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Preparation and evaluation of an experimental luting glass ionomer cement to be used in dentistry

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Abstract The aim of this paper is to compare the fluoride-releasing and mechanical properties of an experimental luting glass ionomer cement, which has a modified composition and a commercial luting cement. The experimental powder was obtained by sol–gel process and then, it was used to prepare the experimental cements. The properties of cement pastes, such as setting time and working time, microhardness and diametral tensile strength were determined. Fluoride release from GICs was evaluated at time intervals of 1, 7, 14, 21 and 28 days in deionized water. Atomic force microscopy (AFM) analyses showed that the surface of the experimental cements is more homogeneous than commercial GICs. The mechanical properties and the measure of liberation of fluoride of the two cements were influenced by ratio powder:liquid and chemical composition of the precursor powders. Experimental cements released less fluoride than commercial cements. However, this liberation was more constant during the analyzed period. Thus, the results obtained in this study indicated that the composition of the experimental powder modified by the niobium can lead the formation of the polysalt matrix with good mechanical properties. In other words, we can say that experimental powder offered considerable promise for exploitation in dental field.

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1 Introduction

Several dental restorative materials containing fluoride, such as glass polyalkenoate cements or glass ionomer cements (GICs), have been developed and these materials are available on the market due to their attractive properties for use in Dentistry, such as the continuous release of fluoride [1–3].

Fluoride is well documented as an anticariogenic agent. Fluoride-releasing from restorative materials may be able to reduce the recurrent caries at the restoration margins [4, 5]. Recurrent caries is the most frequent cause for the failure of dental restorations [6, 7]. A variety of mechanisms are involved in the anticariogenic effects of fluoride, including the formation of fluorapatite that has lower solubility than the original carbonated apatite, the enhancement of remineralization, interference of ionic bonding during pellicle and plaque formation, and the inhibition of microbial growth and metabolism [8–10]. Fluoride released from restorative materials can inhibit caries through all these mechanisms although it seems likely that the enhancement of remineralization is the major mechanisms by which fluoride released from restorative materials is effective [7]. These anticariogenic and bacteriostatic effects vary widely among different materials and largely depend upon the amount of fluoride that material releases.

Another important advantage of GICs is their ability to absorb fluoride from exogenous sources. Thus, the

exhausted cement can be recharge with a fluoride application to maintain cariostatic capability. Therefore, the GICs act as a continuous reservoir for fluoride, which is released from cement over a long period [3, 11–13].

However, only the fluoride releasing is not enough to evaluate the properties of the cements. Because, other properties, such as setting time, working time and the mechanical properties should be considered. Most of these properties depend on the composition of the glasses [3, 4, 7] and in this context, different formulations of glasses have been researched and proposed for use in Dentistry.

The glasses firstly studied by Wilson and Kent were calcium-fluoro-alumino-silicate and the method of preparation was conventional fusion method at temperatures ranging from 1100 to 1550°C depending on the composition [1]. However, there are evidences that this method of preparation has been showed problems associated to variation in the final glass composition due to fluorine loss during melting. This fluorine loss is uncontrolled and results in variable composition between batches. The inability to control the melt composition has led to difficulties in correlating the glass composition to cement mechanical properties [14].

On the other hand, chemical methods of preparation of glasses such as sol–gel process can be used to overcome the problems observed in fusion method, because this method offers several processing advantages, mainly due to high chemical homogeneity and composition control, and low processing temperatures [15, 16].

In recent times, new formulations of glasses have been developed aiming the use as cement formers. In this context, the objective of this paper is to evaluate the properties of GICs which were prepared from the system conventional SiO_2–Al_2O_3–Nb_2O_5–CaO–CaF_2 modified by the presence of niobium. Other papers have shown the biocompatibility of niobium is high and this metal is added to improve the chemical durability of some bioglasses. This fact may reflect an increased the chemical resistance of GICs used in Dentistry [16, 17].

The present paper describes and to evaluate the properties of a commercial and experimental GIC, which was prepared from SiO_2–Al_2O_3–Nb_2O_5–CaO–CaF_2 glass powder.

2 Materials and Methods

2.1 Preparation and characterization of precursor powder of GICs

The precursor powder of experimental cements, an ion-leachable glass based on the $4.5SiO_2$–$3Al_2O_3$–xNb_2O_5–$2CaO$–$3CaF_2$ system was prepared using the sol–gel method in the composition range of $0.10 < x < 1.0$.

The raw reagents used to prepare the powders were tetraethoxysilane (TEOS, 99%, Aldrich), aluminum nitrate nona-hydrated (99%, Synth) calcium nitrate (99%, Synth), niobium citrate solution and H_2SiF_6 (fluorosilicic acid).

In the sol–gel procedure, TEOS was first hydrolyzed in ethanol using an open vessel under continuous stirring at room temperature for one hour. The previously dissolved aluminum and calcium salts were then added drop wise to the hydrolyzed TEOS solution. Afterwards niobium citrate solution and fluorosilicic acid were added to the solution. The fully mixed solution was then heated with continuous stirring to 80°C, till gelation occurred. In order to obtain the powder sample, the gel was dried at 80°C, pulverized and then heated at 600°C for 2 h using an electrical furnace.

The powder prepared by the sol gel method was analyzed by X-ray diffraction (XRD) using Cu Kα radiation, 42 KV, 0.020° min^{-1} and scan range between 20° and 70°.

2.2 Cement preparation

The experimental powder after the undergoing the heating process at 600°C were passed through a sieve with a mesh opening of 25 μm, and were then used to produce the cements.

The experimental GICs were prepared at room temperature by mixing the powder with aqueous solutions 45–50% (m/m) of poly(acrylic acid)—PAA—MW 23,0000 and aqueous solution (10%-m/m) of tartaric acid. The commercial restorative specimens were made using a powder:liquid (P:L) ratio of 2:1 (m/m) according to the manufacturer's instructions.

2.3 Cement characterization

The manipulative properties of cement pastes were determined by evaluation of the consistency of the mixture of powder with organic acid solution.

After setting for 1 and 24 h, the microhardness of the specimens was determined. The microhardness of the specimens was determined using a microhardness tester (HMV-Shimadzu). The Vickers microhardness (HV) test was performed at room temperature using a diamond indenter with 50 g load and 30 s dwell time. Five measurements were made on the surface of each specimen. For each material investigated were analyzed ten specimens ($n = 10$).

The diametral tensile strength tests were performed on cement cylinders 2.0 mm in diameter × 4.0 mm in height. The testing procedure was based on the ISO standard (ISO 7489: 1986). These tests were carried out using an

Universal Testing Machine (MEM-2000 model) with a crosshead speed of 0.5 mm/min and a 50 kgf load cell, until fracture.

The microstructure of GICs was examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa).

2.3.1 *Measurement of fluoride release by using ion-selective electrode (ISE)*

The specimens were immersed and stored in individual plastic containers with 6 mL deionized water at 37°C. At time of fluoride determination, each specimen was removed from its container and the storage solution decanted for analysis. The specimen was returned to a container with a fresh 6 mL deionized water, and storage was continued.

The determination of fluoride release was made by using an Orion ionanalyser connected to a fluoride ion selective electrode up to 28 days. An equal volume of TISAB (total ionic strength adjustment buffer) was added to 6 mL to each sample. This mixture was then placed into a selective electrode. The electrode was cleaned carefully and dried between measurements. Readings were converted to μg F^-/mm^2 using a standard calibration curve.

3 Results

XRD (Fig. 1) showed that the commercial and experimental powder prepared by the sol–gel method at 600°C were completely amorphous.

The properties of the commercial and experimental cements are shown in Table 1. The experimental GICs prepared using powder:liquid ratio equal to 2:1 or 1.5:1 had no adequate manipulative properties. However, the experimental GICs prepared with a ratio equal to 1:1 had the manipulative properties and working time and setting time similar to the commercial GICs.

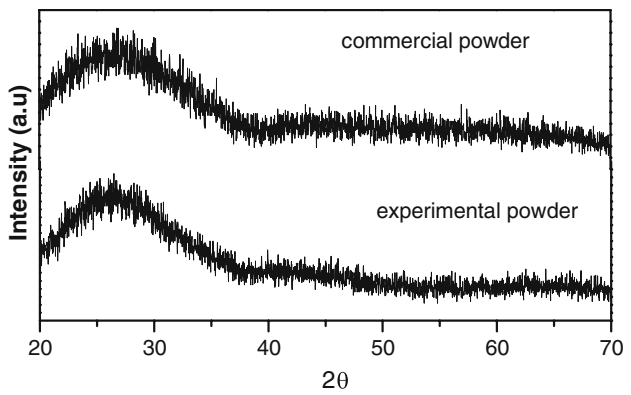

Fig. 1 XRD pattern of precursor powders of experimental and commercial GICs

Table 1 Working and initial setting time of tested cements

GIC	P:L (mass/mass)	Working time (min)	Setting time (min)
Commercial	2:1	5.5–7.0	8.0–10
Experimental	1:1	3.5–5.0	6.0–12

Table 2 Microhardness and diametral tensile strength of tested cements

GIC	Microhardeness (HV) 1 h	Microhardeness (HV) 24 h	Diametral tensile strength (MPa)
Commercial	18.3 ± 1.0	24.2 ± 0.5	14.0 ± 3.0
Experimental	11 ± 0.80	21.2 ± 3.7	7.5 ± 0.9

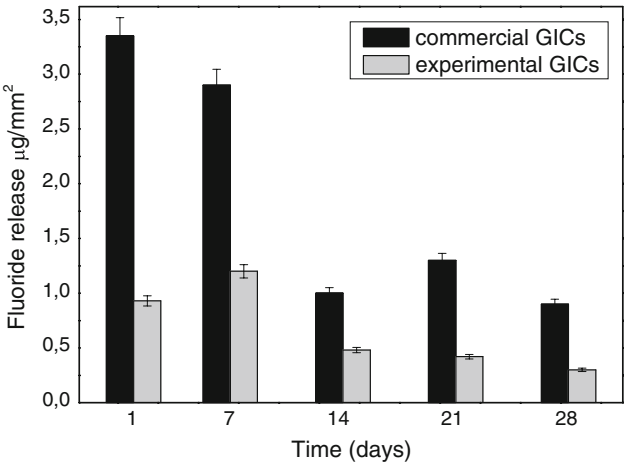

Fig. 2 Concentration of fluoride released by experimental and commercial GICs over 28 days

The diametral tensile strength of the experimental GICs was lower than commercial GICs due to the reduction of ratio powder/liquid (Table 2).

The cumulative concentration (μg/mm^2) of fluoride released from the cements specimens during 28 day storage in deionized water are shown in Fig. 2. The pattern of release for commercial and experimental GICs was similar, but there were great differences in the amount of fluoride released from tested GICs.

The images obtained using AFM for experimental and commercial cements, are illustrated in the Fig. 3. Observing these images, it is possible to observe differences among the two surfaces of cements.

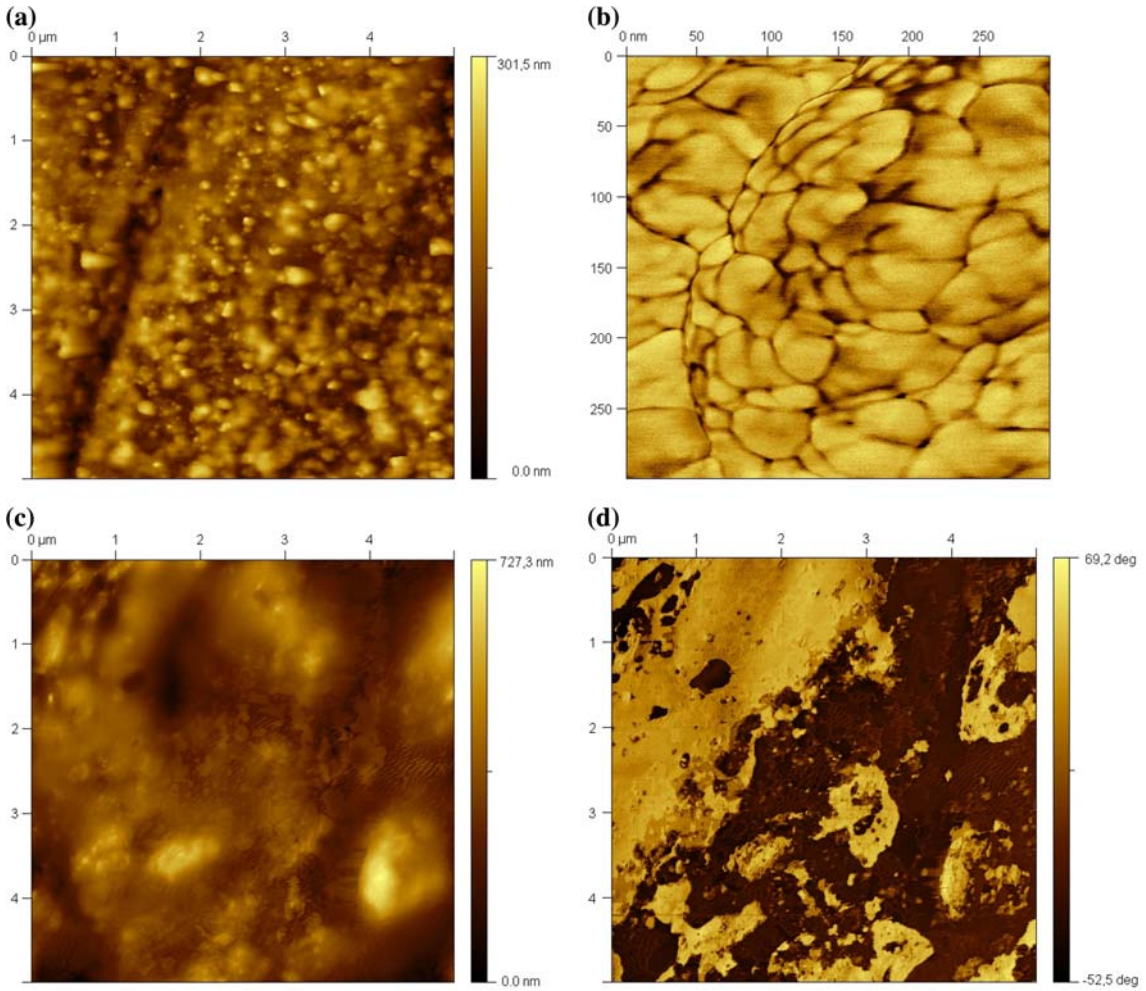

Fig. 3 AFM images for experimental (**a**, **b**) and commercial cements (**c**, **d**)

4 Discussion

As can be seen in Fig. 1, the result of XRD demonstrates that the chemical processing has been successfully applied to prepare a experimental powder with structure similar to commercial powder at temperatures below 1000°C.

It can be observed that there is a relationship between the strength of the cements and the powder:liquid ratio. This observation is according to several papers which report that the powder:liquid ratio affects the mechanical properties of the GICs.

The results of microhardness tests showed that the means values of experimental GICs was not 50% lower than commercial GICs. Thus, this fact indicates that the composition of glass used to prepare the experimental cements could yield cements with mechanical properties similar to commercial GICs. The presence of other ions in the composition of glasses such as niobium could lead to the improvement of mechanical properties. Because, Nb^{5+} cations bond the structural units Si–O or Al–O forming a common network with strong Si–O–Nb–Al bonds [17]. Thus, the polysalt matrix formed in the setting reaction of GICs, contain these bonds which could have favourable effects on the cements properties such as mechanical properties. As well as, it can be observed in the results obtained in the microhardness tests.

For the GICs tested, there were great differences in the amount of fluoride released. The greatest release occured on the first day, after which the amount diminished gradually until a relatively constant rate was reached.

Experimental GICs showed constant levels of fluoride release from 14 day. The differences among in amount of fluoride released among commercial and experimental cements may be attributed to differences in glass composition, ground glass particle size, physicochemical properties and powder-liquid ratio, which may affect fluoride release.

Our present findings, the fluoride release from experimental GICs was lower than that commercial cements mainly due to powder:liquid ratio used in the preparation of cements or the quantitative differences among the cements may be attributed to differences in initial fluoride content of precursor glasses. Besides, the glass network of experimental GICs has strong bonds which could reduce the fluoride release.

Although, the experimental GICs liberate amounts of fluoride significantly lower than commercial GICs. It was observed a rate of fluoride-releasing constant from 14 day. This characteristic is clinically important because experimental GICs may liberate low amounts of fluoride constantly to surrounding dental tissue reducing the incidence of caries. This behavior was not observed for commercial GICs. For commercial GICs higher levels of fluoride were released initially, but this release fell rapidly. On the other hand, the use of experimental GICs would be preferable due to constant and lower amounts of fluoride released during the period studied.

The cement experimental sample presents granular texture with nanoparticles (Fig. 3a, b). Besides, we can observe that the experimental cements have a surface more homogeneous in comparison with the surface of commercial cement (Fig. 3c, d).

Based in this preliminary study, about the properties of experimental GICs, we can conclude that these results obtained encourage further applications of the proposed glass in the preparation of new formulations of dental cements.

5 Conclusion

Experimental GICs were prepared from glass powder synthesized by the chemical method. This powder was obtained at 600°C and has a differentiated composition of conventional powders used to prepare the dental cements.

According to results showed in this paper, the experimental GICs released fluoride constantly and lower amounts during the period studied. It can be assumed that mechanical properties of experimental GICs such as microhardness were similar to commercial GICs. This advantageous property can be attributed to the presence of niobium in the experimental powder in which it differs from all other commercial luting cements.

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