significance of the effect of different storage time intervals (24,72 and 168 hrs) on VHNof the different investigated groups

Storage Time intervals / Groups	1st interval Mean ±SD		2nd interval Mean ±SD		3rd interval Mean ±SD		P-value
Group1	54.9±2.9	A	55.0±3.5	A	56.8±3.6	A	0.3
Group2	50.8±2.3*	B	53.6±3.6*	Ab	54.3±4.2*	A	0.019*
Group3	45.3±5.38*	Cb	39.1±4.8*	Bd	44.8±6.7*	B	0.03*
Group4	37.1±8.76	D	32.0±4.9*	Bc	40.4±8.3*	Cb	0.05*
P-value	0.000*		0.000*				

Means with the same letter within each column and treatment are not significantly different at p=0.05.
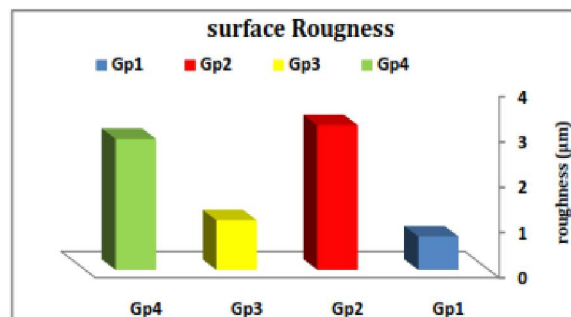
1.14 Surface roughness

The statistical analyses for surface roughness among different investigated groups are presented in **Table** and
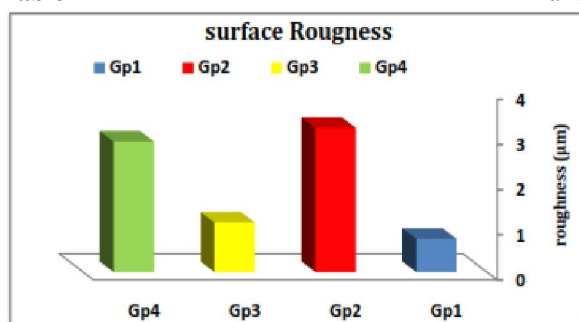
FigureV. Surface roughness of Group 1, Group 2 and Group3 group4; recorded (0.74±0.24, 3.2±0.99, 1.1±0.12, and 2.9±0.94μm^2) respectively. **Group 2** showed the highest significant surface roughness recorded (3.2±0.99 μm^2), whereas group **1** was the lowest one (0.74±0.2 μm^2). On other hand, there was no significant difference recorded in surface roughness between **group 2** and **4** (3.2±0.99, and 2.9±0.94 μm^2) respectively.

Table V.3.7: Descriptive statistics and test of significance for surface roughness (μm^2) of different investigated groups.

Groups	Mean ±SD (μm^2)		p-value ≤ among each colum
Gp1	0.74±0.24	D	
Gp2	3.2±.99	A	0.000
Gp3	1.1±.12	C	
Gp4	2.9±.94	Ba	

FigureV.3.7 Histogram show surface roughness of all investigated groups

4. Discussion

Various modifications and the developments of glass powder and polymer liquid have been introduced to improve its antimicrobial effect in turn mechanical and physical properties of GICs might be altered consequently durability[18]. The properties of a conventional GIC are influenced by the glass-powder and chemical composition of the polymer liquid. Chitosan was selected as chemical additive to modify and improve the different properties of conventional glass ionomer. Three concentrations of chitosan were selected in this study and prepared in form of aqueous solution dissolved in acetic acid to be studied after mixing with polycarboxylic acid. CGIC powder / polycarboxylic acid: chitosan liquid 1: (0.75:0.25, 0.5:0.5 and 0.25:0.75 v/v) standard tests for efficiency and their effect on the mechanical and physical properties.

The nature of setting reaction of conventional glass ionomer is an acid base reaction between the acidic polyelectrolyte and the aluminosilicate glass. poly acid released hydrogen ions that attacks glass to release poly cations and fluoride ions. These ions, probably metal fluoride complexes react with the poly-anions to form a salt gel matrix. The $AL^{+}3$ ions appear to be site bound, resulting in a matrix resistant to flow. During initial setting reaction in the first 3hours, calcium ions react with polycarboxylate chains subsequently the trivalent aluminum ions react for at least 48hrs.[4]

Addition of chitosan might be altered the working and setting time of glass ionomer. Working time is the time elapsed between starting the mix till the material can be manipulated clinically. Whereas setting time is the time from starting mixing till hardening of material.[19] In ours study, the working time of glass ionomer cement **group 1** was (4.76±0.41) min that decreased after chitosan addition regardless the percentage of chitosan. This might be attributed to the nature of CH reaction, as CH in the present study was used with acetic acid mixed with poly acrylic acid liquid. CH can be considered a strong base as it possesses primary free amino groups (NH3+) when dissolved with polyacrylic acid.[14] The reaction had taken place between amino (-NH2) group of CH and the functional group (OH group and C=O group) of GIC. Since CH possess hydroxyl and acetamide groups, they bind to hydroxyl group of powder particles and carboxylic groups of poly acrylic acid by hydrogen bonding, which decreased the working time. In addition, it may react with –Si–O–Si– units at the surface of the glass particles, leading to the formation of –Si–OH groups[20] Also, increased CH percentage might be led to rapid reaction with the same polymeric chain of chitosan and segregations of the chain especially if the concentration was same or exceeded the polyacrylic acid percentage as in group 3 and 4; CH: PAA was 1:1 and 1.5:1. These decreased working and setting time but might be affecting mechanical and physical properties.[2]

Furthermore, increased percentage of chitosan as in **Group 3,4** might be led to more increasing in viscosity of cements and rapidly hardened than free conventional glass ionomer[21] Another factor might be explained the decreased working and setting time when chitosan percentage increased which is an exothermic reaction or heat evolution. More polymeric contents are accompanied by more heat evolution might be fasten the working time and setting time.[4,22]

Increased percentage of CH in GIC was recorded the highest significant water sorption and solubility; **Group 4** at 72 and 168hrs; (105±7.9 and 41.1±29.4), respectively. When the tested samples are stored in water, two different mechanisms occur. First there will be uptake of water producing an increased weight (sorption) and leaching or dissolution of components from the material disks into the stored media (solubility) leading to reduction in weight. The property of sorption includes combination of both adsorption and absorption. Adsorption is a surface phenomenon while absorption involves penetration of liquid molecules into the structure of the solid material mainly through diffusion.[5,19] Amount of sorption and solubility depend on various factors such as type of material, composition of matrix, filler particles, efficiency of polymerization, and immersion media used as well as physicochemical nature of material surface; an Isoelectric point of material investigated and surface roughness.[23]

The high liability of chitosan for water sorption is directly affected also to different physicochemical factors include electrophoretic kinetic nature for chitosan and other ions after immersion in water that controlled by temperature and pH storage media in addition to ion concentrations precipitated in storage media.[23] CH has hydrophilic nature in polymerization linkages. In addition to the presence of amine and hydroxyl groups on the chitosan moiety, where is the most probable site for the accommodation of the additional water. The presence of hydroxyl, carboxyl groups in polycarboxylic acid and their resultant polymer make them more hydrophilic and more prone to water sorption consequently water solubility.[24]

The more water sorption was enhanced when cement was containing more percentage of chitosan exceeding the percentage of polyacrylic acid as in group 4. The segregation effect of chitosan increased the agglomeration of amino groups that were positively charged. Consequently, OH^- ions adsorbed to cement disks and H^+ increased away led to lowered pH value of storage media.[23] The sorbet water acted as a plasticizer, separated the polymeric chains consequently reduced their bond strength hence the solubility was increased.[25]

Increased chitosan addition to glass ionomer, decreased the surface hardness. **Group 1** was recorded the highest significant hardness number at all-time intervals 24, 72, 168 hrs storage among all groups, whereas group 4 was the least one. Hardness is a surface property represented the resistance of scratch and indentation of the surface.[5] This might be due to all the above discussed factors; the nature of setting reaction, water sorption and solubility. Conventional glass ionomer has an acid-base reaction that occurs in a slow and continuous manner. This reaction, which forms the cross-link of polycarboxylate chains, is a continuous process and lasts for 48hrs, consequently hardness developed by time in agreement with[26 & 27]. The final microstructure of CGIC is formed mainly from unreacted glass particles surrounded by silica gel embedded in multi poly cross linked ions matrix. Glass particles have high hardness.[19] These results were assured by XRD results as group 1 showed the highest percentage of inorganic crystal 45% more than other groups, nearly about 50% from matrix. On another hand, when chitosan was added, the polymeric structure was incorporated into the matrix network on expanse of inorganic crystals. Polymers have lower surface hardness than glass particles. Consequently, the surface hardness adversely affected by increasing chitosan%, in agreement with.[28]

Furthermore, the decreased surface hardness was adversely affected by increased water sorption and solubility that were accompanied the high chitosan percentage. Where group 4 was recorded the highest water sorption, it revealed the least hardness number among all different groups at all-time intervals; (39.1±4.8,32.0±4.9 and 40.4±8.3 VHN).[28]

Surface roughness is one of the most important surface properties with clinical prevalence and further clinical success of any restoration. Smooth surfaces can increase the wear resistance of surface, in addition to aesthetic aspect of restorative materials might be improved. On the other hand, rough surfaces allow proliferation of many caries-inducing microorganisms and plaque retention causing gingival irritation.[29]

In our study, **group 1** was the least significant surface roughness recorded (0.74±0.2μm) whereas **group 4** was the greatest one (2.9±0.94μm). Many factors can control the surface roughness of glass ionomer restoration as, particles homogeneity, size, shape and their distribution in matrix. Among the different investigated groups, the microstructure of **group 1** was the least heterogeneous one, whereas the chitosan containing matrix was heterogeneous in nature. In addition to the higher viscosity nature when percentage of chitosan increased. As the percentage of chitosan increased, the viscosity of matrix increased due to develop of polymerization process. During the progress of viscosity, the structure might be incorporated voids consequently micro-roughness, this assured from decreased working time rather than CGI; (4.76±0.41 and 3.60±.44min), respectively. Furthermore, the manual mixing of powder and liquid of glass ionomer cement might allow the incorporation of air bubbles during mixing.[30] The conventional GIC is usually supplied as a powder and polyacid liquid. When the polyacid is present in solution, an increase in the viscosity of the liquid occurs, making the cement paste progressively more difficult to manipulate.[4]

Whereas group 4 and 3 have higher chitosan and higher viscosity during mixing due to progress of polymerization process, they possessed more liability for voids incorporation, consequently more micro-roughness compared to group 1, in agreement with[31]. Solubility might be other contributing factor that encouraged the surface roughness in glass ionomer restoration. Group 4, recorded the highest solubility value on contrarily to group1[7].

It was obviously that in the present study, there was no linear regression found between surface roughness and hardness, so it can be concluded that the surface roughness of GICs might be affected by other factors like the discussed rather than their surface harnesses.[7,32]

The null hypothesis of this investigation is that using chitosan liquid to modify poly-acrylic acid liquid might decrease setting time, improve water sorption and solubility hence surface hardness will increase and roughness will decrease. The addition of chitosan would be decreased the working and setting time but adversely affected water sorption and solubility in addition to surface hardness. Thus the null hypothesis was partially rejected.

Conclusion:

Under limitation of this study, the following can be concluded: when CH: PCA up to (0.25:0.75), (0.5:0.5) and (0.75:0.25).

• Increasing chitosan amount decreased both working and setting time of conventional glass ionomer cement.

• Increasing chitosan amount adversely affected water sorption and water solubility in addition to surface hardness.

• Generally, addition of chitosan in liquid form to PAA has detrimental effect on surface durability on GI.

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