Determination of the properties of an experimental glass polyalkenoate cement prepared from niobium silicate powder containing fluoride

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\textbf{A R T I C L E   I N F O}

\textbf{Article history:}
Received 17 August 2006
Received in revised form 2 February 2007
Accepted 14 March 2007

\textbf{Keywords:}
Niobium
Cement
Sol–gel

\textbf{A B S T R A C T}

Objectives. The purpose of this paper is to modify the conventional calcium fluoro-alumino-silicate glass, which is used in the formation of glass ionomer cements (CIGs) by the niobium addition and to study the properties of GICs obtained.

Materials and methods. Sol–gel process was used to prepare the powder at lower temperature than fusion method. Glass-ceramic powder obtained in this way was used to prepare the GICs. The properties such as working and setting times, microhardness and diametral tensile strength were evaluated for the experimental GICs and a commercial luting cement.

Results. The ideal powder:liquid (P:L) ratio determined to prepare the experimental GICs was equal to 1:1. The cements prepared using this ratio showed working and setting times similar to the commercial GICs. In mechanical tests it was observed that microhardness and diametral tensile strength of the experimental GICs decreased significantly with the reduction of P:L ratio. On the other hand, the results obtained in microhardness tests indicated that the presence of niobium was a positive factor.

Significance. The chemical process allows the development of glass-ceramic powder at 600 ℃ which is the goal of the present paper. It was concluded that GICs containing niobium might be used in dental applications and these results encourage further researches on other compositions.

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1. Introduction

Glass polyalkenoate cements or glass ionomer cements (GICs) are currently used for various dental applications. More than 20 years of clinical experience promoted them as versatile materials, due to their simple handling and relative tolerance to variations in clinical techniques.

The GICs are products of the acid/base setting reaction between an ion-leachable glass powder and a polyalkenoic acid generally poly(acrylic acid) in aqueous solution [1]. During the cement forming reaction, the surface of the glass particle is degraded by the organic acid, releasing ions such as Al\(^{3+}\) and Ca\(^{2+}\) [1,2]. These released cations are chelated by the carboxylate groups of the polymer and serve to cross-link the
polycacid chains. Thus, the set cement consists of a pollysalt matrix embedded with glass particles [3].

These materials have a number of properties, which make them highly suitable for application in dentistry. Chemical diffusion-based adhesion to enamel and dentin [2,4] and fluoride release are some of their important properties. The exhausted glass ionomer cements can be recharged with a fluoride application to maintain cariostatic capability. Besides, the GICs have high biocompatibility [4]. Despite these good properties, disadvantages such as early water sensitivity, poor strength and reduced occlusal wear resistance, have limited the use of conventional GICs in clinical application.

The GICs were first developed by Wilson and Kent and have undergone continuous development, improvement, and diversification. New researches have been made to improve the properties of conventional GICs by modification of the glass formulations using other methods of preparation.

Calcium fluoro-alumino-silicate glasses may be regarded as the basic type from which GICs are derived. These systems are prepared by the fusion method at temperatures ranging from 1200 to 1550 °C, depending on the composition. In this process, fluorine is lost from the melt. This fluorine loss is uncontrolled and results in variable composition between batches [5].

Alternatively, soft chemistry has been used for synthesis of glasses because this route yields more homogeneous materials using lower processing temperatures than the conventional fusion method. Besides, the sol–gel process has the potential to yield glasses which cannot be otherwise prepared by the conventional melting method due to their high melting points [6].

Considerable efforts have been made to improve the properties of GICs using other types of glass powders derived from calcium fluoro-alumino-silicate systems with new components. Therefore, it is very important to carry out research about the presence of other ions in the composition of glasses. In this context, vitreous systems containing niobium have been of great interest due to their structural versatility and useful applications. According to Samuneva and Dimitrov, the chemical resistance of silicate glasses can be enhanced by Nb2O5 addition that exerts a favorable effect on a number of physical and chemical properties in silicate systems [7]. On the other hand, due to the fact that some bioglasses have low resistance to a humid environment, niobium is added to improve the chemical durability. Thus, the addition of niobium would improve the chemical resistance of cements used as materials for the restoration or luting agent for the attachment of devices.

The use of glasses based on SiO2-Al2O3-K2NbF7-CaO system, as GIC formers, has not been found in the literature. The proposed system has the potential to form GICs with good mechanical properties and to result in the dental cement with a good cost–benefit relationship.

The aim of this study is the preparation of niobium fluoro-alumino-silicate glass powder by the sol–gel process for use as cement formers. The properties of experimental luting cements and of commercial powders were compared.

2. Materials and methods

2.1. Preparation of precursor powder of GICs

The precursor powder of cements, an ion-leachable glass based on the 4.5SiO2-3Al2O3-xK2NbF7-2CaO system was prepared using the sol–gel method in the composition range 0.10 < x < 1.0.

The raw reagents used to prepare the powders were tetraethoxysilane (TEOS, 99%, Aldrich), aluminum nitrate 9 hydrate, crystal (99%, Synth) calcium nitrate (99%, Synth) and K2NbF7 (potassium fluoroniobate).

In the sol–gel route, TEOS was first hydrolyzed in ethanol using an open vessel under continuous stirring at room temperature for 1 h. The previously dissolved aluminum and calcium salts were then added drop wise to the hydrolyzed TEOS solution. Afterwards, K2NbF7 was added to the solution. The fully mixed solution was then heated with continuous stirring to 80 °C, when gelation occurred. In order to obtain the powder sample, the gel was dried at 80 °C, pulverized and then fired at 600 °C for 2 h using an electrical furnace.

2.2. Cement preparation

The powder prepared by the sol–gel process was passed through a sieve with a mesh opening of 25 μm, and then was used to produce the cement.

The experimental luting GICs were prepared at room temperature by mixing the powder prepared by the sol–gel process with aqueous solutions 45–50% (m/m) of poly(acrylic acid) – PAA – MW 230,000 and aqueous solution (10%, m/m) of tartaric acid. The commercial luting specimens were made using a powder:liquid (P:L) ratio of 2:1. This P:L ratio (m/m) is in accordance with the manufacturer’s instructions.

2.3. Cement characterization

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

After setting for 24h, the microhardness and diametral tensile tests of the specimens were determined. The microhardness of the specimens was determined using a microhardness tester (HMV, Shimadzu). The Knoop hardness number (KHN) 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 five specimens were analyzed (n = 10).

Diametral tensile tests were performed using disks of 2 mm diameter and 4 mm thickness. The tests were carried out using a Universal Testing Machine (MEM-2000 model) with a crosshead speed of 0.5 mm/min and a 50 kgf load cell, until fracture.

Fourier transform infrared spectroscopy (FTIR) and magic-angle spinning nuclear magnetic resonance 27Al MAS NMR were used to investigate structural aspects of the experimental GICs after the setting reaction. NMR spectra were acquired using a spectrometer (Varian Unity Inova 300). 27Al
3. Results

The powder prepared at 600 °C by the sol–gel process was analyzed by X-ray powder diffraction (XRD) to identify the crystal phases. In Fig. 1, four peaks were observed, corresponding to the presence of fluorite.

In the initial studies, the ideal powder:liquid (P:L, m/m) ratio was determined for experimental GICs. This ratio is the most important factor affecting all the other GICs properties. Thus, it represents a compromise and must be chosen with care. Table 1 shows the properties of the experimental cement pastes and of the commercial GICs. These results show that the properties of these cements were different due to the surface area of the powders (Table 2).

FTIR was used to investigate the poly(acrylic acid)/powder reaction kinetics. FTIR spectra obtained at 10 min and 24 h after the start of mixing are shown in Fig. 2. The general features observed were a progressive conversion of acid –COOH groups to salt –COO⁻ groups as metal salts were formed [8,9].

In the Al MAS NMR (Fig. 3) spectrum of the powder prepared by the sol–gel route two peaks were observed. The first peak around 55 ppm, can be assigned to aluminum tetrahedrally coordinated Al⁴⁺ in the aluminosilicate network and the second observed around –2 ppm corresponds to aluminum octahedrally coordinated Al⁶⁺ [10]. Fig. 4 shows the spectrum...
Al MAS NMR obtained for the experimental GIC 24 h after the start of mixing. In this spectrum, it is possible to observe that the peak assigned to Al⁶⁺ in Fig. 3, increased in intensity. This demonstrates that Al³⁺ ions were released from powder reacted with carboxylate groups of poly(acrylic acid).

The mechanical properties of experimental GICs were strongly influenced by P:L ratio. There was a decrease in the values of the properties when the P:L was decreased from 1 to 0.5.

4. Discussion

As can be seen in Fig. 1 the powder containing Nb and fluoride is a glass–ceramic presenting the crystalline phase of fluorite (CaF₂). On the other hand, fluorite has also been shown to crystallize in glasses prepared by the conventional melting method at temperatures below the glass transition temperature. Therefore, the results in this study were in accordance with previous reports of crystallization in calcium fluoro-alumino-silicate glasses.

The properties of GICs prepared from the powder prepared by sol–gel and commercial material are shown in Table 1. Certain broad conclusions can be drawn about the effect of P:L ratio on cement properties. The manipulation of the experimental cement pastes using ratio equal to 2:1 was difficult, because they had little workability. For this reason other P:L ratios were tested for the preparation of the experimental GICs. A decrease in the P:L ratio significantly prolonged the working and setting times.

None of the experimental GICs prepared with P:L equal to 2:1 or 1.5:1 had adequate working and setting times. It was not possible to use the same P:L ratio (2:1) of commercial GICs due to the fact that the experimental powder had a greater surface area than the commercial powder (Table 2). Thus, the manipulative properties of cements were not adequate because of rapid setting characteristics and consequently the working time of cement pastes decreased. Experimental GICs prepared with a ratio equal to 1:1 had the most favorable manipulative properties and the paste had a good working time.

On neutralization of organic acid the main characteristic is loss of bands around 1250 and 1710 cm⁻¹ assigned to C–O and C=O stretch of poly(acrylic acid) in the FTIR spectra. Loss of these bands is due to formation of polyacrylate salts [8,9].

As can be seen in the FTIR spectra (Fig. 2) the bands observed around 1700 cm⁻¹ (after 10 min) were substituted progressively and other bands can be observed in the spectra. These bands around 1460 and 1640 cm⁻¹ (after 24 h) could be assigned to symmetric and asymmetric COO⁻ stretch of aluminum polyacrylate salt and the bands around 1380 cm⁻¹ assigned to symmetric COO⁻ stretch of calcium polyacrylate. These data confirm that the reaction between the particles of the powder and poly(acrylic acid) solution was completed within 24 h after that cement had been prepared.

The Al NMR spectra indicated that the acid attack occurred at the surface of the particles breaking the Si–O–Al bonds and, at the same time, Al³⁺ ions were released from the network to cross-link COO⁻ groups of polyacid leading to the formation of aluminum polyacrylate salt [10,11], which is responsible for the setting reaction of the cements. This observation coincides with the results obtained in the FTIR spectra.

The mechanical properties of commercial luting cements and experimental cements are presented in Table 3. These results showed that the tensile strength of experimental GICs was lower than that of the commercial luting tested. The mean values and standard deviations for all of the experimental GICs tested depended to some extent on P:L ratio.

It can be observed that there is a linear relationship between the strength of the GICs and the P:L ratio. In fact, Wilson and collaborators [12] reported that the physical properties of dental cements depend on a number of variables including chemical formulation and P:L ratio. Other published papers on the properties of commercial GICs report that P:L ratio affects the strength of the cements [13,14]. Thus, higher P:L ratios are used by the manufactures to yield cements with attractive mechanical properties.

The results of microhardness tests showed that the experimental GICs had higher mean values of the KHN than commercial GICs. This result indicates that the insertion of niobium in the polysalt matrix of GICs could have a positive effect leading to the improvement of mechanical properties.

Based on this initial study, new research is needed on other compositions in order to establish the effect of the niobium addition on the properties of the cements as well as tests for the evaluation of biological properties. This work is now in progress in the authors’ laboratory.

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**Table 3 – Mechanical properties of experimental GICs**

<table>
<thead>
<tr>
<th>GICs</th>
<th>P:L ratio (m/m)</th>
<th>Diametral tensile strength 24 h (MPa)</th>
<th>Microhardness (KHN), 24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>2:1</td>
<td>12 (3.4)</td>
<td>16.4 (4.0)</td>
</tr>
<tr>
<td>Experimental</td>
<td>1:1</td>
<td>7.0 (1.0)</td>
<td>19 (5.5)</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.5:1</td>
<td>2.3 (0.4)</td>
<td>6.1 (1.7)</td>
</tr>
</tbody>
</table>

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**Fig. 4 – Al²⁷ MAS NMR spectrum of experimental GIC 24 h after mixing.**
5. Conclusion

In this study, new experimental GICs were developed from calcium fluoro-alumino-silicate glass containing niobium, with partially crystallized fluorite phase. The sol–gel method allowed the preparation of this glass–ceramic powder at 600°C. Although the powder presents a crystalline phase of CaF2 it reacts with poly(acrylic acid) to form the GICs. According to the results obtained, it can be assumed that the decreased mechanical strength of experimental GICs is due to the fact that significant amount of powder was reduced in the preparation of cement pastes due to the high surface area of powder prepared by sol–gel.

On the other hand, microhardness results prove the fact that the niobium addition would improve the mechanical properties of cements. Further exploitation of niobium polyacrylate cements is clearly possible and continued development of new formulations should result in even more resistance materials.

Acknowledgements

The authors acknowledge financial support provided by Brazilian research financing institution FAPESP.

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