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Sol-gel methods for synthesis of aluminosilicates for dental applications

Alexandre Cestari[1]

Federal Institute of Education, Science and Technology of São Paulo – IFSP – Campus Matão, Brazil

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ABSTRACT

Introduction: Amorphous aluminosilicates glasses containing fluorine, phosphorus and calcium are used as a component of the glass ionomer dental cement. This cement is used as a restorative, basis or filling material, but presents lower mechanical resistance than resin-modified materials. The Sol-Gel method is a possible route for preparation of glasses with lower temperature and energy consumption, with higher homogeneity and with uniform and nanometric particles, compared to the industrial methods Glass ionomer cements with uniform, homogeneous and nanometric particles can present higher mechanical resistance than commercial ionomers.

Objectives: The aim of this work was to adapt the Sol-Gel methods to produce new aluminosilicate glass particles by non-hydrolytic, hydrolytic acid and hydrolytic basic routes, to improve glass ionomer cements characteristics. Three materials were synthesized with the same composition, to evaluate the properties of the glasses produced from the different methods, because multicomponent oxides are difficult to prepare with homogeneity. The objective was to develop a new route to produce new glass particles for ionomer cements with possible higher resistance.

Characterization methods: The particles were characterized by thermal analysis (TG, DTA, DSC), transmission electron microscopy (TEM), X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). The glasses were tested with polyacrylic acid to form the glass ionomer cement by the setting reaction.

Conclusions: It was possible to produce distinct materials for dental applications and a sample presented superior characteristics (homogeneity, nanometric particles, and homogenous elemental distribution) than commercial glasses for ionomer cements. The new route for glass production can possible improve the mechanical resistance of the ionomer cements.

1. Introduction

The aluminosilicates consist of an inorganic polymer network or mixed oxide, based on a silicon and aluminum matrix, with amorphous structure (glass type). This material is used in dentistry as the basis for the restorative material named glass ionomer cement [1].

This cement has interesting physical and chemical properties, mainly the higher adhesion than other restorative materials, lower shrinkage, proven biocompatibility with the dental pulp and cariostatic properties due to continuous release of fluoride ions during the life of the restoration [2,3].

The release of fluoride also promotes the teeth remineralization, which are composed of hydroxyapatite, forming superficial fluoroapatite. This merger also makes the teeth structure more resistant to acid attack from food and beverages [4].

Sol-gel silica and vitreous materials (bioglass) are being studied as substitutes for bone implants and as dental materials due to the interactions with the bone structure composed of hydroxyapatite ($Ca_5(PO_4)_3OH$). Some amorphous materials can also promote the osseointegration and osteoinduction with bone growth [5].

Vitroceramics and materials with the crystalline phases fluoroapatite ($Ca_5(PO_4)_3F$) and mullite ($3Al_2O_3{\cdot}2SiO_2$) provides biocompatibility and appreciable integration to the bones. Nano hydroxiapatite can also be merged with glass materials to improve the biocompatibility for bone replacements and ionomer dental matrices [6–8].

News researches are being made about glass ionomers to improve mechanical and chemical properties, especially micro hardness and fracture resistance. A large number of cross-link is essential to ensure superior wear resistance, compressive strength, micro hardness and low solubility. The glasses made by the

[1] Address: R. Stéfano D'Avassi, 625. Nova Cidade, Matão – SP. CEP: 15991-502, Brazil.

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Table 1
Composition proposed by S. G. Griffin.

Element	Molar ratio
Si	4.5
Al	6.0
P	3.0
Ca	5.0
F	2.0
O	29.5

industrial routes present low homogeneity and micro particles that decrease the resistance of the dental cement [6–8].

The glass ionomer cement is used as a restorative, basis or filling material, but presents lower mechanical resistance than resin-modified materials. In this study, three oxides with the same composition ($4{\cdot}5SiO_2$-$3{\cdot}0Al_2O_3$-$1{\cdot}5P_2O_5$-$4{\cdot}0CaO$-$1{\cdot}0CaF_2$) were synthesized by the Sol-gel methods: non-hydrolytic, hydrolytic with acid catalyst and hydrolytic with basic catalyst, to evaluate the properties of the materials produced by the different routes, because multicomponent oxides are difficult to prepare with homogeneity. The objective of this work was to develop a new route to produce new glass particles for ionomer cements with possible higher resistance.

2. Experimental

2.1. Materials

The produced materials were based with the composition proposed by S. G. Griffin, according to Table 1 [9].

The non-hydrolytic Sol-Gel method previously described by Cestari et al. produced aluminosilicates for dental applications and in this work it was modified to synthesize an oxide (sample Ci1), with 1.995 g of $AlCl_3$ (Sigma-Aldrich), 1.824 g of $AlPO_4$ (Sigma-Aldrich), 0.389 g of CaF_2 (Sigma-Aldrich), 3.273 g of $Ca(NO_3)_2$ (Sigma-Aldrich), 170 mL of anhydrous ethanol (Tedia) and 5 mL of TEOS (Tetraethyl orthosilicate, Sigma-Aldrich) [10,11].

The reaction system was in reflux, with magnetic stirring, heated at 110 °C and with inert atmosphere of Argon during 4 h. After the reaction, the solvent was evaporated and the gel was dried at 110 °C. After drying, the material was homogenized and a white solid with small particles was obtained.

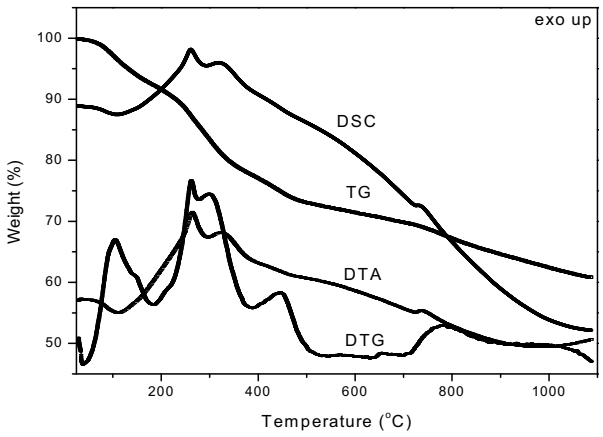

Fig. 1. Thermal analysis of the sample Ci1.

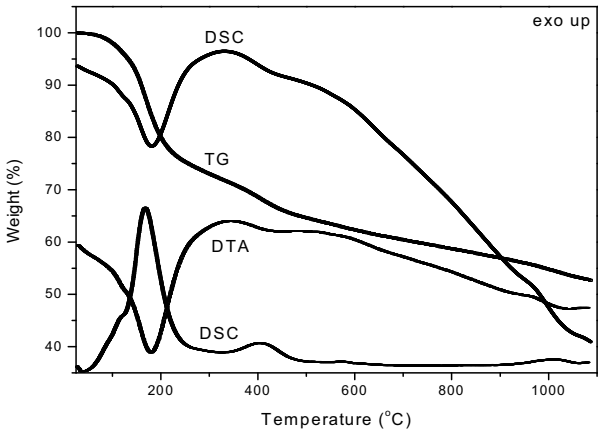

Fig. 2. Thermal analyses of the sample Ci2.

The material synthesized by hydrolytic method with acid catalyst (sample Ci2), was made with 3.056 g of aluminum isopropoxide (Sigma-Aldrich), 0.389 g of CaF_2, 1.825 g of $AlPO_4$, 4.709 g of $Ca(NO_3)_2{\cdot}4H_2O$, 90 mL of anhydrous ethanol, 30 mL of distilled water, 70 mL of hydrochloric acid at 36% (Vetec) and 5 mL of TEOS.

The reaction medium was magnetic stirred during 7 days, at room temperature and the obtained gel was dried at 110 °C and homogenized, to obtain a fine white powder.

For the material synthesized by the hydrolytic method with basic catalyst (sample Ci3), it was used the same quantities of reagents of the sample Ci2, replacing the hydrochloric acid by 80 mL of aqueous ammonia at 28% (Vetec).

All materials were heat treated at 380 °C and 600 °C for removal of residual solvent inside the pores, by-products and other organic residues.

2.2. Characterization

2.2.1. X-ray diffractions

The measures of X-ray diffractions (XRD) were performed in a Shimadzu diffractometer, model 6100, with Cu Kα (λ = 1.54 Å), 40 kV and 30 mA, from 5 to 60 theta, with resolution of 0.05.

2.2.2. Scanning electron microscopy coupled with energy dispersive spectroscopy

The scanning electron microscopy (SEM) was performed in a Zeiss microscope, model EVO 50, coupled to an energy dispersive

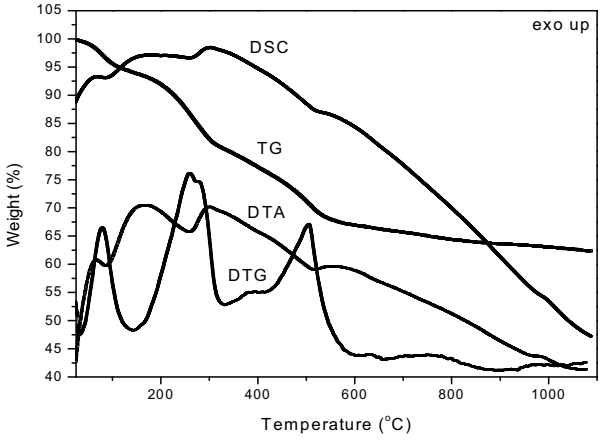

Fig. 3. Thermal analysis of the sample Ci3.