PHYSICO-CHEMICAL PARAMETERS OF TETRAETHYL ORTHOSILICATE

Viorica SIMON[1], Antonina GRITCO-TODIRASCU[2], Liliana-Mihaela IVAN[2]

Biomaterials are widely used in different fields of medicine from disposable medical devices to indefinitely implanted prostheses. Their main characteristic is biocompatibility which means that it must be accepted by the body where they need to be transplanted. Tetraethyl orthosilicate (TEOS) is one of the precursors in preparation of aluminosilicate materials using in dental implants, having the chemical formula $Si(OC_2H_5)_4$. In this paper, the main physico-chemical parameters of TEOS were calculated and corroborated with the results obtained from experimental data.

Keywords: tetraethyl orthosilicate, molecular modeling, optimized geometry, dipole moment, a precursor for dental implants

1. Introduction

A synthetic material, inert from systemic and pharmacologic points of view, used to partially replace a living tissue or designed in order to be incorporated in human body is named biomaterial. The biomaterial performance is determined by the interaction between the human body and the material. The biomaterial – human body interaction takes place at the interface of living tissue – implant and it is defined by the human body tolerance to biomaterials [1].

Among other conditions imposed for good implant functionality, the main characteristic of all biomaterials is the biocompatibility, implying the accept of the implant by the neighboring tissues and by the organism [2, 3].

Tetraethyl orthosilicate (TEOS) is one of the precursors used for preparation of the dental bioceramics, having the chemical formula $C_8H_{20}O_4Si$.

The experimental study was completed with quantum-chemical studies in order to establish the behavior of the samples in simulated body fluid (SBF).

2. Experimental

Tetraethyl orthosilicate (TEOS) having organic component in its structure, is used as precursor for SiO_2 (silicon dioxide) in order to obtain bioceramics for

[1] "Babes-Bolyai University", Faculty of Physics, Cluj-Napoca, Romania, e-mail: viosimon@phys.ubbcluj.ro

[2] "Alexandru Ioan Cuza" University, Faculty of Physics, Iasi, Romania, e-mail: antoninagritco@yahoo.com; mihaelaivan2002@yahoo.com

dental implants. In our case the obtained biomaterials have the composition illustrated in Table 1 and were synthesized by sol-gel method in the Laboratories of Experimental Interdisciplinary Institute (ICEI) of Cluj-Napoca [4].

Table 1

Sample composition in wt %

Sample / Composition	$Si O_2$	Al_2O_3	B_2O_3	BaO	ZnO	fluorides
S1	45	10	17	20	0	8
S2	40	10	10	0	30	10

The preparation was made in water solutions, adding concentrate ammonia slowly until pH of 8,5 is reached.

In order to study the vitroceramics biocompatibility after preparation, the bioceramics were immersed in 50 ml of SBF for 21 days at 37°C temperature in thermostat.

The prepared biomaterials were analyzed using DTA and FTIR, both, before and after immersion in SBF. The FTIR spectra, were recorded with a FT/IR 610 JASCO spectrometer at room temperature, the registrations were made in the spectral range 400- 4000 cm^{-1}.

The natrium concentration, pH and conductivity in SBF, at different interval of time, were estimated in order to establish possible changes due to the interactions with vitreous samples. The analyses were made at room temperature with a Consort C833 multimeter. SBF solution was prepared after Kokubo [5].

The ratio between the surface in contact with SBF of the samples and the volume of SBF in which they were saked, was approximately of 4 m^{-1}.

The parameters measured for SBF before and after soaking the vitreous ceramics in it, are approximately the same (Table 2), demonstrating that between SBF and ceramics there is not any ionic exchange.

Table 2

The measurements recorded before and after soaking in SBF

	First day	After 7 days	After 14 days	After 21 days
pH	7.11	6.93	6.91	6.89
Conductivity (mSv)	19.5	22.8	23.4	24.3
Na^+ concentration	1.05×10^{-1}	1.55×10^{-1}	1.09×10^{-1}	1.08×10^{-1}

3. Results and Discussions

The molecular modeling asks the reconstruction of the main structural and energetic parameters of the studied molecular system, comparable with those resulted from experiments. The quantum mechanical methods permit the estimation of some parameters which cannot be identified by experimental means.

The structural and energetic parameters of TEOS were established using HyperChem program with PM3 method [6]. The values of the computed parameters are listed in Table 3. A remarkable stability given by the high value of the total energy and the hidrophobicity indicated by the positive value of log P result from the data of Table 2. TEOS has the dipole moment of about 2.66 D and the polarizability of about 20.31 $Å^3$.

Tabel 3

The structural and energetic parameters of TEOS

QSAR Parameters		Energetic Parameters	
Surface area ($Å^2$)	452.94	Total energy (kcal/mol)	-57886
Volume ($Å^3$)	713.99	Heat of formation (kcal/mol)	-327
Hydration energy (kcal/mol)	-2.30	Binding energy (kcal/mol)	-3083
log P	1.74	E_{HOMO} (eV)	-9.83
Refractivity ($Å^3$)	48.26	E_{LUMO} (eV)	1.03
Polarizability ($Å^3$)	20.31	Dipole moment (D)	2.66

The energy gap, ΔE=10.86 eV, indicates a low reactivity and electronic transitions with frequencies from far UV. The values of these parameters recommend TEOS as a good precursor for dental implants. Tetrahedral structure of TEOS and the covalent bonds of the 4 atoms of oxygen with identical substituents ensure a certain symmetry to the compound characterized by a good stability (Fig. 1).

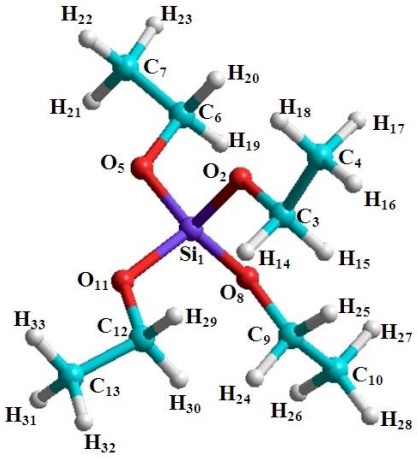

Fig. 1 The optimized structure of TEOS: turquoise - carbon, white - hydrogen, red - oxygen, violet – silicon

The silicon atom is covalently bonded by four identical bonds oriented towards the four tetrahedron peak.

Table 4

Angles between atomic bonds and dihedral angles

Angles	(^{0})	Angles	(^{0})
O11-Si1-O2	108.82	Si1-O8-C9-H24	-59.17
Si1-O8-C9	120	Si1-O11-C12-H29	-57.77
O2-Si1-O8	107.82	Si1-O2-C3-H15	59.22
O5-Si1-O11	113.52	O2-Si1-O8-C9	-175.57
Si1-O5-C6	119.3	C13-C12-O11-Si1	-179.32
Si1-O11-C12	120	Si1-O2-C3-C4	180
Si1-O2-C3	117.56	Si1-O5-C6-C7	180
O5-Si1-O8	113.52	Si1-O8-C9-C10	179.33
Si1-O11-C12-H30	59.19	C13-C12-O11-Si1	-179.32

From the value of the angles between the bonds in TEOS (Table 4) it results quasitetrahedral symmetry of the central silicon atom.

The charges located near the constituent atoms of TEOS are presented in Fig. 2 a), from which it results a similar distribution of atomic charges for the four substituents of silicon. Also, the bond lengths of TEOS are listed in Fig. 2 b).

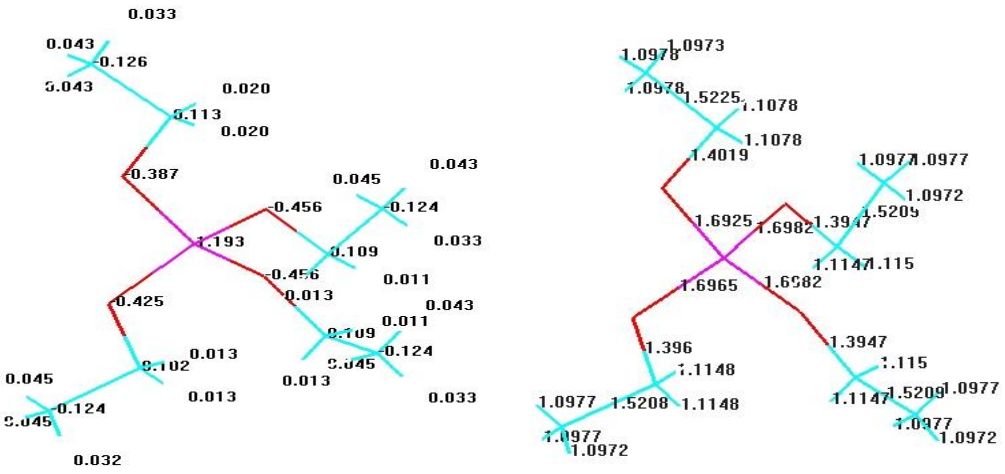

Fig. 2 The charges neighbouring the component atoms (a) and the lengths of the interatomic bonds of TEOS (b)

Table 5

Wavenumbers of some vibrational bands in our [4,7] samples and in TEOS with $Ca(OH)_2$ [8]

TEOS ($Al_2O_3 \cdot 2SiO_2$)	**TEOS +Ca $(OH)_2$**	**Frequency assignement**
440 cm^{-1}	458 cm^{-1}	Bending vibrations of Si-O-Si bonds
720 cm^{-1}	713 cm^{-1}	Al-O stretching vibrations

875 cm^{-1}	874 cm^{-1}	Al-O vibrations in AlO4 units
1040 cm^{-1}	1056 cm^{-1}	SI-O-Si for samples obtained by sol-gel method
1180 cm^{-1}	1165 cm^{-1}	Stretching vibrations of Si-O-Si bonds
1640 cm^{-1}	1635 cm^{-1}	Bending vibrations of the H-OH bond from adsorbed water

The characteristics bands of biomaterials [9,10] with TEOS [11] in IR spectra have appropriate values of wave numbers in both samples, as it results form Table 5.

4. Conclusions

1. Spectral and thermal data demonstrated the coverage of glass samples used in silane dental implants as a coupling agent, and the fact that no major changes were noted after immersion in SBF.
2. High stability, rigidity and hydrophobicity of TEOS have been established by using HyperChem program with PM3 method.
3. The quantum mechanical calculations prove the utilization of TEOS as a precursor for dental implant biomaterials, which demonstrates the veridicity of previously published results.
4. TEOS can be considered a good precursor for dental implants due to its remarkable stability of the structure, rigidity and hydrophobicity.

R E F E R E N C E S

[1]. *J. B. Park, R. S. Lakes*, Biomaterials: An Introduction, Kluwer Academic Publishers, 1992.
[2]. *V. Șimon*, Fizica Biomaterialelor (Phisics of biomaterials), Presa Universitară Clujeană, Cluj-Napoca, 2002.
[3]. *V. Pop, I. Chicinaș, N. Jumate*, Fizica biomaterialelor. Metode experimentale (Physics of biomaterials. Experimental methods), Presa Universitară Clujeană, Cluj-Napoca, 2001.
[4]. *A.Gritco, M. Moldovan, R. Grecu and V. Simon*, "Thermal and Infrared Analyses of Aluminosilicate Glass Systems for Dental Implants", in J. Optoelectron. Adv Mater, **vol. 7**, *no* 6, Dec. 2005, pp. 2845-2849.
[5]. *T. Kokubo, H. Kushitani, S. Sakka, T. Yamamuro*, "Solutions able to reproduce in vivo surface-structure changes in bioavtive glass-ceramic A-W" in J. Biomed. Mater. Res., **vol. 24**, no. 6, Jun. 1990, pp. 721-734.
[6]. www.hyper.com
[7]. *V. Simon, D. Eniu, A. Gritco and S. Simon*, "Thermal and Spectroscopic Investigation of Sol-Gel Derived Aluminosilicate Bioglass Matrices" in J.Optoelectron. Adv. Mater., **vol. 9**, no. 11, nov. 2007, pp. 3368 – 3371.
[8]. *A. M. Barberena-Fernandez, P. M. Carmona-Quiroga and M. T. Blanco-Varela*, "Interaction of TEOS with Cementitious Materials: Chem. And Physical Effects", in Cement and Concrete Composites, vol. 55, 2015, pp. 145-152.

[9]. *Robert M. Silverstein, Francis X. Webster, David J. Kiemle, David L. Bryce*, Spectrometric Identification of Organic Compounds, 4th ed., J. Wiley & Sons, New York, 1981.
[10]. *L. David, O. Cozar, C. Cristea, L. Gaina*, Identificarea Structurii Moleculare prin Metode Spectroscopice (Identification of Molecular Structure by Spectroscopic Methods), Presa Universitară Clujeană, Cluj-Napoca, 2004.
[11]. *M. Martínez-Ibáñez, M.J. Juan-Díaz, I. Lara-Saez, A. Coso, J. Franco, M. Gurruchaga and J. Suay Antón, I. J. Goñi* , in Mater SCI Mater Med., vol. 27, no. 4, Apr. 2016 pp. 80.