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Synthesis of glass ionomer cement gels using tetraethylorthosilicate xerogels in presence of a polymeric matrix

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A matrix of galactopyranose, tetraethylorthosilicate xerogels were used to synthesize glass ionomer gels. The purpose was to produce gels of glass ionomer cement in the presence of a polysaccharide by means of the sol-gel method. The gels were characterized by scanning electron microscope, analysis for fractal dimension, energy dispersive X-ray and watershed segmentation method. According to the results, the gels were successfully synthesized with TEOS xerogels in the presence of a polymeric network in solution. Among other things, the peaks/μm^2 count corresponding to the surface properties of the characterized gels have a normal distribution with ranges between 17 and 22 nm. Also, the analysis of fractal dimension that represents the similarity of the roughness of the surface of the gels has a value of 2.508.

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Keywords: Glass ionomer cement gels, Tetraethylorthosilicate, Polymeric matrix, Sol-gel, Scanning electron microscopy

1. Introduction

The synthesis of materials for diverse applications in areas such as industry, tissue engineering and dental restorations has attracted the attention of a large number of researchers due to the great progress on the development and characterization of new biomaterials. The use of various cements such as glass ionomer, zinc phosphate, zinc polycarboxylate, resin modified glass ionomer (RMGI), zinc oxide eugenol, resin cements among others, has worked as the basis for the synthesis of new materials [1-3]. Several models have been described for the preparation of various composites using glass ionomer in the presence of polymers for the study of its molecular interaction [4]. Similarly, the use of various polymer molecules such as vinyl polyacids bound to the glass ionomer, is another strategy in the development of dental materials [5]. Other researchers have used derivatives of natural amino acids bound to the glass ionomer to form microstructures and study their mechanical strength [6]. Likewise, the use of various structures such as magnesium nanoparticles has been performed for the study of antibacterial functions with glass ionomers [7]. The manufacture of new aluminum-free glass ionomers using magnesium, strontium, SiO_2 among others, has been incorporated to study flexural and mechanical properties [8]. The use of tetraethylorthosilicate (TEOS) has also been performed to synthesize glass ionomer composites incorporating hydroxyapatite [9]. In other studies, bioactive silica incorporated into glass ionomer has been synthesized with TEOS [10]. Additionally, the work by Ismail et al. reported the use of TEOS to modify the properties of glass ionomer cements [11]. In this context, we are reporting the synthesis of glass ionomer cement gels with TEOS in presence of a polymeric matrix of galactopyranose.

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2. Experimental section

2.1. Synthesis of Tetraethylorthosilicate xerogels

An alkoxide solution was prepared mixing 3.7 ml TEOS and 9.5 ml ethanol in a beaker, then 5.0 ml water and 9.5 ml ethanol were mixed in another beaker. Subsequently, 0.200 ml, ~5 drops of ammonium fluoride/ammonium hydroxide were added, this solution is named catalyst solution. The catalysis solution was put into the alkoxide solution and was mixed in a magnetic stirrer. After, this solution was put into molds and let resting by 30 min at room temperature to form the gel. Once the gel was formed, it was put under ethanol and let aging for 24 hours. Subsequently, an exchange in 200 ml of ethanol was made for 4 times over a week.

2.2. Synthesis of glass ionomer cement gels with TEOS

The elaboration of the glass ionomer cement gels was carried out as follows: a solution was prepared using 50 mg of glass ionomer cement (Sci-Pharm 50-02 Inc. USA) and 2 ml of hydrochloric acid (10% w/v Sigma-Aldrich USA). Last, this solution was stirred in a magnetic stirrer for 1h. Subsequently, 50 mg of TEOS xerogels previously treated were added, thereafter a solution containing 3 ml of a polymeric matrix of chemically pure grade polysaccharide (1-3 linked β-D galactapyranose and 1.4 linked 3.6 anyhdro-α-L-galactopyranose Sigma-Aldrich USA) to 0.2% -1.0%, preheated to 50 °C was added, in this way different experiments were performed modifying the final volume to know the density of the gels, all components were gently shaken for 5 minutes and deposited in circular molds until gels were formed for 30 minutes, then some gels were cut for analysis with a surgical scalpel blade No. 11 (Swann-Morton Ltd England) in a transversal direction, the specimen sizes were 3 x 3 mm approximately. Finally, the gels were aged at room temperature for 5 days and characterized by scanning electron microscopy SEM (JEOL JSM 7000F, JEOL, Tokyo, Japan) and the images were processed using a software for fractal dimension (software version 8.0 Mountains Lab USA), energy dispersive spectroscopy (EDX) and watershed segmentation analysis.

2.3. Mechanical test

To perform the mechanical tests of the polymeric matrix and the glass ionomer gels with TEOS, this procedure was followed: in a first step, a specimen of the polymer matrix was placed at a temperature of -5 ° C and -10 ° C respectively for 10 hours in a Fisherbrand Isotemp-Fisher Scientific /Value Lab Freezer. In a second step, a specimen of the glass ionomer gels was processed in the presence of TEOS, which was stored at a temperature of -5 to -30 ° C for 10 hours. After each processing time in relation to temperature, each one of the specimens with dimensions of approximately 3 x 3 mm, were taken out to perform the impact tests with a Gardner Impact Tester equipment according to ASTM D 2794 method.

2.4. Viability test

To determine the viability of the glass ionomer cement gels with TEOS, a biocompatibility test was performed by preparing a simulated body fluid solution (SBF) containing Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3- 4.2, $HPO_4{}^{2-}$ 1.0, and $SO_4{}^{2-}$ 0.5 mM at pH 7.0 in distilled water respectively, (solution 1). Later, another solution was prepared containing bidistilled water to which 50 mg of Collagen from chicken sternal cartilage (Sigma Aldrich), 10 ml of acetic acid at pH 3.0 (5 mg/ml) and 100 mg of the powders containing the gels were added, (solution 2). Then 300 ml of solution 1 were added to solution 2 and the mixture was shaken in a SSI3 SHEL –LAB/shaking incubator and stored for 24 hours at 8°C. The excess fluid was then removed and dried overnight. Once the samples were dry, these were analyzed using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Characterization of Glass ionomer cement gels with TEOS by SEM

Fig. 1 shows the TEOS xerogels in absence of glass ionomer, it can be seen that the xerogels have different morphology and size, it is also observed that the surface is not porous.

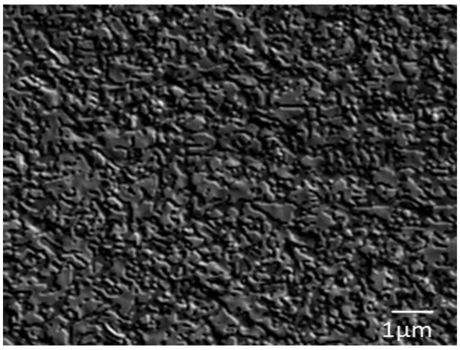


Fig. 1. SEM image of TEOS xerogels.

In Fig. 2 the morphology of the Glass ionomer cement gels with TEOS in SEM is observed, this image reveals the formation of pores with homogeneous morphology, circular particles are seen inside the pores and also outside. The observation in SEM leads to establish the homogeneous formation of the surface. The process of formation of gels indicated by the SEM micrographs is a kinematically controlled process, rather than thermodynamically controlled process. In this manner, the system evolves and organizes in such a state or structure that is consistent with the lowering of the total free energy of the system, including the free energies present in volume as well as free energies present in interface. The energies can be elastic strain energies due to the misfit between the various phases as well as between the actual system and the substrate. The interface energy leads to the selection of those surface and interface that have the lowest energies. The gels kinematically controlled are governed by the variables such as deposition, time and metallic surface diffusion fluxes. The structure that is being formed is the result of the interplay of these processes acting simultaneously during the deposition process of metallic precursor. Finally, depending on the different precursors the growth rate is minimum even in presence of other medium acids or bases. Furthermore, growth rate also depends on the concentration of dispersing medium.

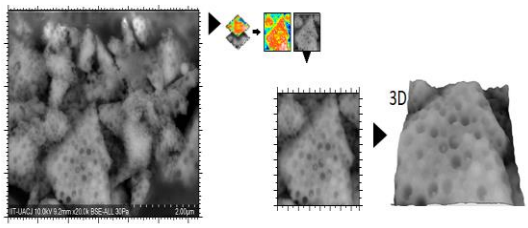
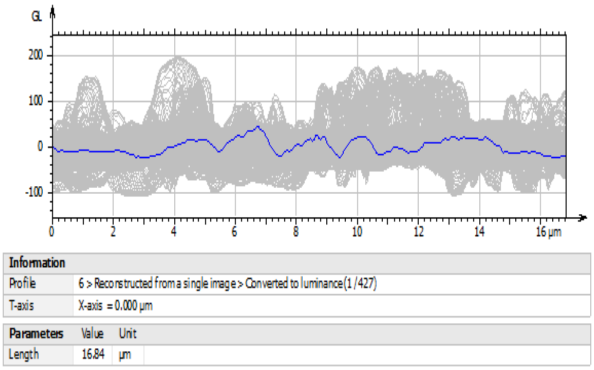


Fig. 2. SEM images of glass ionomer cement gels with TEOS.

3.3. Profiles of roughness

The Fig. 3 shows the extract north-south profiles of roughness of the gels' surface. In it can be observed the existence of (grooves) with a mostly irregular morphology and a variation in their depth and height, the characteristics data are shown in Table 1.



Information	
Profile	6 > Reconstructed from a single image > Converted to luminance(1 /427)
T-axis	X-axis = 0.000 µm

Parameters	Value	Unit
Length	16.84	µm

Fig. 3. Profiles of roughness of glass ionomer cement gels with TEOS.

Table 1. Values of roughness of glass ionomer cement gels with TEOS.

Sq	3.005 nm	Root-mean-square height
Ssk	0.3140	Skewness
Sku	0.3210	Kurtosis
Sp	12.99 nm	Maximum peak height
Sv	12.35 nm	Maximum pit height
Sz	25.90 nm	Maximum height
Sa	2.395 nm	Arithmetic mean height

3.4. Watershed segmentation analysis

The peak /µm^2 count can be seen in the histogram in Fig. 4 which were characterized by the watershed segmentation method and have a normal distribution with a standard deviation of 8 nm, additionally, the maximum peaks were found to be in a range of 17 to 22 nm.

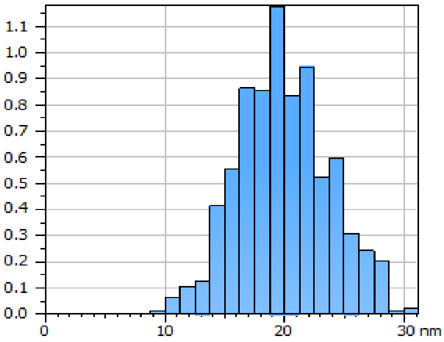
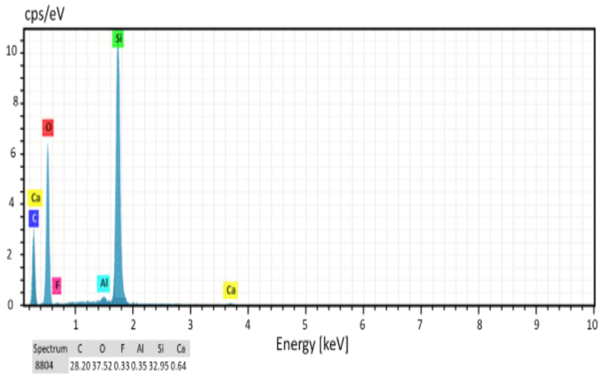


Fig. 4. Peak count histogram of glass ionomer cement gels with TEOS.

3.5. Energy dispersive X-ray analysis

The energy dispersive spectrometer studies (EDX) show the elemental chemical composition of the glass ionomer cement gels where Carbon, Oxygen, Fluor, Al, Si and Ca can be observed, Fig. 5.

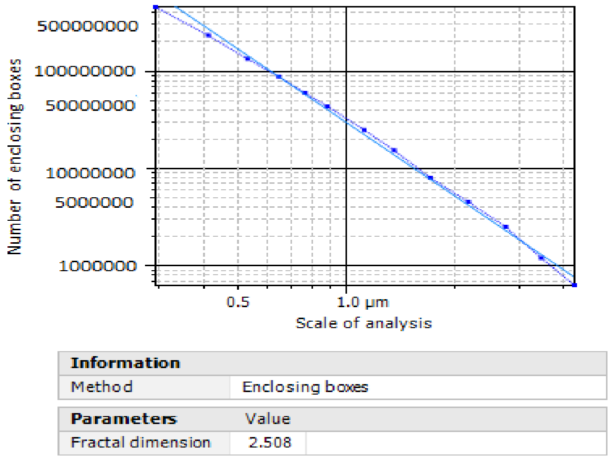


Spectrum	C	O	F	Al	Si	Ca
8804	28.20	37.52	0.33	0.35	32.95	0.64

Fig. 5. EDX spectrum of glass ionomer cement gels with TEOS.

3.6. Fractal dimension analysis

Fig. 6 is representative of the fractal dimension analysis performed on glass ionomer cement gels with TEOS where 13 points were analyzed on the grooves to know the pattern of the edges using the following formula: log S = D log L -------> D = log S / log L. Where S (13) is the size of the fractal, L is the measurement scale (2.78) and D is the unknown fractal dimension. The result of the fractal dimension is related to the morphology of the edges since an irregular surface is present, which is continuous and characterized by its geometric shape that is due to the participation of the polysaccharide matrix. In this way, the value of the fractal dimension indicates that the base of the gels' geometric shape is circular. According to the result obtained on the fractal dimension, which has a value of, approximately 2.508, it can be inferred that there is a self-similarity on its surface marked by the values of roughness that gives us a real idea of its extent since its parts retain the same one-dimensional shape, Fig. 6. This behavior can be explained by the homogenous deposition of the polymer chains of galactopyranose before of the polymerization process to form dimensional networks.



Information	
Method	Enclosing boxes

Parameters	Value
Fractal dimension	2.508

Fig. 6. Fractal dimension of glass ionomer cement gels with TEOS.

3.7. Study of density of glass ionomer cements gels

The Fig. 7 shows the density analysis of the glass ionomer cement gels in presence of TEOS, in this image a change in the density related to the amount of polysaccharide and the final volume can be clearly seen from an increase of 2.25 g and 2.5 g respectively. Likewise, the gradual increases of the polymer from 0.5 g to 2.0 g do not seem to represent changes in the density of the gels because the forces of the cross-linked networks are not compacted by the concentration of the polysaccharide. Among other things, the study of the density of the gels summarized in the Fig. 7, which in this case is between 0.13 and 0.16 g/cm^3, suggests a relationship between the decrease in density and the increase in the final volume of the glass ionomer cement gels from a concentration of 0.2% and 1.0 %, from here the complexity of some systems made with polymers is deduced to know exactly its density, which demonstrates the importance of the management of internal variables and the molecular interactions of the different metal precursors.

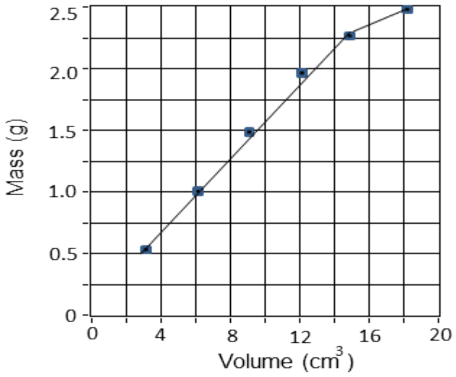
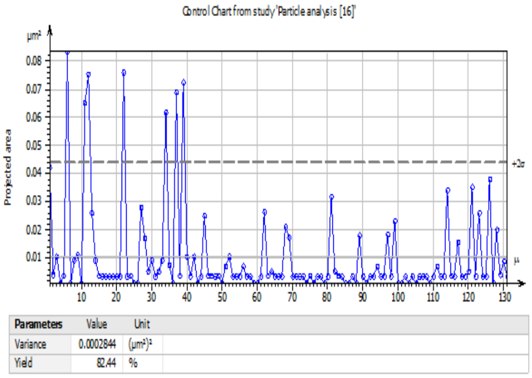


Fig. 7. Density of glass ionomer cement gels with TEOS.

3.8. Particle analysis

Fig. 8 shows the following values: variance with 0.0002844 µm^2, and 82.44 %, which corresponds to the yield of particles, the x-axis represents the number of particles and the y-axis the value in µm^2.



Parameters	Value	Unit
Variance	0.0002844	(µm²)²
Yield	82.44	%

Fig. 8. Particle analysis.

Fig. 9 shows the coefficient of determination R2, it can be seen that the points are on the regression line, the value of R2 is 1, which determines that the results obtained can be replicated, in this way our model explains 100% of the value of the variable.

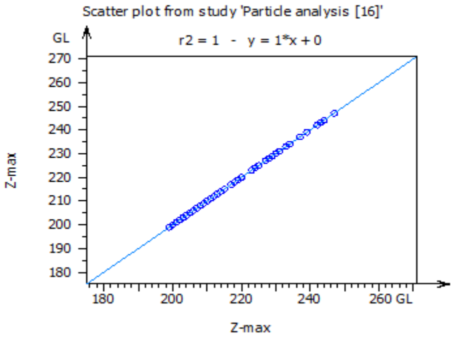


Fig. 9. Coefficient of determination R2.

3.9. Mechanical analysis

Fig. 10 shows the analysis of the mechanical properties of the polysaccharide matrix in the absence of glass ionomer particles and TEOS, it can be seen that the sample that was processed at -5 and -10 ° C, showed a resistance of 1 lb at -5 ° C before fracturing. Fig. 11. Shows the matrix of the polysaccharide in SEM after the impact test.

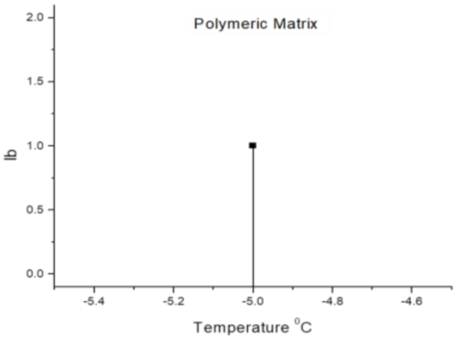


Fig. 10. Impact test of the polymeric matrix.

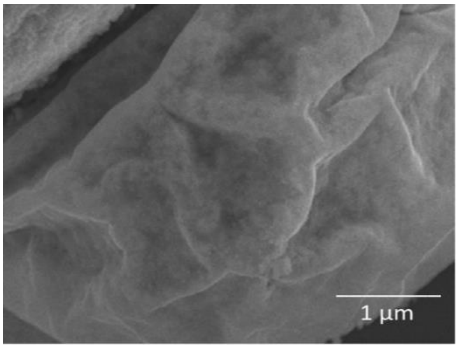


Fig. 11. Polymeric matrix in SEM.

Fig. 12 shows the analysis of the glass ionomer gel in the presence of TEOS, which was maintained in ranges of -5 to -30 ° C, the specimen showed a fracture resistance of 18 lb. and then fractured. The results show evidence that the impact resistance is increased due to the presence of glass ionomer and TEOS at low temperature, compared to the sample of the polymer matrix in the absence of glass ionomer and TEOS, (Fig. 10).

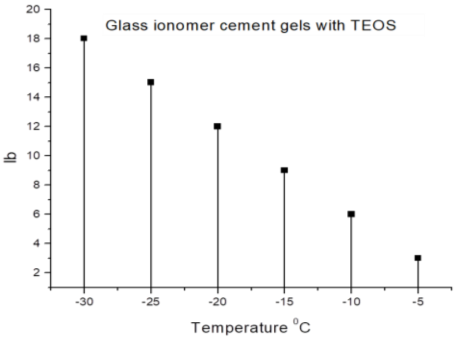


Fig. 12. Impact test of glass ionomer cement gel with TEOS.

Fig. 13 shows the SEM image of the gel after the impact test. The behavior of glass ionomer gels in the presence of TEOS can be caused by the transfer of the stress applied to the polymer matrix on the glass ionomer and TEOS particles, existing a cohesive force between the matrix and the particles that make up the gels, restricting the movement of the polysaccharide fibers, thereby making the gels harder and more resistant. Likewise, the presence of TEOS xerogels gives the gels the characteristic of thermicity behaving as an insulator against low temperatures, since the low temperature to which the gels were subjected would be expected to cause an increase in the fragility of the gels due to the absorption of less energy to break the material, a fact that in this case did not happen.

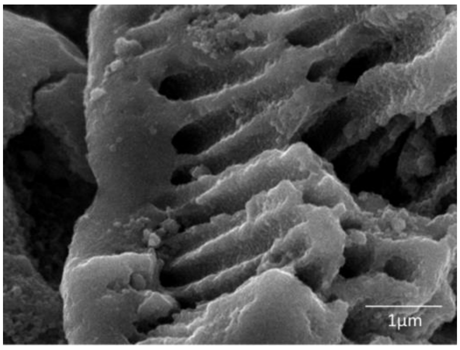


Fig. 13. Micrograph in SEM of glass ionomer cement gel with TEOS.

3.10. Viability analysis

The Fig. 14 (a) and (b), shows the sample of glass ionomer cement gel with TEOS in presence of Collagen from chicken sternal cartilage. The gels present a different morphology, the surface covered by the collagen fibers can be observed clearly [12]. Additionally, the surface has a smooth and rough appearance, probably due to the fact that the temperature and the concentration of the collagen play an important role in increasing the density of the fibers in the gels. Likewise, there is a hydrophobic behavior that can have an intermolecular relationship between the collagen fibers, organizing them into dense blocks covering the gels.

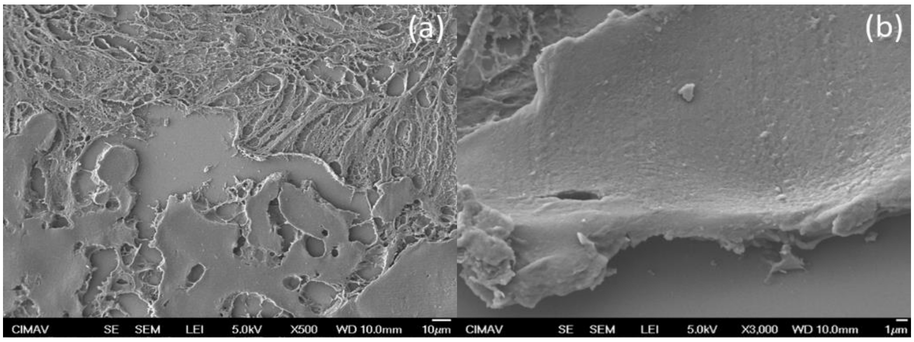


Fig. 14. (a) and (b), glass ionomer cement gel with TEOS in presence of Collagen from chicken sternal cartilage.

4. Conclusions

The results show that the interaction of tetraethylorthosilicate and the polymeric matrix are potential elements to generate glass ionomer cement gels. The roughness results represented by a morphological homogeneity and a normal distribution in the peak/μm^2 with values between 17 and 22 nm, show that the galactopyranose matrix is an excellent mechanism for maintaining the system of interaction with metal precursors. Furthermore, stability control was possible by standardizing the concentration of the polymer in solution which was 0.2% to 1.0%.

The maintenance in the concentration of galactopyranose can form stronger interpenetrated networks, this allows a more homogeneous incorporation of metal precursors with an increase in its functionality. SEM images of the gels during the impact tests support the fact that the polymeric matrix in the presence of glass ionomer and TEOS has a higher resistance than the matrix in the absence of these elements. In reference to the interaction shown in SEM images between the gels and the collagen fibers, we confirm an excellent compatibility of organic and inorganic molecules in this system. In addition, with this technique it would be possible to analyze several events as concentration of polymer, impact strength, biocompatibility, pH and drying time.

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