Effect of Sodium Bicarbonate Additions on the Physical, Mechanical and Bioactive Property of Sol-Gel Bioglass

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Abstract. Porous bioceramics are the materials of choice for non-load bearing bone implants. Calcium phosphates and bioglass are widely used due to excellent biocompatibility. The primary function of porous bioceramics are as filler material for bone defects. In this research, 10% amount of sodium bicarbonates (Na₂HCO₃) were mixed with sol-gel derived glass powder (SiO₂-CaO-P₂O₅) and sintered at 700 °C for 3 hours. It was found that, additions of sodium bicarbonate induced a foaming effect during sintering of bioglass thus increased the porosity content of the glass-ceramics obtained. However, the increased in porosity significantly reduced the compressive strength of the crystallized glass. The increased in porosity content and formation of sodium related phases within the crystallized glass matrix after sintering resulted in enhancement of its in vitro bioactivity property when tested in SBF solution.

1 Introduction

Macroporous structure in the range of 100 to 300 µm can promote tissue ingrowth and enable bone ingrowth as well as the formation of capillary to occur [1-2]. Bioglass with macroporous structure within this range of pore size is required to fulfil the requirement as an implant scaffold. This scaffold structure can be achieved by preparing porous bioglass by using several different methods such as polymeric templating and foaming agent [3-7]. The component of Na₂O in the sol-gel derived glass is important due to addition of network modifier cations; such as sodium (Na²⁺), non-bridging oxygen (NBO) bonds can be introduced through the disruption of structure. This NBO bonds may increase dissolution from the glass surface promoting the formation silica layer thus improve the bioactivity of bioglass [3-4]. It is necessary for the deposition of Ca²⁺ and P⁵⁺ ionic species that lead to the bonding and crystallization of apatite layer. Other than that, presence of Na₂O composition in bioglass resulted in the formation of sodium-related crystalline phases after sintering. This crystalline phases which are hard yet biodegradable can increased the bioactivity property of sol-gel derived bioglass [8]. Na₂O also is typically used for lowering the melting temperature in conventional melt-derived glasses [9].

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Our previous studies has found that sintered sol-gel derived glass with macroporous structure and higher mechanical properties can be obtained by the presence of specific Na$_2$O content [10-11]. Typically, Na$_2$O component in bioglass composition was obtained by hydrolisis reactions of sodium nitrate precursor in acidic solution which is added during a sol-gel process. Sodium bicarbonate (NaHCO$_3$) is commonly known as baking soda, bread soda, bicarbonate of soda, and cooking soda. It has many uses, ranging from cooking to cleaning and personal hygiene. Its physical appearance is usually a white, odourless, fine powder and has alkaline or basic properties. It dissolves in water, so it is water-soluble and it is nonflammable [12]. Several previous studies were carried out on the preparation of scaffold material using sodium bicarbonate as foaming agent [13-15]. However, no studies has yet been done in the application of sodium bicarbonate as the source of sodium in sol-gel derived glass composition and at the same time acts as pore forming agent. Thus, the aim of this study is to investigate the effect of sodium bicarbonate additions on the physical, mechanical and bioactivity properties of ternary glass composition made by sol-gel method. In this study, the comparison between ternary sol-gel derived glass and sol-gel derived glass with added sodium bicarbonate were discussed and presented.

2 Methodology

Gel-glasses with novel compositions of 60% SiO$_2$ – 37.5% CaO – 2.5% P$_2$O$_5$ (in mol%) were initially prepared via acid catalyzed sol-gel method. The reagents and precursors used to prepare these gel-glasses includes nitric acid (HNO$_3$, 1 M, Sigma Aldrich), tetraethyl orthosilicate (TEOS, Si(OC$_2$H$_5$)$_4$, Sigma Aldrich (99.0%)), tetraethyl phosphate (TEP, OP(OC$_2$H$_5$)$_4$, Merck (99.0%)), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O, Merck (99.0% - 102.0%)) and sodium bicarbonate (Na$_2$HCO$_3$, Merck (96.5%)). At first, 1 ml of nitric acid was mixed with 40 ml of deionized water and stirred continuously using magnetic stirrer for 5 minutes. Then, followed by addition of precursor with the sequence of 10.0 ml TEOS, 2.0 ml of TEP and 8.0 gm of calcium nitrate tetrahydrate. Each of these reagents were dissolved into the solution one by one after being stirred for 40 minutes in between them. For Na-BG, 3.0 gm of sodium nitrate was added and dissolved into the solution. The sol then casted into teflon mold for gelation process. The gel obtained then been subjected to aging at 60 °C for 24 hours followed by drying at 120 °C for 48 hours. The dried gel then heated at 600 °C for 3 hours for stabilization before grinded into fine powder using agate and mortar.

The glass powders were then pressed into 12 mm diameter pellets via uniaxial hydraulic press and sinter at temperature of 700 °C with soaking time and heating rate of 3 hours and 5 °C/min respectively. For compression test, six pellets with 6.00 mm diameter and 10.00 mm height were prepared for each sample parameter. The compression test (Instron 8874) was done with maximum load capacity and speed of 5 kN and 20 seconds respectively. The sintered pellets were immersed into simulated body fluid (SBF) (prepared by following the ISO 23317:2007(E)) solution for 7 days for in vitro bioactivity test. Samples (before and after immersed in SBF solution) were characterized for surface morphology by using Scanning Electron Microscopy (SEM) model JOEL JSM6460LA) and phases analysis using X-ray Diffraction (XRD) model BRUKER D2. The percentage of porosity and densification of glass-ceramic were obtained by dividing bulk density (obtained from Archimedes principle) with rule of mixture (obtained from qualitative analysis based on XRD). Meanwhile, percentage of weight loss and diameter shrinkage of samples were calculated based on the particular data measured before and after sintering process.
3 Results and discussions

The XRD pattern of BG (in figure 1) showed the presence of hydroxyapatite (Ca_{10}(PO_4)_{6}(OH)) (JCPDS Card No. 9-432) as the major phase. While, β-tricalcium phosphate (Ca_3(PO_4)_2) phase and also known as (β-TCP) (JCPDS No: 70-2065) as minor phases. Song Wang et al., (2017), also had found that when temperature reached to 700 °C the β-tricalcium phosphate (β-TCP) phase appeared [16]. However, the split of (211) and (112) reflections is not complete due to the fact that the HA is not fully crystallized. This phenomenon is due to the fact that the atoms in BG sample was not obtain sufficient energy for atom rearrangement at the HA lattice to induce complete crystallization [16]. The XRD pattern of Na-BG (in Figure 2) showed the formation of similar crystalline phases after sintering as BG, however, sodium calcium silicate (Na_2Ca_2Si_3O_9) (JCPDS No: 75-1685) and sodium calcium hydrogen phosphate (NaCa(HPO_4)_2) (JCPDS No: 50-1758) phases were formed. Sodium calcium silicate (Na_2Ca_2Si_3O_9) (known as combeite) can influence the bioactivity property [17]. Meanwhile, formation of sodium calcium hydrogen phosphate (NaCa(HPO_4)_2) which related to calcium phosphate in bioglass can enhanced the properties in bone tissue engineering [17]. Thus, this results showed that both BG and Na-BG samples has been crystallized and became glass-ceramic compound after sintering at 700 °C.

Fig. 1. XRD diffractogram for BG sample

Fig. 2. XRD diffractogram for Na-BG sample.
Table 1 showed the physical and mechanical properties of BG and Na-BG samples. It was found that, the presence of sodium bicarbonate in bioglass affected in higher porosity, higher weight loss (40 wt.%) while reduced in body densification of the glass-ceramics. During sintering process, the decomposition of sodium bicarbonate should be occurred and foaming effect has been taken place. This is also explained by previous study where during sintering, the sodium bicarbonate was decomposed into sodium carbonate, carbon dioxide (CO$_2$) and vapour (H$_2$O) [18]. The release of carbon dioxide (CO$_2$) gaseous and vapour during sintering caused a foaming effect. The foaming effect occurred was in line with diameter expansion at 3.33% experienced by Na-BG compared with BG which exhibited diameter shrinkage at 6.38%. Furthermore, higher weight loss experienced by Na-BG also was due to the decomposition of sodium bicarbonate content in the glass matrice. As explained by Galusek et al., (2013), during the intermediate phase of sintering, the microstructure of samples was undergoing rapid inter-particle neck growth and coalescence [18]. Atoms diffused into the empty space creating the grain boundaries interface. The diffusing action was driven by energy, usually provided by the high temperature during sintering in the form of heat energy reported by M. N. Rahman (2003). As a result, the movement of atoms get into the empty space will cause the sample to shrink [19]. The compressive strength for BG and Na-BG were 3.3 MPa and 1.2 MPa respectively. The compression strength of Na-BG was apparently much lower compared to BG due to the porosity content of Na-BG was higher. This suggested that porosity of bioglass significantly affected its compressive strength property. The entrapped carbon dioxide gas produced during foaming effect created some holes and channel inside the Na-BG sample which then attributed to the relatively lower compression strength [20].

| Properties               | Sample       |
|--------------------------|--------------|
|                         | BG           | Na-BG        |
| Weight loss              | 24.0%        | 40.0%        |
| Diameter shrinkage/expansion | 6.38%    | -3.33%      |
| Densification            | 70.0%        | 55.0%        |
| Porosity                 | 30.0%        | 46.0%        |
| Compressive strength     | 3.3 MPa      | 1.2 MPa      |

Figure 3 (a) showed the morphology of BG which consisted of inhomogeneous grains, rough surface and apparent porous structure. This was due to the bioglass particles used for sample preparations were inhomogeneous in particle sizes, thus easily produced stress concentration on the surface. Meanwhile, the addition of sodium bicarbonate into bioglass matrice significantly formed glass-ceramic morphology with higher pores structure and larger pore sizes (Figure 3 (b)). This is in par with the sample physical properties which
showed the addition of sodium bicarbonate into bioglass formed higher porosity and lower densification of the glass-ceramic obtained.

Fig. 3. Surface morphology of (a) BG and (b) Na-BG both at 500X magnification.

Higher porosity content formed on the Na-BG morphology was particularly due to the foaming effect resulted from release of gaseous during sintering. The high porous structure on the morphology should be the main factor which attributed to lower compression strength of Na-BG. The compressive strength of Na-BG however was under the minimum strength required as scaffold materials for bone implant materials. Because of that, this samples would serve as a better candidate as filler materials in bone defected area instead of scaffolding materials.

The morphology image of BG after immersed in SBF solution for 7 days is shown in Figure 4 (a). The morphology was accumulated by inhomogeneous grains, crack-like and severe pores structures. Under the effect of water erosion and ion exchange between bioactive glass sample and SBF solution, cracks were formed as result of the dual function of physical and chemical reaction [21]. It was clear that, no apatite-like layer was formed on its surface thus indicate the low bioactivity property of BG. Meanwhile, morphology of Na-BG was characterized by the formation of homogenous structure and clearly apatite-like layer was completely cover its surface after soaked in SBF solution for 7 days (Figure 4 (b)). This indicate that the ionic dissolution rate of Na-BG was significantly higher compared to BG. According to Liu et al. (2013), the addition of sodium in bioglass sample was important in favoring the apatite formation. The presence of sodium and calcium network modifier cations interrupt the bridging oxygen (BO) bond which causes the formation of non-bridging (NBO) bond that improved the dissolution and bioactivity of glass and fasten HCA nucleation [22]. Furthermore, ion exchange reaction between Ca$^{2+}$ ions from bioglass network and H$^+$ from SBF solution took place at the corner of crack easily [19]. Other than that, higher porosity is required to offer sufficient space to reactive site for tissue growth and nutrient supply within the bone graft [23]. This result showed that, increased in porosity structure will increase the bioactive property of bioglass-ceramics due to higher HCA formation.
Fig. 4. Surface morphology of (a) BG and (b) Na-BG after immersed in SBF solution for 7 days.

Conclusion

In conclusion, additions of sodium bicarbonate were succeeded in increasing the porosity content of sintered sol-gel derived glass besides allowing the presence of sodium related crystallized phases. Both of this factor has improved the sol-gel glass in vitro bioactivity property when tested in SBF solution. However, the increased in porosity content significantly reduced the compressive strength of the sintered glass. Because of that, sodium contained-BG samples have high potential as the material of choice for bioactive filler materials in bone defects problem.

References

1. V. Karageorgiou, D. Kaplan. Porosity of 3D biomaterial scaffolds and osteogenesis. *Biomaterials*, **26**(27), pp.5474-5491 (2005)
2. X. Liu, M. Rahaman, Y. Liu, B. Bal, L. Bonewald. Enhanced bone regeneration in rat calvarial defects implanted with surface-modified and BMP-loaded bioactive glass (13-93) scaffolds. *Acta Biomaterialia*, **9**(7), pp.7506-7517 (2013)
3. I. Sabree, J. Gough, B. Derby. Mechanical properties of porous ceramic scaffolds: Influence of internal dimensions. *Ceramics International*, **41**(7), pp.8425-8432 (2015)
4. X. Liu, M. Rahaman, Q. Fu. Bone regeneration in strong porous bioactive glass (13-93) scaffolds with an oriented microstructure implanted in rat calvarial defects. *Acta Biomaterialia*, **9**(1), pp.4889-4898 (2013)
5. Q. Chen, I. Thompson, A. Boccaccini. 45S5 Bioglass®-derived glass–ceramic scaffolds for bone tissue engineering. *Biomaterials*, **27**(11), pp.2414-2425 (2006)
6. J. Jones, L. Ehrenfried, L. Hench. Optimising bioactive glass scaffolds for bone tissue engineering. *Biomaterials*, **27**(7), pp.964-973 (2006)
7. Z. Wu, R. Hill, J. Jones. Optimizing the Processing of Porous Melt-Derived Bioactive Glass Scaffolds. *Bioceramics Development and Applications*, **1**, pp.1-4. (2010)
8. K. Xie, L. Zhang, X. Yang, X. Wang, G. Yang, L. Zhang, H. Shao, Y. He, Ji. Fu, Z. Gou. Biomedical Glass I (2015)
9. Q. Chen, Y. Li, L. Jin, J. M. W. Quinn, and P. A. Komesaroff: Acta Biomater. 6 (2010)
10. S.N.F. Adam., J. Banjuraizah, Z. Furuz. Sol Gel Synthesis and Preparation of Macroporous Glass: Effect of Sodium Nitrate Addition. International Journal of Current Research in Science, Engineering & Technology, 1 (2018)
11. Zainudin, S., S.N.F. Adam, D.S.Che Halin, M. Yusof, J. Banjuraizah Z. Furuz,. Preparation and Characterization of Macro Porous Glass-Ceramics as Bioactive Scaffold Material. Solid State Phenomena, 281, pp.83-89 (2018)
12. Sodium Bicarbonate Supplements and Exercise Performance*, Healthline. [Online], Available: https://www.healthline.com/nutrition/baking-soda-and__performance [Accessed: 09- Dec- 2018].
13. X. Shen, J. Ruan, Z. Zhou, H. Zhang. Fabrication of porous scaffolds using NaHCO₃ particulates as the porogen material. Journal of Wuhhan University of Technology-Mater. Sci. Ed., 22(2), pp.279-283 (2007)
14. F. Dehghani, N. Annabi. Engineering porous scaffolds using gas-based techniques. Current Opinion in Biotechnology, 22(5), pp.661-666 (2011)
15. M. Fauzi, N. Du, H. Osman, A.G. Supri. Effect of Sodium Bicarbonate as Blowing Agent on Production of Epoxy Shape Memory Foam using Aqueous Processing Method. Sains Malaysian, 44(6), pp.869-874 (2015)
16. I. Hung, W. Shih, M. Hon, M. Wang. The Properties of Sintered Calcium Phosphate with [Ca]/[P] = 1.50. International Journal of Molecular Sciences, 13(12), pp.13569-13586 (2012)
17. J. Chen, L. Zeng, X. Chen, T. Liao, J. Zheng. Preparation and characterization of bioactive glass tablets and evaluation of bioactivity and cytotoxicity in vitro. Bioactive Materials, 3(3), pp.315-321 (2018)
18. S. Wang, Y. Wang, K. Sun, X. Sun. Low temperature preparation of α-tricalcium phosphate and its mechanical properties. Processing and Application of Ceramics, 11(2), pp.100-105 (2017)
19. M. N. Rahaman. Ceramics Processing and Sintering, 2003.
20. E. Aguilar-Reyes, C. León-Patiño, B. Jacinto-Díaz, L. Lefebvre. Structural Characterization and Mechanical Evaluation of Bioactive Glass 45S5 Foams Obtained by a Powder Technology Approach. Journal of the American Ceramic Society, 95(12), pp.3776-3780 (2012)
21. R. Li, A.E. Clark, L.L. Hench. An investigation of bioactive glass powders by sol-gel processing. Journal of Applied Biomaterials, 2,231-9 (1991)
22. M. Trivedi. An Impact of Biofield Treatment on Spectroscopic Characterization of Pharmaceutical Compounds. Modern Chemistry & Applications, 3(03) (2015)
23. N. Gupta, D. Santhiya, Mesoporous bioactive glass and its applications. Bioactive Glasses (Second Edition). pp. 63-85 (2018)