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The effect of applying a new formulation of $CaCl_2$ on surface hardness of conventional glass ionomer (In-vitro Study)

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ABSTRACT

Background: Glass ionomer cements (GIC) have excellent biocompatibility and fluoride release properties; however, they suffer from moisture sensitivity and low mechanical properties. Calcium chloride ($CaCl_2$) in solution form improved the surface hardness of GIC. Some authors suggested the preparation of a new formulation of $CaCl_2$ to be more stable in application. Surface hardness was measured at baseline and after the pH-cycling protocol. ***Aim of the study:*** To evaluate the effect of $CaCl_2$ application in both solution and gel forms on the surface hardness of the GIC at baseline and after pH cycling. ***Materials and Methods:*** Thirty disc-shaped specimens were prepared from Fuji IX GIC and divided into three groups according to different surface treatments, (n=10); group 1 (control), group 2 ($CaCl_2$ solution) and group 3 ($CaCl_2$ in gel form). pH-cycling protocol was done for all specimens using 5% acetic acid (pH=3) twice /day, rinsed, dried and then stored in distilled water. This protocol was thus repeated for 14 days. Surface hardness was measured twice, at baseline and after pH-cycling. ***Results:*** At baseline and after pH-cycling, the control group showed the lowest mean hardness. Two other $CaCl_2$ gel and $CaCl_2$ sol. showed insignificant differences between each other. pH-cycling resulted in a significant decrease in surface hardness in all groups compared to baseline. ***Conclusions:*** Both $CaCl_2$ forms improved surface hardness of self-setting GICs. Yet, handling the gel-form was easier. pH-cycling protocol deteriorated the surface hardness values of all groups.

Keywords: Calcium chloride, Fuji IX, Glass ionomer cement, pH-cycling, Surface hardness.

INTRODUCTION

In the early 1970s, in clinical dentistry glass ionomer cements (GICs), water-based cements, were discovered and broadly used as restorative and preventative materials.[1]

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Due to their anti-cariogenic properties, good biocompatibility, similar thermal coefficient of expansion to that of dentin and chemical adhesion to dentin and enamel. GICs were preferred as restorative dental materials for treating incipient caries lesions, specifically in high caries-risk patients such as children.[2–7]

However, GICs are vulnerable to humidity, leading to low initial surface hardness. As a result, the development of their final strong structure is always postponed.[8,9] A weak, porous, and soft cement prone to surface fissures occurs from water contamination and inadequate setting reactions during the first stage of GIC setting, lowering its wear resistance and surface hardness.[10]

The cross-linking of polyalkenoic acids' carboxylate groups with Ca^{2+} (Calcium) and Al^{3+} (Aluminum) ions produced from glass particles is the main setting reaction of GIC. Accordingly, different methods were employed to improve the setting reaction of the GIC, aiming to enhance different mechanical and physical properties.[11,12]

Previous studies,[13-15] mentioned that the concentration of Ca^{2+} on the restoration's surface should be increased for the acid–base reaction's improvement between both the carboxylate groups (–COO−) of the polyalkenoic acids and Ca^{2+} of the glass particles of the cement, thus raising the crosslinking potential and improving different mechanical properties, such as: surface hardness.

Surface hardness is an indicator of the mechanical properties of the GIC that predicts the wear resistance and survival of the material. Therefore, it is expected that if the surface hardness is decreased, the longevity of the restoration would be directly affected by the oral environmental conditions.[16]

Calcium chloride ($CaCl_2$) has been previously used as a liquid component with the introduction of the modified calcium silicate-based materials (Biodentine). It served as a hydrosoluble polymer and water-reducing agent, thereby accelerating its setting time. In fact, as an accelerator, it helped in solving the problem of slow setting time of the other capping materials as MTA.[17]

This led to the acceptance of the idea of using this chemical agent in other materials that suffer from slow setting reaction as glass ionomers by other researchers, such as **Dionysopoulos** D. et al.[18] and Shiozawa M. et al.[19] They found that the chemical enhancement methods, by the application of $CaCl_2$ solution on the GIC, showed positive results in improving the performance of GIC during setting, enabling faster and superior - mechanical properties.[20-22]

However, they recommended using a gel form of $CaCl_2$ in higher concentrations to give better results and to be more stable during handling. So, it was an opportunity to prepare a new formulation in a gel form to test its efficiency compared to the sol form. Moreover, Menne-Happ U. et al.[23] also acknowledged that a longer period of application and a higher concentration of $CaCl_2$ solution could raise the calcium absorbed amount inside the cement, leading to a surface hardness increase. Accordingly, 42.7 weight % $CaCl_2$ in both solution and gel forms were applied on the top surface of the GIC for 2 minutes. The new $CaCl_2$ gel formulation was prepared in the Inorganic chemistry labs of the Faculty of science, at Suez Canal University. Therefore, the aim of this study was to compare the effect of Calcium chloride solution and Calcium chloride gel on the surface hardness of conventional Fuji IX GIC twice, at baseline and after pH-cycling.

The null hypothesis of the current study was that there would be no differences between the surface hardness of conventional glass ionomer setting reaction treated by Calcium chloride solution, and Calcium chloride in gel form in the enhancement of the GIC surface hardness.

MATERIALS AND METHODS

Materials:

A conventional GIC (shade A3.5) was tested in this investigation **(GC Fuji IX GP®, GC, America).**

Calcium chloride gel preparation:

The gel form was prepared by dissolving Carbopol 940 polymer in 50 ml distilled water and gelatin powder in another 50 ml of warm distilled water containing anhydrous $CaCl_2$, then mixing them with $CaCl_2$ for 2 hours. The final gel was then stored in tightly closed sealed syringes and kept safe in the refrigerator until being used.

Specimen preparation:

30 disc-shaped specimens, 6 mm in diameter and 2 mm in thickness, of **GC Fuji IX GP®, GC America,** were prepared using cylindrical Teflon molds. Each capsule was activated and mixed for 10 s (recommended time) by an amalgamator **(IMIS-M3, Macao, China).** The material was injected immediately into the mold after being loaded onto a glass ionomer applicator. A polyester strip (0.05 mm thick) was placed onto a glass slab, before mixing the cement, then the mold was placed over it to produce a standardized surface finish and to remove excessive materials. After setting, for test and control

groups, the specimens were removed from the mold and the material's excess around the edge of the mold was removed carefully using a surgical blade. The specimens were then examined from the top surface under an optical microscope (×10 magnification) to ensure they contained no air bubbles or cracks. Subsequently, specimens were stored in plastic containers containing deionized water at 37 ± 1 °C for 24 h in order to complete the greatest part of the GIC setting reaction.

Experimental groups:

The specimens were distributed randomly into 3 groups, 10 specimens each. After mixing, Group 1 (control) specimens were left to set in the mold without any treatment. In Group 2 (Calcium Chloride ($CaCl_2$) solution) 42.7 weight % $CaCl_2$ solution was applied on the top surface of the GIC specimens for 2 minutes during setting and then rinsed. Finally, In Group 3 (Calcium Chloride ($CaCl_2$)) in gel form), specimens were rubbed with $CaCl_2$ gel on the top surface of GIC for 2 minutes during setting and then rinsed. **Figure (1)** showed both forms of $CaCl_2$.

Evaluation of surface hardness:

The surface hardness of the specimens was evaluated at baseline and after pH-cycling. It was determined at baseline using a

Figure (1): a) $CaCl_2$_Sol. **b)** $CaCl_2$_Gel.

Digital Display Vickers Micro-hardness Tester **(Model HVS-50, Laizhou Huayin Testing Instrument Co., Ltd. China)** with a Vickers diamond indenter and a 20X objective lens. A load of 100g was applied to the surface of the specimens for 15 seconds. Three indentations, which were equally placed over a circle and not closer than 0.5 mm to the adjacent indentations, were made on the surface of each specimen. The diagonals' length of the indentations was measured by a built-in scaled microscope and Vickers values were then converted into micro-hardness values.

Micro-hardness calculation:

Micro-hardness was obtained using the following equation:

HV=1.854 P/d²

$$HV = 1.854\ P/d^2$$

Where, **HV** is Vickers hardness in Kgf/mm^2, P is the load in Kgf and d is the length of the diagonals in mm.

pH-cycling:

Specimens were exposed to 5% acetic acid as an erosive medium twice daily for 10 min, for a period of 14 days. **Waterproof pH Meter and Temperature Tester Adwa (AD11), Hungary** was used to measure the acidic pH. Acidity measurements were performed once and then rinsed. The mean pH of acetic acid was 3. Following each erosive pH-cycle, the samples were rinsed and kept at 37°C in distilled water until the following erosive pH-cycle. The samples were sent to be re-evaluated for surface hardness after the 14-day pH-cycling.

Statistical Analysis

Data were presented as mean and standard deviation (SD). Data were explored for normality using Kolmogorov-Smirnov and Shapiro-Wilk tests. Two-way ANOVA

was used to compare between tested groups and the pH-cycle followed by pairwise comparison with Bonferroni correction. $P \leq 0.05$ was used at a significant level. Statistical analysis was performed with IBM SPSS Statistics for Windows, Version 26.0. Armonk, NY: IBM Corp.

RESULTS

Table (1) and **Figure (2)** showed statistically insignificant differences between

Table (1): Mean and SD for Hardness for different tested groups.

		Control		$CaCl_2$ gel		$CaCl_2$ sol.		p-value
		Mean	SD	Mean	SD	Mean	SD	
Microhardness	**Baseline**	46.44^{a}	1.26	48.96^{b}	2.00	48.37^{b}	1.53	0.007*
	pH Cycle	42.38^{a}	1.45	45.77^{b}	1.87	45.50^{b}	1.18	0.005*
	p-value	<0.001*		0.003*		0.007*		

**: significant at p ≤ 0.05.*
Different letters within each row indicate significant differences.

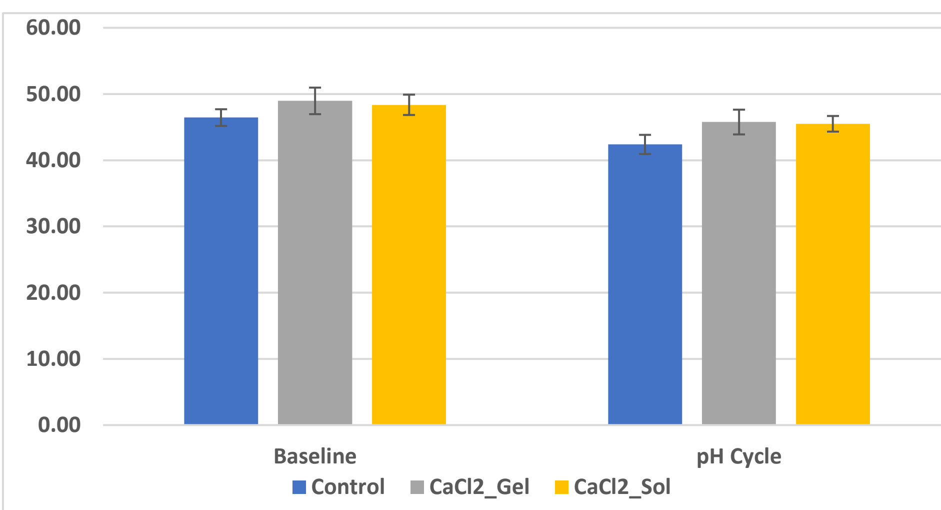

Figure (2): Bar chart showing the mean values for different tested groups.

tested groups, at baseline. Comparing the control group to the other two test groups, the control group displayed the least significant mean hardness. After pH-cycling, the surface hardness significantly decreased in all groups, as shown in **Figure (3)**. The control group showed the lowest significant mean hardness compared to all groups while $CaCl_2$ gel, and $CaCl_2$ sol showed insignificant differences.

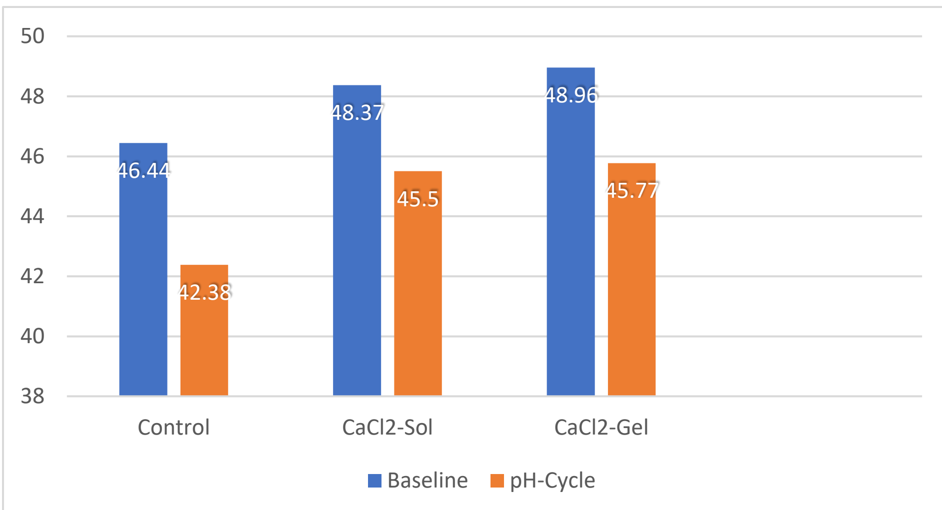

Figure (3): Bar chart showing the mean values for the pH cycling.

DISCUSSION

Chemical enhancement of the GIC properties with the application of calcium chloride in solution form has been proved to increase the mechanical properties of the glass ionomer restorations as $CaCl_2$ solution can raise the calcium absorbed amount inside the cement, leading to a surface hardness increase. A gel form was recommended by previous researchers,[18,24,25] in order to be more stable and interact more with the restoration's surface.

Therefore, in the current study, a higher concentration of $CaCl_2$ (42.7 weight %) was used for a longer period (2 minutes) in both solution and gel form as recommended by Menne-Happ U. et al.[23]; No previous literature discussed using a gel form of $CaCl_2$. Thus a gel form of $CaCl_2$ was prepared to improve the handling properties of the $CaCl_2$.

The oral environment is aggressive, which may jeopardize the tooth structure as well as the restorative materials. The erosive nature of the different acidic beverages and foods added to our daily nutrition, as well as cariogenic acids, can be the major source of risk to the existing restoration. Francisconi L. et al (2008),[26] proved that the degradation of GIC after acid attacks resulted in a decrease in the material's surface hardness.[27]

As a method for challenging the acid attacks' resistance of GICs, previous studies established the obligatory resemblance of oral cavity condition with change in pH, simulating the salivary medium in the mouth. Amongst the aggressive nutritive products added to everyone's daily diets altering the oral environment, is acetic acid. Accordingly, GIC specimens were soaked in a chemically prepared 5% acetic acid with pH 3, for 10 minutes twice a day, for 14 days to resemble the acidic challenge in the clinical situation.[27,28]

Therefore, the aim of this invitro study was to evaluate the effect of calcium chloride application in both solution and gel forms on the surface hardness of the glass ionomer cement at baseline and after pH cycling.

The results of this study revealed a significant enhancement in surface hardness of Fuji IX GIC specimens that were surface treated by calcium chloride solution and calcium chloride gel compared to the control untreated specimens.

Many studies,[23,29-31] agreed with the present study results in which there was an enhancement in the surface hardness of the used GIC after the application of calcium chloride.

Regarding the chemical enhancement of the GIC, and Dionysopoulos D. et al. (2018)[18], Shiozawa M. et al (2013)[19], explained their findings based on calcium chloride ($CaCl_2$) solutions' application on the GIC such that by raising the Ca^{2+} concentration on the restoration's surface; thus, improving the acid–base reaction between the polyalkenoic acids' carboxylate groups (–COO−) and Ca^{2+} of the cement's glass particles. The main setting reaction of GIC is the cross-linking of the polyalkenoic acids' carboxylate groups with the ions released from glass particles, Al^{3+} and Ca^{2+}. The polycarboxylate network formation's progress is caused by the upturn of the GIC's surface hardness, which is ascribed to the absorption of Ca^{2+} cations onto the material's surface; the cations rather form chemical bonds with the remaining non-reacted carboxylic acid groups in the cement matrix than with the $CaCl_2$ precipitates on the material's surface.[13-15]

The results of the current study also demonstrated that pH cycling had significant adverse effects on the surface hardness of all test and control groups; all groups showed a reduction in surface hardness, however the control untreated group showed a higher decrease compared to the test groups.

These results were in agreement with the study of Francisconi L. et al (2008),[26] which explained that the acid attack degraded the fluoroaluminosilicate glass of the GICs, thereby releasing fluoride, aluminum and calcium ions which reduced the surface hardness. Also, Honório H. et al. (2008),[32] stated that both types of GICs (resin-modified and conventional) resulted in significantly major surface hardness reduction as a result of the erosive pH cycling when compared with saliva (the control medium) and other different restorative materials. These results could be illustrated by affirming that the breakdown of the siliceous hydrogel layer of the GIC caused degradation of the matrix of GIC glass particles after an acid attack. Moreover, Wongkhantee et al.,[33] noticed a decrease in the RMGI's surface hardness after alternative immersion in cola drink and saliva for 10 cycles of 5 seconds, due to the long period of acidic exposure. The findings of the results could be based on the conventional GIC's acid resistance, which is quite low.

Accordingly, the null hypotheses were rejected as the results showed differences between applying $CaCl_2$ solution and $CaCl_2$ gel at baseline, as well as after the pH cycling protocol, the three groups' surface hardness experienced adverse effects.

Although using $CaCl_2$ in both forms could improve the microhardness of conventional GIC; yet this improvement is still liable to deteriorate under harsh oral conditions. Further studies are thus needed to improve the GIC's mechanical properties as it is still considered one of the most promising restorative materials. Also, further studies are needed to incorporate $CaCl_2$ solution in the formulation of glass ionomer cements to act as an accelerator for their setting reaction, thus enhancing its mechanical properties especially in the early maturation phase.

CONCLUSION

1. The treatments used in the current study could enhance the surface hardness of GIC.
2. pH cycling protocol was detrimental to the surface hardness of all control and treated GIC specimens.
3. The form of $CaCl_2$ (either solution or gel form) did not differ in its effect in enhancing GIC surface hardness, however, the handling of the gel was easier.

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