

physical Properties of (SiO₂-CaCl₂) Doped with 3-methacryloxypropyl Trimethoxysilane (MAPTMS)

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IN this study, TEOS - CaCl₂ and Mixed TEOS-MAPTMS-CaCl₂ were synthesized via sol-gel method and evaluated as a bioactive bone substitute. The hydrolysis and condensation were achieved in an (ethanol/water) solution. The ratio of silane to water to ethanol was 1:3:3. Bioactivity of the samples was premeditated via in-vitro test by inundation in simulated body fluid (SBF) to assess the creation of a hydroxyl apatite (HA) layer on the surface of the samples. Structural characterization of the prepared samples was done using Thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and fourier transform infrared (FTIR) spectroscopy. Elemental Analysis was performed using a UV-Vis Spectrophotometer. Results showed the creation of a layer of hydroxyl apatite (HA) on the surface of the samples. It was found that, sample contain hydrocarbon chain (sample doped with MAPTMS) need higher temperature to lose water and ethanol, i.e. organic precursor increases the thermal stability of the samples. In addition a layer of HA were deposited on the surfaces of the two samples after soaking in SBF for 33 days.

Keywords: Biomaterials, SBF, Hybrid, Sol-gel, Hydroxyapatite, (Methacryloyloxy) propyl, Tetraethyl orthosilicate.

Introduction

The sol-gel process is a synthetic procedure that allow creating organic-inorganic hybrid (O-I) materials[1]. In this work, (SiO₂-CaCl₂) and (SiO₂-CaCl₂) doped with (MAPTMS) were synthesized by sol-gel method. Organic-inorganic hybrid materials merge some characteristic of organic compounds (easy processing with traditional techniques, elasticity and organic functionalities) with the characteristic of inorganic oxides (hardness, thermal stability, chemical stability and transparency); so they can show exceptional mechanical properties and excellent thermal and photostability [2]. O-I crossbred materials can be syntheses at room temperature (T° C) via sol-gel process [3], [4]Ancamide 805, Ancamide 2050, Ancamide 2353, Epicure 3164, Jeffamine D-400, etc., at different epoxy to amine equivalent ratios. The formulated hybrid coatings were cured at laboratory temperature and humidity for more than 20 days and subjected to different tests. The hybrid coatings were analyzed using Fourier transform infrared spectroscopy (FTIR). Earlier researches have already showed that the essential requirement

for artificial materials to achieve bone-bonding properties is the formation of a hydroxyapatite layer on the artificial materials surface in the living body [5]. Hydroxyapatite creation ability can be achieved *in-vitro* using a simulated body fluid (SBF) that has a composition similar to inorganic composition of living body fluid. on the formation of hydroxyapatite layers on the sample in SBF has shown that hydroxyapatite formation was stimulated not only by the release of Ca ions from the sample, but also by the formation of silanol (Si-OH) groups that may encourage heterogeneous nucleation of hydroxyapatite on the sample [6], [7]. In this work, we prepared two samples, the first one is inorganic material from TEOS and CaCl₂ and the second one is a hybrid material from γ -methacryloxypropyltrimethoxysilane (MAPTMS), tetraethyl orthosilicate (TEOS) and CaCl₂. The organic precursor, for example MAPTMS, has carbon chain which can work as network modifiers. so the presence of these modifiers, the sample acquire extra properties (e.g., hydrophobicity, flexibility) relying on the type of the organic group used [8]. We assume preparing pure TEOS - CaCl₂ and Mixed TEOS-MAPTMS-CaCl₂ by mixing the TEOS or

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TEOS-MAPTMS hybrid with calcium salts such as (CaCl_2) will encourage the deposition of bioactive apatite in the (SBF) [9] which accordingly makes it appropriate for bone regeneration. TGA, FTIR and XRD have been applied to check the validity of this hypothesis.

Materials and Methods

Samples preparation

($\text{SiO}_2\text{-CaCl}_2$) and ($\text{SiO}_2\text{-CaCl}_2$) doped with (MAPTMS) were synthesized by sol-gel method by dissolving suitable amounts of Tetraethyl orthosilicate (TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$, sigma aldrish Co., Germany) and distilled water in ethanol (sigma aldrish Co., Germany). The TEOS / EtOH / H_2O mixture was stirred at location temperature for ten minutes. Then HCl (sigma aldrish Co., Germany) was added to attain acid hydrolysis to avert phase separation. The TEOS / EtOH / H_2O / HCl mixture was stirred for additional ten minutes at location temperature. 3-(Methacryloyloxy)propyl trimethoxysilane ((MAPTMS); $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, purchased from Alfa Aesar Co., Germany) was added to the prepared solution (only in the hybrid sample (sMT) as shown in Table 1). Different molar ratios TEOS: MAPTMS of [(1:0) and (1:4)] [sT and sMT] respectively were suggested. The molar ratio of silane to water to ethanol of 1:3:3 was applied. The prepared solution was stirred for four hours at location temperature. Lastly, 0.12 grams of Calcium Chloride (CaCl_2) (sigma aldrish Co., Germany) was added to the prepared solution to rise the bioactivity of the samples. The mixture was stirred ten minutes also at location temperature. Then it was stirred for four hours at 50°C to attain the sol-gel conversion (Condensation process). The gelation state was informed at which the flow stops in the beaker when tilted. The resultant gel was dried at 120°C in a drying oven for six days. eventually, the selected samples were crushed in the agate mortar where some characterization techniques were subsequently been applied.

TABLE 1. Chemical composition of the samples (in ml).

Sample	0	4
TEOS: MAPTMS	1:0	1:4
TEOS	14.799	2.886
MAPTMS	0	12.289
Ethanol	11.610	11.323
H_2O	3.5896	3.500

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Characterization Techniques

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT) was done on a SETARAM DTA-TG labsys™ Evolution-1750 equipment, with $\alpha\text{-Al}_2\text{O}_3$ powders as a reference material. Samples of 5 mg crushed powder were set into an Al_2O_3 crucible and the measurements were performed in the temperature range $23\text{--}800^\circ\text{C}$ (heating rate $10^\circ\text{C}/\text{min}$) in air.

Fourier transform infrared spectrometer (FT-IR)

At location temperature, FTIR absorption spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} by the spectrometer (FT-IR-400, JASCO, Japan). The two samples were prepared by typical method by mixing up about 2 mg of powder sample with 200 mg of potassium bromide (KBr), which was posteriorly compressed into disc using an evacuated die. Background data was documented before assembling spectra from the samples and was subtracted from the spectra of the sample.

X-Ray Diffraction (XRD)

The amorphous nature of the pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT) was certified by recording XRD patterns of the crushed powder of the two samples using X-ray diffractometer (BRUKER Germany, D8 ADVANCE) using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 0.154060\text{ nm}$), scanning rate 0.10° in the 2θ ranging from 10° to 100° step time 1 sec. at 40,000 V and 0.04 A.

In-vitro Bioactivity Analysis

Soaking in SBF.

The *in-vitro* bioactivity of the two samples (0.6 gram of powder) was examined by immersing in 36 ml of (SBF) for each sample [Table 2]. The pH of the SBF was buffered at 7.4. The samples were immersed in a plastic beaker in a thermodynamic shaking-water bath at constant separation and incubated for 33 days at 37°C . After 33 days of immersion, the samples were taken out from the SBF, rinsed by distilled water and dried at location temperature.

pH measurement

The pH of the SBF solution was measured using a pH meter (Jenway 3510). The alteration in pH of the SBF of the pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT) and SBF without any sample (control) was recorded at pre-determined time intervals.

TABLE 2 . Reagents for SBF preparation.

Tris	1.0 m HCl	NaCl	NaHCO ₃	KCl	K ₂ HPO ₄ ·3H ₂ O	CaCl ₂	Na ₂ SO ₄	MgCl ₂ ·6H ₂ O
6.057 g	39 ml	8.006 g	0.352 g	0.223 g	0.228 g	0.277 g	0.071 g	0.304 g

Elemental Analysis by Spectrophotometer

A 10 mL sample of SBF is taken from each test tube after 0, 1, 3, 6, 10, 13, 22 and 33 days from the beginning of the immersion. And stored frozen until analyzed for determining the concentration of Ca and P by using UV-Vis Spectrophotometer (Jenway 4600 UV/Vis. Spectrophotometer, England), using biological kits. Calcium ions were measured using (Biodiagnostic) at 585 nm. Inorganic phosphorus was measured using (Bio Adwic T29) at =700 nm. All the samples were read three times and taken the average.

Results and Discussion

Thermal gravimetric analysis (TGA)

The knowing of the thermal behavior of materials is of excessive importance, in determining their preferable processing conditions. Thermal gravimetric analysis (TGA) is a significant tool for thermal stability studies of the materials. It permits determining the temperature range at which a heated specimen undergoes a main conformational change by recording the thermal weight loss profile.

TGA analysis was used to estimate the thermal stability of pure TEOS - CaCl₂ (sT) and Mixed TEOS-MAPTMS-CaCl₂ (sMT) via sol-gel process (10 °C / min in nitrogen atmosphere). It permits determining the temperature range at which the heated sample undergoes a main conformational change by means of recording the thermal weight loss profile.

Figure (1): Shows TGA curves (25-800 °C temperature range) pure TEOS - CaCl₂ (sT) and

Mixed TEOS-MAPTMS-CaCl₂ (sMT). In order to follow up some considerable effects, the weight loss was studied in three intervals: (I), (II) and (III).

The initial weight loss (Region I) in the two samples is considered to be the consequence of the removal of the condensation by-products, ethanol and water (8.3% weight loss) [10]. It was found that, sample contain hydrocarbon chain (sample doped with MAPTMS) need higher temperature to lose water and ethanol, i.e. more water and ethanol being released when the system does not contain MAPTMS.

The second weight loss (Region II), in sample (sT) is due to the evaporation of the trapped ethanol and water molecules inside the small pores (5.91% weight loss) [11]. But in sample (sMT) is due to the partial thermal degradation of organic matter in the hybrid [12]. It occurs from 370 up to 560 °C (40% weight loss), this indicates that, to avert the burning of the organic precursor from the hybrid, the hybrid should be cured while being prepared at a temperature which does not exceeds 370 °C. In other words, 120 °C is a appropriate temperature for curing the hybrid.

The third weight loss stage (Region III) at 560-800 °C in sample (sMT) (4.16% weight loss) is due to the complete burning of organic precursor in the hybrid [13]. From the TGA curve, it is obvious that, the weight loss increase in the sample which contain a carbon chain (organic precursor). In addition, 120 °C is a suitable temperature for curing these hybrids.

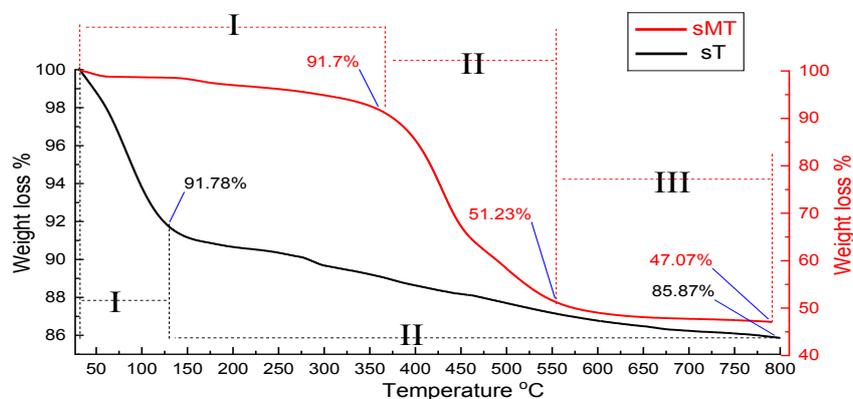


Fig. 1. shows TGA curves of pure TEOS - CaCl₂ (sT) and Mixed TEOS-MAPTMS-CaCl₂ (sMT).

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT). are shown in Fig (2). FTIR spectra of the two samples showed the major specific bands of silica network. the band found near 445 cm^{-1} is ascribed to Si-O-Si out of plane bending [14], while the peak at 800 cm^{-1} is because of the symmetric Si-O-Si stretching vibrations [15]. The peak at 1080 cm^{-1} , is attributed to Si-O-Si stretching vibration in SiO_4 tetrahedra [16]. the Characteristic bands of MAPTMS showed at (1721 , 1640 , 1465 , 1320 and finally at 1150 cm^{-1}). The band at 1721 cm^{-1} is attributed to the stretching vibrations of C=O (carbonyl groups) of MAPTMS [17], [18]. while the band at 1640 cm^{-1} is attributed to C=C group of the methacrylate groups from the organic precursor [19], [20]. Band at 1320 cm^{-1} is ascribed to asymmetric stretching vibrations of C-O in C-O-C bond. Bands at (1150 and 1465 cm^{-1}) are ascribed to deformation vibrations of C-H in CH_3 and CH_2 bonds, respectively [21] [22]. Band at 2960 cm^{-1} attributed to stretching vibra-

tions of C-H bonds in alkyl [23]. The broad band between 3100 and 3700 cm^{-1} is attributed to the OH stretching vibrations [24]. $\delta \text{ C=O}$ is detected at 600 cm^{-1} . The band at 700 cm^{-1} accredited to Si-C. The grouping of these bonds exhibits the wide band of Si-O-C at 1050 cm^{-1} [25] which is characteristic for -Si-O-C bond that appeared in the hybrid sample (sMT) while this band was not observed in sample (sT) (MAPTMS /TEOS, 0/1) [26] and these results indicated that, the organic precursor still present in the hybrid sample which confirms the same result obtained from the TGA curve which is $120 \text{ }^\circ\text{C}$ is a suitable temperature for curing these hybrids.

X-ray Diffraction (XRD)

Fig (3): presents XRD pattern of pure TEOS - CaCl_2 (sT) and MAPTMS-TEOS- CaCl_2 hybrid (sMT). The two samples in amorphous state characterized by the wide diffraction bands centered at and for sample (ST) and sample (SMT) respectively indicating the internal disorder of the prepared samples[27].

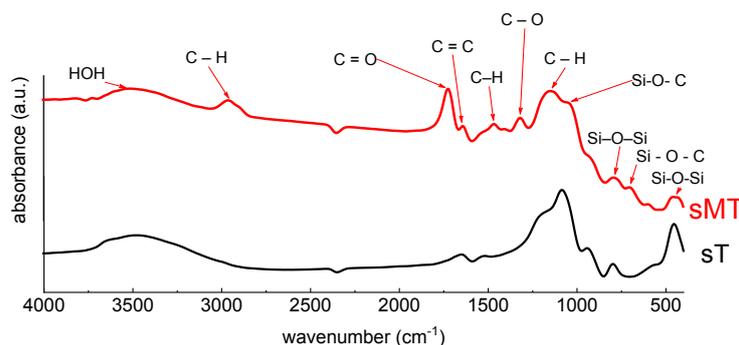


Fig. 2. Representative FTIR absorption spectra of pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT).

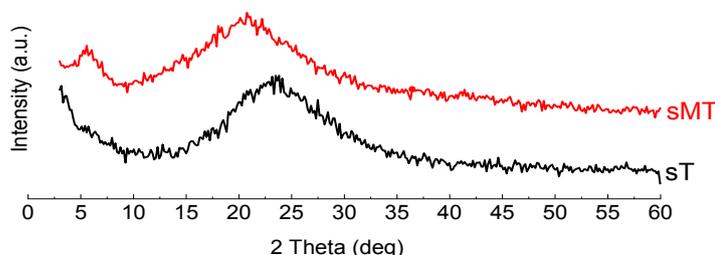


Fig. 3. Powder XRD patterns of pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT).

pH measurements

The pH measurement is very important to study the dissolution process of the samples soaked in physiological solutions. Two factors lead to increase pH of SBF; the first is the ion exchange between the protons H⁺ in SBF and the modifying cations of sample, and the second is the saturation of SBF by acid silica[28].

Figure (4), shows the variation in pH of SBF solution through dissolution of pure TEOS - CaCl₂ (sT) and Mixed TEOS-MAPTMS-CaCl₂ (sMT). It is detected that, during the first day of immersion in SBF, there is a fluctuation in pH value of the two samples. After 1 day up to 20 days of immersion, the pH decreases, that may be attributed to cations consumption from the SBF solution. The cations consumption is the initial step in the precipitation process of bone-like apatite from SBF solution. The pH increased after 20 to 33 days in SBF immersed as a consequence of partial dissolution that grants an idea about the high reactivity of these samples. These facts agree with the formation mechanisms of the hydroxyl apatite layer on the surface of the samples, i.e., in an exchange takes place between Ca²⁺ and H₃O⁺ ions from the solution. Such exchanges provoke an increase in pH that accordingly favors the formation of apatite nuclei on the silanol groups in the samples surface.

The fluctuation in pH value of the two samples may be described when considering the result of two opposite processes: the release of Ca²⁺ from

the surface, and the consumption of Ca²⁺ due to the formation of hydroxyl apatite layer. Therefore, when the releasing rate of Ca²⁺ is higher than the consumption rate, the pH will increase, or else, the pH will decrease[29].

Calcium concentration

The alteration in concentration of Ca ions can show the competition condition between the rate of dissolution and precipitation processes. The concentration of calcium in SBF solution is almost 100 mg/l. The Ca concentration was found to be increased more than 100 mg/l, this means that the dissolution rate is faster than the precipitation rate.

Fig (5) shows the change of concentration of Ca ions after immersion the two samples in SBF solution. The calcium concentration appears to increase at the initial stage for the two samples. This increase in calcium concentration is induced by the release of calcium ions from the samples. The decrease of calcium concentration from 1 up to 6 days in sample (sMT) and from 1 up to 10 days in sample (sT) may be due to the consumption of calcium ions through apatite formation on their surfaces[30] a revised simulated body fluid (R-SBF).

At the middle stage, the increase in the Ca concentration observed for sample (sT) from 10-13 day in SBF and for sample (sMT) from 6-22 day in SBF is attributed to dissolution of the samples.

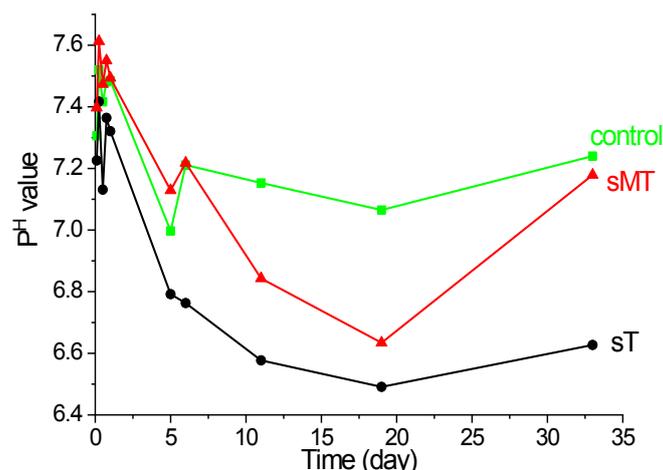


Fig.4. Change in pH of SBF solution during dissolution of pure TEOS - CaCl₂ (sT) and Mixed TEOS-MAPTMS-CaCl₂ (sMT).

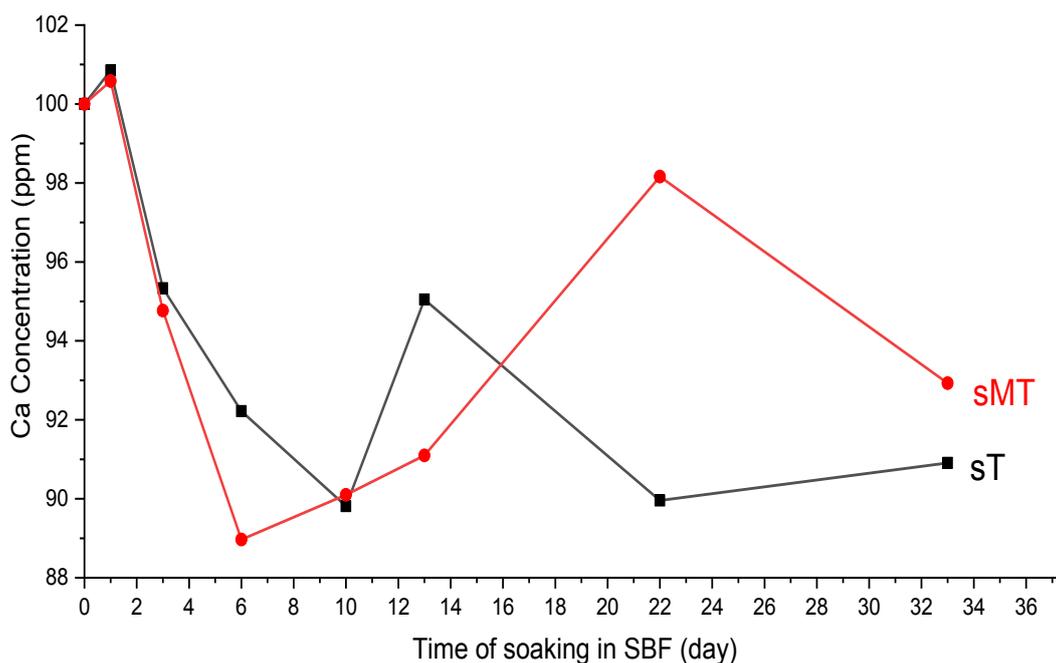


Fig.5. The concentration of Ca^{2+} ions of pure TEOS - CaCl_2 (sT) and Mixed TEOS-MAPTMS- CaCl_2 (sMT) after soaking in SBF solution for 33 days.

At the final stage, the decreasing in the Ca^{2+} ions concentration in SBF is attributed to the rapid growth of the apatite nuclei formed on the surface of the samples that beat the release rate of calcium ions to the solution. The pH varied according to Ca^{2+} concentration variations, because of Ca^{2+} ions in the samples exchanged with H^+ or H_3O^+ in the SBF[31] many aspects of this strategy remain unknown. We investigated possible fitness costs of hyperparasitism as influenced by host size. Our study was conducted with the facultative hyperparasitoid *Pachycrepoideus dubius* Ashmead (Hymenoptera: Pteromalidae).

Phosphorus concentration

Fig (6) shows the concentration of P^{5+} ions after 33 days soaking of the samples in SBF solution. Before immersion phosphate ion concentration in SBF is 30 ppm only. After immersion of the samples in SBF for 33 days, at 24 h it is noted that phosphate concentration in the two samples decreased to approximately 20 ppm indicating the consumption of phosphate in the SBF due to precipitation of P^{5+} ions on the surface of the samples. From day 2 to day 10 phosphorus concentration decreased gradually in sample (sMT) which contain organic precursor while the phosphorus concentration in sample

(sT) lightly increased from day 2 to day 6 then it rapidly decreases from day 6 to day 10 since the sample (sT) is pure TEOS - CaCl_2 phosphorus concentration increased rapidly from 10 up to 12 days due to formation of a layer of HA on the surface of the two samples. Then it showed approximately a constant value from 12 up to 33 days. This decrease in phosphorus concentration maybe due to the consumption of phosphate ions through the formation of apatite on the surfaces of the two samples [32].

Conclusion

- Pure TEOS - CaCl_2 and Mixed TEOS-MAPTMS- CaCl_2 were synthesized successfully via sol-gel method. The hybrid networks combined (TEOS) as inorganic material and MAPTMES as organic material. The bioactivity of these samples was investigated by in-vitro testing in (SBF) for 33 days, and characterized by TGA, DSC, XRD and FTIR. Results showed that layers of HA were deposited on the surfaces of samples.
- From the TGA data, it is clear that, the weight loss increases in the sample which contain organic precursor. In addition, 120 °C is a suitable temperature for curing these hybrids.

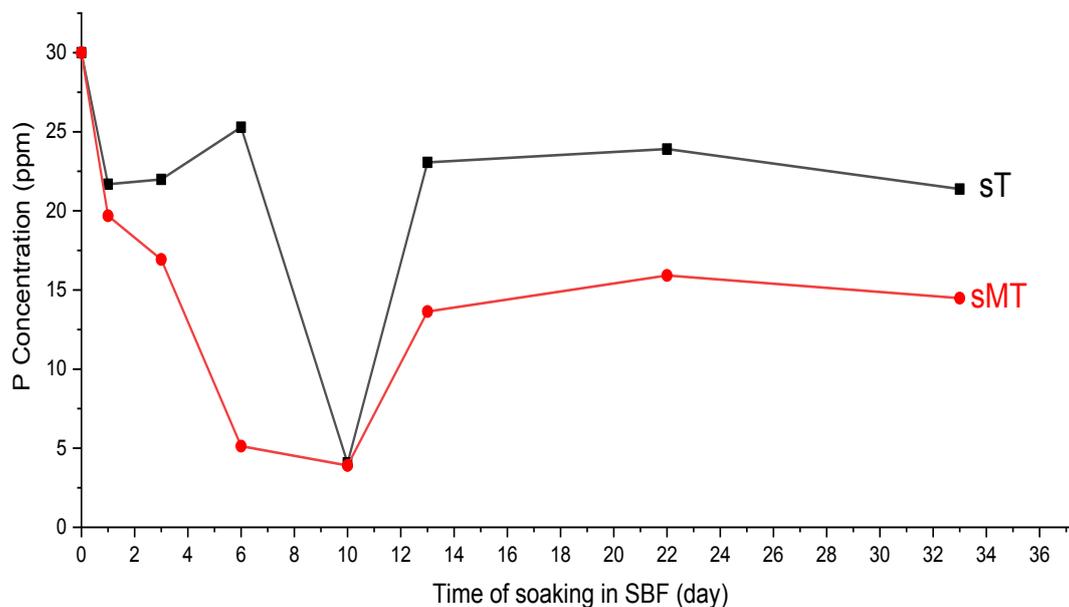


Fig.6. The concentration of Ca²⁺ ions of pure TEOS - CaCl₂ (sT) and Mixed TEOS-MAPTMS-CaCl₂ (sMT) after soaking in SBF solution for 33 days.

References

- R. P. C. L. Sousa, B. Ferreira, M. Azenha, S. P. G. Costa, C. J. R. Silva, and R. B. Figueira, "PDMS based hybrid sol-gel materials for sensing applications in alkaline environments: Synthesis and characterization," *Polymers (Basel)*, vol. 12, no. 2, 2020, doi: 10.3390/polym12020371.
- Y. Wang, B. Li, L. Zhang, Q. Zuo, L. Liu, and P. Li, "Improved photoluminescence properties of a novel europium(III) complex covalently grafted to organically modified silicates," *J. Colloid Interface Sci.*, vol. 349, no. 2, pp. 505–511, 2010, doi: 10.1016/j.jcis.2010.05.047.
- D. K. Chattopadhyay and D. C. Webster, "Hybrid coatings from novel silane-modified glycidyl carbamate resins and amine crosslinkers," *Prog. Org. Coatings*, vol. 66, no. 1, pp. 73–85, 2009, doi: 10.1016/j.porgcoat.2009.06.004.
- A. Kayan, "Inorganic-organic hybrid materials and their adsorbent properties," *Adv. Compos. Hybrid Mater.*, vol. 2, no. 1, pp. 34–45, 2019, doi: 10.1007/s42114-018-0073-y.
- L. L. Hench, "Bioceramics: From Concept to Clinic," *J. Am. Ceram. Soc.*, vol. 74, no. 7, pp. 1487–1510, Jul. 1991, doi: 10.1111/j.1151-2916.1991.tb07132.x.
- L. Of, "Mechanism of apatite formation on CaO-SiO₂-P₂O₅ glasses in a simulated body fluid," vol. 143, pp. 84–92, 1992.
- P. Li *et al.*, "Apatite formation induced by silica gel in a simulated body fluid," *J. Am. Ceram. Soc.*, vol. 75, no. 8, pp. 2094–2097, 1992.
- O. H. Park, Y. J. Eo, Y. K. Choi, and B. S. Bae, "Preparation and optical properties of silica-poly(ethylene oxide) hybrid materials," *J. Sol-Gel Sci. Technol.*, vol. 16, no. 3, pp. 235–241, 1999, doi: 10.1023/A:1008717219952.
- T. Kokubo *et al.*, "Ca, P-rich layer formed on high-strength bioactive glass-ceramic A-W," *J. Biomed. Mater. Res.*, vol. 24, no. 3, pp. 331–343, Mar. 1990, doi: 10.1002/jbm.820240306.
- H. Y. Park, D. P. Kang, M. K. Na, H. W. Lee, H. H. Lee, and D. S. Shin, "Characteristics of organic-inorganic hybrid coating films synthesized from colloidal silica-silane sol," *J. Electroceramics*, vol. 22, no. 1–3, pp. 309–314, Feb. 2009, doi: 10.1007/s10832-007-9355-4.
- A. V. Rao, R. R. Kalesh, and G. M. Pajonk, "Hydrophobicity and physical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component," *J. Mater. Sci.*, vol. 38, no. 21, pp. 4407–4413, 2003, doi: 10.1023/A:1026311905523.

12. I. E. Soliman, A. A. Elhadad, A. Mubarak, and K. T. Ereiba, "CHARACTERIZATION OF ORGANOSILICA HYBRID MATERIALS DERIVED FROM TETRAETHYLORTHOSILANE (TEOS) AND VINYLTRIMETHOXYSILANE (VTES) CHARACTERIZATION OF ORGANOSILICA HYBRID MATERIALS DERIVED FROM TETRAETHYLORTHOSILANE (TEOS) AND VINYLTRIMETHOXYSILANE (VTES," no. September, 2016.
13. C. Jing, X. Xu, and J. Hou, "Synthesis of sub-micro-sized solid alpha alumina fibers with smooth surfaces by sol-gel method," *J. Sol-Gel Sci. Technol.*, vol. 45, no. 1, pp. 109–113, Jan. 2008, doi: 10.1007/s10971-007-1644-5.
14. R. K. Nariyal, P. Kothari, and B. Bisht, "FTIR Measurements of SiO₂ Glass Prepared by Sol-Gel Technique," *Chem. Sci. Trans.*, vol. 3, no. 3, pp. 1064–1066, 2014, doi: 10.7598/cst2014.816.
15. M. Kumar, B. P. Tripathi, and V. K. Shahi, "Ionic transport phenomenon across sol-gel derived organic-inorganic composite mono-valent cation selective membranes," *J. Memb. Sci.*, vol. 340, no. 1–2, pp. 52–61, 2009, doi: 10.1016/j.memsci.2009.05.010.
16. N. P. Bansal, "Low Temperature Synthesis of CaO-SiO₂ Glasses Having Stable Liquid-Liquid Immiscibility by Sol-Gel Process," *J. Mater. Sci.*, vol. 27, no. 11, pp. 2922–2933, 1992, doi: 10.1007/BF01154101.
17. S. Alay Aksoy, C. Alkan, M. S. Tözüm, S. Demirbağ, R. Altun Anayurt, and Y. Ulcay, "Preparation and textile application of poly(methyl methacrylate-co-methacrylic acid)/n-octadecane and n-eicosane microcapsules," *J. Text. Inst.*, vol. 108, no. 1, pp. 30–41, 2017, doi: 10.1080/00405000.2015.1133128.
18. P. Rodi, I. Milo, M. Lekka, F. Andreatta, and L. Fedrizzi, "Progress in Organic Coatings Corrosion behaviour and chemical stability of transparent hybrid sol-gel coatings deposited on aluminium in acidic and alkaline solutions," no. February, 2018, doi: 10.1016/j.porgcoat.2018.02.025.
19. S. T. Examiners, M. Kellom, J. M. Examiners, and N. S. Council, "Aida Khayyami Low Temperature Sol-Gel on Polymeric Substrate," 2015.
20. P. Rodi, A. Mertelj, M. Borov, A. Ben, D. Mihailovi, and I. Milo, "Surface & Coatings Technology Composition , structure and morphology of hybrid acrylate-based sol – gel coatings containing Si and Zr composed for protective applications," vol. 286, pp. 388–396, 2016, doi: 10.1016/j.surfcoat.2015.12.036.
21. P. Innocenzi and G. Brusatin, "A comparative FTIR study of thermal and photo-polymerization processes in hybrid sol-gel films," *J. Non. Cryst. Solids*, vol. 333, no. 2, pp. 137–142, 2004, doi: 10.1016/j.jnoncrysol.2003.09.043.
22. M. Pantoja, B. Diaz-Benito, F. Velasco, J. Abenojar, and J. C. del Real, "Analysis of hydrolysis process of ??-methacryloxypropyltrimethoxysilane and its influence on the formation of silane coatings on 6063 aluminum alloy," *Appl. Surf. Sci.*, vol. 255, no. 12, pp. 6386–6390, 2009, doi: 10.1016/j.apsusc.2009.02.022.
23. L. Brigo, a. Pistore, G. Grencci, a. Carpentiero, F. Romanato, and G. Brusatin, "New hybrid organic-inorganic sol-gel positive resist," *Microelectron. Eng.*, vol. 87, no. 5–8, pp. 947–950, 2010, doi: 10.1016/j.mee.2009.11.151.
24. J. P. Matinlinna, M. Özcan, L. V. J. Lassila, and P. K. Vallittu, "The effect of a 3-methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane blend and tris(3-trimethoxysilylpropyl)isocyanurate on the shear bond strength of composite resin to titanium metal," *Dent. Mater.*, vol. 20, no. 9, pp. 804–813, 2004, doi: 10.1016/j.dental.2003.10.009.
25. teresa OH and C. K. Choi, "Comparison between SiOC Thin Film by plasma enhance chemical vapor deposition and SiO₂ Thin Film by Fourier Transform Infrared Spectroscopy," *J. Korean Phys. Soc.*, vol. 56, no. 4, pp. 1150–1155, 2010, doi: 10.3938/jkps.56.1150.
26. K. Paljar, S. Orlić, E. Tkalčec, and H. Ivanković, "CHARACTERIZATION OF ORGANIC-INORGANIC HYBRIDS PREPARED FROM POLY(METHYL METHACRYLATE) AND ORGANICALLY MODIFIED Si – ALKOXYDE," *Chem. Eng.*, pp. 158–165, 2006.
27. S. Musić, N. Filipović-Vinceković, and L. Sekovanić, "Precipitation of amorphous SiO₂ particles and their properties," *Brazilian J. Chem. Eng.*, vol. 28, no. 1, pp. 89–94, 2011, doi: 10.1590/S0104-66322011000100011.
28. F. Mezahi, A. L.- Giro, H. Oudadesse, and A. Harabi, "Reactivity kinetics of 52S4 glass in the quaternary system SiO₂ – CaO – Na₂O – P₂O₅ : In fl uence of the synthesis process :

- Melting versus sol – gel,” *J. Non. Cryst. Solids*, vol. 361, pp. 111–118, 2013, doi: 10.1016/j.jnoncrysol.2012.10.013.
29. Z. Zhou, J. Ruan, J. Zou, and Z. Zhou, “Preparation and bioactivity of sol-gel macroporous bioactive glass,” vol. 15, no. 3, pp. 290–296, 2008.
30. Y. Zhang, M. Mizuno, M. Yanagisawa, and H. Takadama, “Bioactive behaviors of porous apatite- and wollastonite-containing glass-ceramic in two kinds of simulated body fluid,” *J. Mater. Res.*, vol. 18, no. 2, pp. 433–441, 2003, doi: 10.1557/JMR.2003.0055.
31. J. Grandgirard, D. Poinot, L. Krespi, J. P. Nénon, and A. M. Cortesero, “Costs of secondary parasitism in the facultative hyperparasitoid *Pachycrepoideus dubius*: Does host size matter?,” *Entomol. Exp. Appl.*, vol. 103, no. 3, pp. 239–248, 2002, doi: 10.1023/A.
32. M. Y. Koh, M. Kamitakahara, I. Y. Kim, K. Kikuta, and C. Ohtsuki, “In vitro apatite formation on organic-inorganic hybrids in the CaO-SiO₂-PO₅/2-poly(tetramethylene oxide) system,” *J. Mater. Sci. Mater. Med.*, vol. 21, no. 2, pp. 385–392, 2010, doi: 10.1007/s10856-009-3868-0.

دراسة الخصائص الفيزيائية لـ (أكسيد السيليكون – كلوريد الكالسيوم) المطعم بـ (MAPTMS) H₂C=C(CH₃)CO₂(CH₂)₃Si(OCH₃)₃

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في هذه الدراسة ، تم تصنيع TEOS-CaCl₂ و TEOS-MAPTMS-CaCl₂ المخلط عبر طريقة sol-gel وتقييمهما كبديل عظمي حيوي. تم تحقيق التحلل المائي والتكثيف في محلول (إيثانول / ماء). كانت نسبة السيلان إلى الماء إلى الإيثانول 1 : 3 : 3. تم تقييم النشاط الحيوي للعينات عن طريق الاختبار في المختبر عن طريق الغمر في سائل الجسم المحاكي (SBF) لتقييم تكوين طبقة هيدروكسيل أباتيت (HA) على سطح العينات. تم إجراء التوصيف الإنشائي للعينات المحضرة باستخدام المنحنى التفاضلي الحرارى (TGA) ، حيود الأشعة السينية (XRD) والتحليل الطيفي للأشعة تحت الحمراء (FTIR). تم إجراء تحليل العناصر باستخدام مقياس الطيف الضوئي UV-Vis. أظهرت النتائج تكوين طبقة من الهيدروكسيل أباتيت (HA) على سطح العينات. وجد أن العينة المحتوية على سلسلة هيدروكربونية (عينة مطعمة بـ MAPTMS) تحتاج إلى درجة حرارة أعلى لتفقد الماء والإيثانول ، أي أن المادة العضوية تزيد من الاستقرار الحراري للعينات. بالإضافة إلى ذلك ، تم ترسيب طبقة من HA على أسطح العينتين بعد الغمر في SBF لمدة 33 يوماً.