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Structure and morphology of chitosan / bioactive glass prepared by sol-gel method

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Abstract — In this study, bioactive glass in ternary system composition SiO_2-CaO-P_2O_5 was synthesized via sol-gel method. The aim of this study is to add a biopolymer which is the chitosan to the solution of 63S bioactive glass. The sol obtained is mixed with a chitosan solution at different percentage (0%, 10%, 30%, 60% and 90%) then heated at 60°C for 10 h and drying at 130°C for 20 h. The powders sintered at 600 °C for 2h and characterized by XRD, FTIR and SEM analyzes. The influence of the addition of chitosan on the structure and morphology of the bioactive glass powders was distinguished and the results showed that the bioactive glass powders have a crystalline structure with the increasing of chitosan rate and this is approved by the XRD and SEM analyses.
Keywords*: Biomaterials, bioactive glass, Sol-Gel method, Chitosan.*

I. INTRODUCTION

Significant interest has been generated in the application of synthetic bioactive materials in tissue engineering. Biomaterials can be produced from many kinds of materials, such as synthetic polymers, metals, ceramics and natural macromolecules that have the proper morphology and properties according to the application requirements [1]. This family of substitutes is particularly suitable for filling bone defects [2] as well as prosthetic coatings in orthopedic surgery, maxillofacial, aestheticians and dental [3, 4]. The main advantages of these synthetic biomaterials are availability, reproducibility and reliability. They must be biocompatible, they should not generate any complication or inflammatory response and also be suitable in their mineral compositions [5]. Hench and al [6] has reviewed the development of bioactive silicate glasses.

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One of the most important reasons for welcoming these kinds of materials is their excellent biocompatibility [7], good bioactivity in comparison with metallic and polymeric biomaterial [8],their osteoconductivity and their biodegradability [9, 10]. In fact, in contact with living tissues, bioactive glasses generate a series of physical and chemical reactions material / bone tissue leading to the formation of hydroxyl carbonate apatite (HCA) layer interface [11, 12], which has a similar composition to the inorganic part of human bone [13, 14].

Sol-gel is the most widely used technique for synthesis of bioactive glass. Sol-gel derived bioactive glass, compared to traditional melt processed, has higher bioactivity and biodegradability [15].

In this investigation, we study the effect of the addition of chitosan, a kind of polysaccharide [16], which is adeacetylated derivative of chitin and has been widely applied in biomedical applications because of its cell compatibility, biodegradability and non-toxic characteristics [17], into the solution of ternary bioactive glass synthesized by sol-gel method. The structure and morphology of ternary

bioactive glass with different rate of chitosan were studied.

II. Synthesis of chitosan / bioactive glass

SiO_2-CaO-P_2O_5 ternary bioactive glass was synthesized via sol-gel method [7]. Initially, tetraethylorthosilicate (TEOS) was added to ethanol as an alcoholic media and the mixture was stirred for 30 min. The following reagents were added in the following sequence, stirring 30 min for each reagent to react completely: the H2O:TEOS molar ratio was 4:1, triethylphosphate (TEP), calcium nitrate tetrahydrate and hydrochloric acid (HCl, 2N).

After the final addition, the solution was stirred for one hour addional. Chitosan solution at a concentration of 2wt% was dissolved in 2% acetic acid. The sol was mixed with the chitosan solution at different volume ratios (chitosan at 0%, 10%, 30%, 60% and 90%) and the mixtures were stirred for 2 h, heated at 60°C for 10 h and dried at 130°C for 20 h. The final products were crushed then sintered at 600 °C for 2 h. The different powders of bioactive glass with and without chitosan noticed BG-0% Ch, BG-10% Ch, BG-30% Ch, BG-60% Ch and BG-90% Ch were characterized by XRD for phase analysis, FTIR for identification of functional groups and scanning electron microscopy (SEM) for the morphology.

III. Results and Discussion

III.1. Characterization of chitosan

III.1.1. XRD analysis of chitosan

X-ray diffraction pattern of chitosan is shown in Fig. 1. The diffractogram of chitosan shows characteristic peaks at 10.4º and 20.4º which coincides with the pattern of the 'L-2 polymorph' of chitosan [18].

The FTIR spectrum of chitosan is shown in Fig.2. The strong and broad band centered at 3440 cm^{-1} which is attributed to the axial stretching of O-H and N-H bonds. The band corresponding to the axial stretching of C-H bonds is observed around 2889 cm^{-1} and the bands centered at 1650 cm^{-1} and 1601 cm^{-1} is assigned to the amide I and amide II vibrations, respectively. The spectrum show also two bands at 1422 cm^{-1} and 1380 cm^{-1} resulting from the coupling of C-N axial stretching and N-H angular deformation and the bands in the range 1088–897 cm^{-1} due to polysaccharide skeleton, including the glycosidic bonds, C-O and C-O-C stretchings [19].

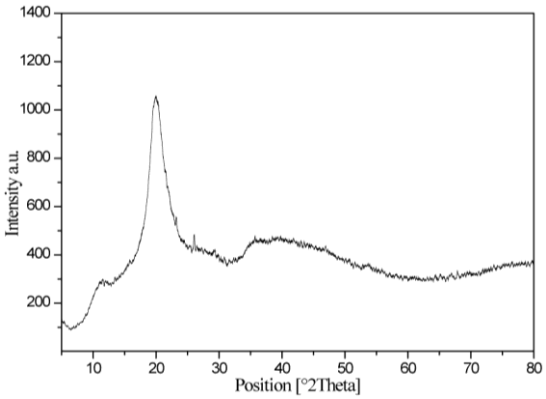

Fig. 1 The diffractogram of chitosan

III.1.2. FTIR analysis of chitosan

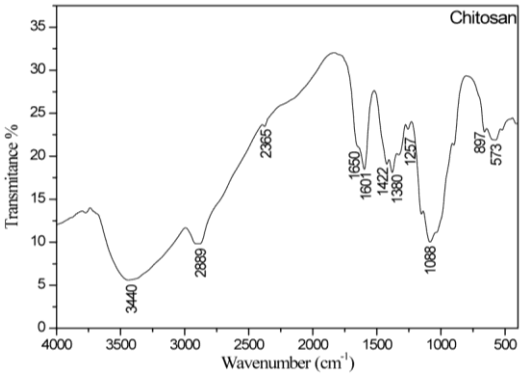

Fig.2 FTIR spectrum of chitosan

III.2. Characterization of bioactive glasses with the addition of chitosan

III.2.1. XRD analysis bioactive glasses

The X-ray diffraction analysis result for the bioactive glass with different rate of chitosan is shown in Fig.3. The samples BG-0% Ch, BG-10% Ch and BG-30% Ch shown the same

paterns, these samples takes amorphous state indicative of the intern disorder and glassy nature of these materials [10, 20]. We observed a crystalline structure in the samples with the rate of 60% and 9% of chitosan, these peaks can be assigned to the wallastonite ($CaSiO_3$) or to the apatite [21 - 23]. The crystallization process depending on the heat treatment conditions [24, 25]. Whereas, In this work we observed that the crystallization depends on the increasing of the rate of chitosan.

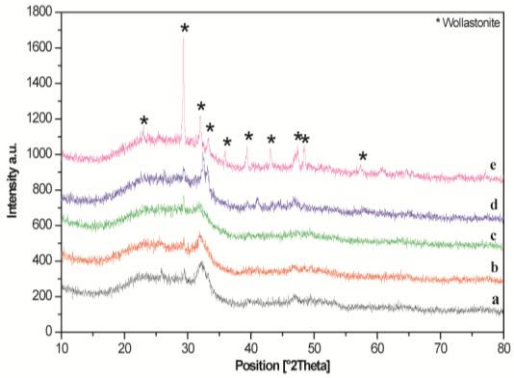

Fig. 3 The diffractograms of bioactive glass powders: (a) BG-0% Ch, (b) BG-10% Ch, (c) BG-30% Ch, (d) BG-60% Ch and (e) BG-90% Ch.

III.2.2. FTIR analysis of bioactive glasses

The effect of chitosan addition is studied by FTIR spectral analysis, which is shown in Fig. 4. The samples shown a strong absorption bands around 1058 cm^{-1} assigned to the Si-O-Si asymmetric bond stretching vibrations, this band became lager with the increasing of the percentage of chitosan especially in the case of 60 and 90 % of chitosan. The band in the 786cm^{-1} is attributed to the symmetric Si-O-Si stretching vibrations [1, 21, 26] this band is almost disappeared for the bioactive glasses with 60 and 90 % of chitosan and the absorption around 455 cm^{-1} due to the vibrational mode of the bending of Si-O-Si [22, 24, 27] which prove that all the samples are mainly composed of a Si-O-Si network. The weak inflection at 1641 cm^{-1} and the broad band centered at 3473 cm^{-1} are assigned to O-H band of adsorbed water and structural hydroxyl group respectively [3, 4, 28] and finally the band at 1440 cm^{-1} is attributed to carbonate group which is appeared also in BG-60% Ch and BG-90% Ch samples.

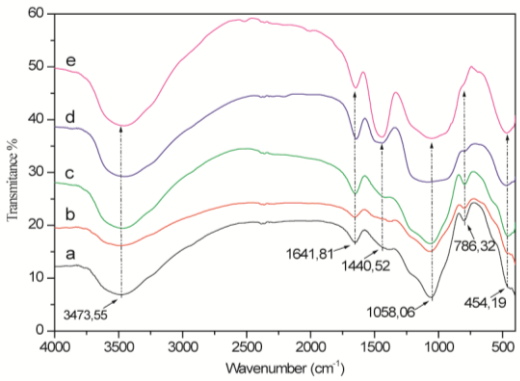

Fig. 4 FTIR spectra of bioactive glass powders 63S: (a) BG-0% Ch, (b) BG-10% Ch, (c) BG-30% Ch, (d) BG-60% Ch and (e) BG-90% Ch.

III.2.3. SEM analysis of bioactive glasses

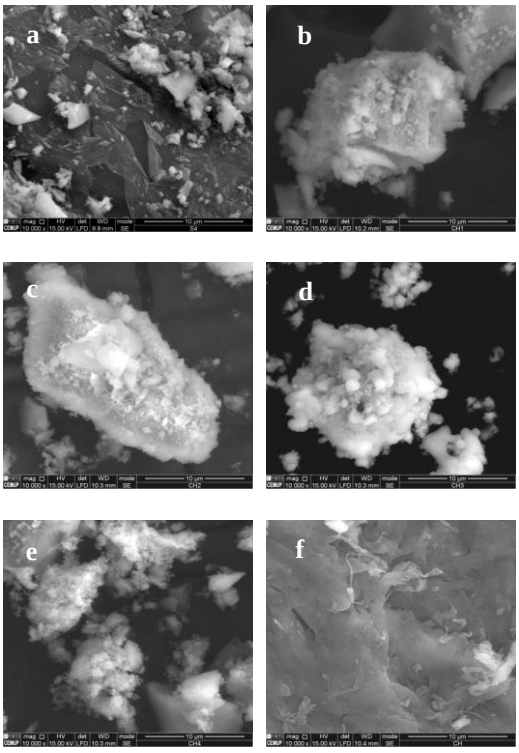

Fig. 5 Morphology of bioactive glass powders: (a) BG-0% Ch, (b) BG-10% Ch, (c) BG-30% Ch, (d) BG-60% Ch and (e) BG-90% Ch, (f) Chitosan (Ch).

The microstructure and the morphology of the bioactive glass powders shows on Fig.5 depends on the rate of the addition of the chitosan. The bioactive glass powder without addition of chitosan (BG-0%Ch) shows a very dense structure with almost zero porosity (Fig. 5a). Whereas, the powders with 10% (Fig. 5b) and 30% on chitosan (Fig. 5b and 5c) shown the same structure which is much similar to the BG-0%Ch with lower density. Powder with 60% chitosan (Fig. 5d) shown spherical particles agglomerated and bioactive glass powder with 90% chitosan (Fig. 5e) showed very small spherical particles with a sponge structure which indicate the crystalline nature of these two powders. These results are in agreement with the results of XRD studies (Fig. 3). Fig. 5f, shows the micrographs of chitosan with a smooth, compact, and homogeneous surface.

IV. CONCLUSION

Different rate of chitosan was added to the solution of bioactive glass precursors synthesized by sol-gel method. The results show that the addition of chitosan influenced the structure and morphology of bioactive glass powders obtained at a fixed sintering temperature of 600°C. X-ray diffraction analysis shows an amorphous structure of the bioactive glass powders with 0, 10 and 30 % of chitosan and a crystalline structure up to 30%. The crystallization process of the bioactive glass powders increased with increasing of the rate of chitosan and SEM analysis is in agreement with XRD analysis.

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