Microstructural evaluation and thermal properties of sol-gel derived silica-titania based porous glasses

Kalim Deshmukh1*, Tomáš Kovářík1, Tomáš Křenek1, Theresia Stich2, Denitsa Docheva2

1New Technologies - Research Center, University of West Bohemia, Plzeň, 30100, Czech Republic.
2Laboratory for Experimental Trauma Surgery, Department of Trauma Surgery, University Regensburg Medical Centre, 93042, Regensburg, Germany.

E-mail: deshmukh@ntc.zcu.cz

Abstract. In recent years, the sol-gel synthesis of porous glasses has drawn widespread attention owing to the convenience and versatility of the sol-gel method. The sol-gel synthesis process mainly involves hydrolysis and condensation of precursors followed by drying and stabilization. In the present study, silica-titania (Si-Ti) based porous glasses with different compositions were synthesized using the sol-gel method. In general, the final properties of sol-gel derived glasses significantly depend on the characteristics such as pore structure, pore size, morphology and the compositions of the precursor materials. The influence of these processing parameters on the microstructural and thermal properties of Si-Ti based glasses has been investigated. The microstructures of the synthesized Si-Ti based porous glasses were investigated using scanning electron microscopy (SEM) and the thermal properties were evaluated using thermogravimetric analysis (TGA) and thermomechanical analysis (TMA). The main objective of the present study is to utilize these Si-Ti porous glasses as a potential biomaterial for bone tissue regeneration. Therefore, to understand this facet of Si-Ti porous glasses, it is essential to investigate their physical and microstructural properties.

Keywords: Sol-gel method, Si-Ti glasses, microstructure, thermal properties.

1. Introduction
The sol-gel method is a simple and reliable wet-chemical technique used for the synthesis of high-quality materials [1]. The sol-gel method is considered as a promising and versatile route to obtain a wide range of materials that can be characterized by nano and microstructures [2] and can be processed into suitable technological products such as fibers [3], coatings [4] and thin films [5] for industrial applications. Recently, the sol-gel method has been accepted by several research groups for the synthesis of a next generation of bioactive glasses with tailored compositions to accomplish the requirements of specific applications [6]. Using the sol-gel method, glasses can be synthesized at lower processing temperatures than the traditional synthesis methods [2]. Sol-gel glasses tend to have improved surface area, surface reactivity and biodegradability [7, 8]. The sol-gel method also provides better control over the homogeneity and purity of the synthesized glasses [2]. The physical and chemical properties of sol-gel glasses depend on the kinetics of hydrolysis and the condensation reactions and also on the type of precursors, compositions, solution pH, temperature and the catalysts.
used during sol-gel synthesis [9]. The porous structure is an intrinsic characteristic of sol-gel based glasses as it is directly associated with the synthesis process [6]. For characterization of the porosity, several features such as pore interconnectivity, pore shape and pore size distribution are generally considered. The porosity characteristics are the key to determine the extent of interaction with cells and the surrounding environment. Hence, the control of pore size and pore structure is the primary need for producing bone substitute materials [6].

Recently, much attention has been drawn towards the synthesis of porous silica-titania (Si-Ti) based glasses because of their intriguing properties such as high thermal and chemical stability, low thermal expansion and tunable refractive index as compared with pure Si or Ti glasses [10, 11]. Si-Ti monoliths with macro and mesoporous structures have been prepared by the sol-gel and phase separation method using various titanium precursors [10]. It has been reported that by using the phase separation method the gel morphology can be controlled to a great extent [12]. Moreover, for the synthesis of Si-Ti glasses by the sol-gel method, controlled hydrolysis is required for achieving homogeneous gels. This is because the hydrolysis and condensation reaction rates of titanium alkoxides are substantially higher than the silicon alkoxides owing to the low electronegativity of Ti and its susceptibility to display several coordinate states [13]. Generally, to compensate for their differences in hydrolysis rates, bulky alkoxy groups for titanium and methoxy or ethoxy groups for silicon are utilized [14, 15]. Besides, using two-step hydrolysis method [16] and the employment of chelating agents such as acetylacetone (Acac) [17, 18] were found to be efficient in obtaining homogeneous Si-Ti based sol-gel glasses. Thus, these studies suggest that homogeneous Si-Ti based glasses can be synthesized simply by extending or altering the sol-gel method. In the present study, different batches of Si-Ti based glasses were fabricated using sol-gel and phase separation method by developing two different protocols and the preliminary results based on their thermal analysis and microstructural evaluation have been reported.

2. Materials and Experimental

2.1. Materials

The following chemical precursors were utilized without further purification for the sol-gel synthesis of Si-Ti porous glasses. Tetraethoxysilane (TEOS) with 98 % purity, titanium isopropoxide (TIP) with 97% purity and molecular weight 284.22 g/mol, Polyethylene glycol (PEG) flakes with average Mn 20,000 and 65 % Nitric acid (HNO₃) were obtained from Sigma Aldrich, Czech Republic.

2.2. Sol-gel Synthesis of Si-Ti based Porous Glasses

In a typical sol-gel synthesis of Si-Ti based porous glasses, metal alkoxides precursors such as TEOS and TIP were used as a source for Si and Ti respectively. 65% HNO₃ was used as catalysts to trigger the hydrolysis reaction and PEG was used as a polymeric component to induce phase separation. The incorporation of organic polymers such as PEG facilitates the control of the morphology. Two batches (B1 and B2) of Si-Ti based sol-gel glasses were prepared using two different protocols (P1 and P2). Table 1 represents the compositions and Figure 1 demonstrates typical steps involved in the sol-gel synthesis of Si-Ti based porous glasses.

| Precursor Materials | B1 (wt %) | B2 (wt %) |
|---------------------|-----------|-----------|
| H₂O                 | 49.213    | 44.803    |
| PEG                 | 1.9685    | 1.7921    |
| 65 % HNO₃           | 9.8425    | 17.921    |
| TEOS                | 36.811    | 33.513    |
| TIP                 | 2.1654    | 1.9713    |
| Total Weight Percent| 100       | 100       |
For the preparation of B1 samples using P1, the following procedure was followed. A known quantity of PEG was dissolved in water and stirred for 15 min. In a separate beaker, a mixture of TEOS and TIP with known quantity was prepared and stirred for 10 min. Later, the prepared solution of PEG/water and TEOS/TIP mixture were added together and stirred for another 10 min. to obtain homogeneous slurry. Subsequently, 65% HNO\textsubscript{3} was added to the obtained homogeneous slurry and stirred for another 10 min. Finally, the resulting solution was stored in closed plastic bottles for ageing. A similar procedure was followed to prepare Si-Ti samples from B2 using P1.

For the preparation of B1 samples using P2, the following procedure was followed. A known quantity of PEG was dissolved in water together with 65% HNO\textsubscript{3} and stirred for 15 min. In a separate beaker, a mixture of TEOS and TIP with known quantity was prepared and stirred for 10 min. Later, the prepared solution of PEG/water and TEOS/TIP mixture were added together and stirred for another 10 min. to obtain homogeneous slurry. Finally, the resulting solution was stored in closed plastic bottles for ageing. A similar procedure was followed to prepare Si-Ti samples from B2 using P2.

2.3. Characterizations
The microstructure of the sol-gel synthesized Si-Ti porous glasses was evaluated using scanning electron microscopy. SEM images were obtained using scanning electron microscope (FEI Quanta 200 instrument) with an accelerating voltage of 15 kV.

The thermomechanical properties of the Si-Ti based porous glasses and the kinetics of their thermal behaviour was evaluated using thermogravimetric analyzer (TGA) by employing Q500 TGA and thermomechanical analyzer Q400 TMA (TA Instruments). The samples were heated from ambient temperatures up to 1000°C in a 75 mL/min flow of N\textsubscript{2} at the heating rate of 10 °C/min.

3. Results and Discussion
3.1. Microstructure Analysis
The potential applications of Si, Si-Ti and various silicate based glasses depend mostly on their microstructure, thus study of porous structure is of primary importance. The most important factor for structure modifications is the relative rates of hydrolysis and condensation reactions. The
microstructural features of sol-gel derived Si-Ti glasses are depicted in Figure 2. It can be seen that all the samples exhibit an interconnected macroporous network structure. Generally, the macropores are formed due to the phase separation induced during sol-gel reaction and gelation helps in anchoring the transitional structure of phase separation [13].

The results show that the microstructural properties are significantly influenced by the proportion of HNO$_3$ and the preparation step. A lower proportion of HNO$_3$ (recipe B1) results in the formation of a porous interconnected structure with an open pore size of 25-40 µm. Applying protocol 2 (P2) resulted in the formation of thicker walls with slight porosity inside the struts (isolated pores 2-5 µm). Open pores in B1P1 samples were identified in the 10-20 µm range. A higher proportion of HNO$_3$ resulted in the formation of a homogeneous interconnected structure with open pore of 2-3 µm (recipe B2). The modification of the process of preparation of gels in this recipe had no effect on the resulting morphology and pore distribution.

Figure 2. SEM micrographs of the Si-Ti based sol-gel glasses
(A) B1P1 (B) B1P2 (C) B2P1 (D) B2P2

3.2. Thermal Analysis

Figure 3 demonstrates TGA and TMA graphs for the Si-Ti based gels. For the B2P2 sample a mass loss of ~ 20% on the TGA curve can be observed in the temperature range 50–140°C (continuously up
to 200°C), due to the removal of adsorbed water and volatile products resulting in the condensation reaction. The highest weight loss in this temperature range is observed in the B2P1 sample (~ 30%), which is attributable to different morphology of the internal porosity of the gels. It is necessary to add that the kinetics of decomposition is the same for all studied samples. The continuous weight decrease in the 200–450°C temperature range can be interpreted as combustion of the organic chains (–O–CH₂–CH₂–O–) in the matrix network [19], accompanied by oxidative decomposition of the PEG side chains interspersed in the silica matrix [20]. In the 550–1000°C range, the weight loss does not continue and the decreased value corresponds to the proportion of temperature-stable Si-based phases.

Thermal expansion/shrinkage behavior can be divided into two temperature regions. The samples disclosed minimum dimensional changes up to 250°C, with overall positive expansion value 0.2113% for B2P2 and negative shrinkage value -0.4074% for B2P1. This temperature region is characterized by a low degree of expansion/shrinkage behavior due to the dimensional stability of gels and the resistance to dehydration of adsorbed water and ethoxide volatile products. A notable shrinkage was observed in the second temperature region above 250 °C, which is caused by thermal decomposition of PEO (above 200°C) and gradual densification (≥ 500 °C) induced by viscous sintering accompanied by the collapse of the porous network [21]. All samples demonstrated similar kinetics of dimensional changes, however, shrinkage slightly differs in total values around -11%.

4. Conclusions
In the present study, two batches of Si-Ti based sol-gel glasses were successfully synthesized using two different protocols and their microstructural and thermal properties were investigated. The sol-gel synthesized Si-Ti based glasses showed excellent thermal stability and less shrinkage as evidenced from TGA and TMA results. The SEM micrographs revealed that Si-Ti based sol-gel glasses exhibits micro/macroporous structure with interconnected pores. Thus, sol-gel method provides a unique opportunity to prepare Si-Ti based glasses from starting compositions. After establishing this, our future work will be more focussed on the production of mesoporous Si-Ti based glasses for their potential bone tissue regeneration applications.
Acknowledgements
This work has been supported by the Bavarian State Ministry of Economy and Media, Energy and Technology (Czech-Bavarian Cross-Border Cooperation Program, INTERREG V, EUS 2014-2020 Objective, MATEGRA-Advanced porous biomaterials functionalized with stem cells for enhanced implant osseointegration, No 201, co-funded by the ERDF and Ministry of Regional Development of the Czech Republic).

References
[1] Vareda JP, Maximiano P, Cunha LP, Ferreira AF, Simoes PN, Duraes L 2018 J. Colloids Interf. Sci. 512 64 http://dx.doi.org/10.1016/j.jcis.2017.10.035
[2] Owens GJ, Singh RK, Foroutan F, Alqasi M, Han CH, Mahaputra C, Kim HW and Knowles JC 2016 Prog. Mater. Sci. 77 1 https://doi.org/10.1016/j.pmatsci.2015.12.001
[3] Gong C, Chen D, Jiao X and Wang Q 2002 J. Mater. Chem. 12 1844
[4] Kim HW, Kim HE and Knowles JC 2004 Biomaterials 25 3351
[5] Nateq MH and Ceccato R 2019 Materials 12 1744 http://dx.doi.org/10.3390/ma12111744
[6] Baino F, Fiume E, Miola M and Verne E 2018 Int. J. Appl. Ceram. Technol. 15 841 https://doi.org/10.1111/ijac.12873
[7] Li N, Jie Q, Zhu S and Wang R 2005 Ceram. Inter. 31 641
[8] Balamurugan A, Sockalingum G, Michel J, Faure J, Banchet V, Wortham L, Bouthors S, Laurent-Maquin D and Balossier G 2006 Mater. Lett. 60 3752
[9] Karasu B, Yanar AO, Kocak A and Kisacik O 2017 El-Cezeri J. Sci. Eng. 4 436 https://doi.org/10.31202/ecjse.323652
[10] Ruzimurado ON 2011 IOP Conf. Ser: Mater. Sci. Eng. 18 032004 https://doi.org/10.1088/1757-899X/18/3/032004
[11] Song CF, Lu MK, Wang SF, Xu D, Yuan DR and Zhou GJ 2003 Inorg. Mater. 39 1529
[12] Nakanishi K and Tanaka N 2007 Acc. Chem. Res. 40 863
[13] Ruzimuradov O, Nurmanov S, Kodani Y, Takahashi R and Yamada I 2012 J. Sol. Gel Sci. Technol 64 684 https://doi.org/10.1007/s10971-012-2903-7
[14] Zhang WH, Lu J, Han B, Li M, Xiu J, Ying P and Li C 2002 Chem. Mater. 14 3413-3421.
[15] Liu G, Liu Y, Yang G, Li S, Zu Y, Zhang W and Jia M 2009 J. Phys. Chem. C 113 (21) 9345 https://doi.org/10.1021/jp900577c
[16] Lenza RFS and Vasconcelos WL 2002 Mater. Res. 5 497-502.
[17] Chena HJ, Wang L and Chiu WY 2007 Mater. Chem. Phys. 101 12
[18] Rupp W, Husing N and Schubert U 2002 J. Mater. Chem. 12 2594
[19] Ştefănescu, M., Stoia, M., Ştefănescu, O. Popa A, Simon M and Ionescu C 2007 J. Therm. Anal. Cal. 88 19
[20] Theodosopoulos, GV, Zisis C, Charalambidis G, Nikolaou V, Coutsolelos AG and Pitsikalis M 2017 Polymers 9 145 https://doi.org/10.3390/polym9040145
[21] Martins O and Almeida RM 2000 J. Sol-Gel Sci. Technol. 19 651