

POLY(DIMETHYLSILOXANE) / TETRAETHYL ORTHOSILICATE MODIFIED HYDROXYAPATITE COMPOSITES: MECHANICAL PROPERTIES AND BIOCOMPATIBILITY EVALUATION

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ABSTRACT

A composite of poly(dimethylsiloxane)/hydroxyapatite (PDMS/HAp) has been developed and its mechanical properties and biocompatibility were assessed. The processing of the composite involved the surface modification of HAp with 5 or 10 %(wt/wt) tetraethyl orthosilicate (TEOS) solutions, followed by mixing in a two roll open mixer with the silicone. The energy dispersive spectroscopy (EDS) spectra indicated evidence of a silane layer in the HAp modified surface. In tensile property measurement, the PDMS/modified-HAp composite showed higher values of tensile strength (2.41 MPa) and lower elongation at break (73.44 %) than the PDMS/unmodified-HAp composite, 2.26 MPa and 365.58 % respectively. In both cases, the composites showed higher values of tensile strength than the original silicone (1.97 MPa). Scanning electron microscopy (SEM) micrographs of the PDMS/unmodified-HAp composite exhibited debonding of the HAp particles from the elastomeric matrix at the fracture surface. On the other hand, HAp particles remained well attached to the matrix in the PDMS/modified-HAp composite. The presence of HAp improved the biocompatibility of the silicone. The soaking of the composites for 7 days in a simulated body fluid (SBF) formed a dense and homogeneous layer of HAp like crystals in the surface of the composites. The surface modification of HAp powders with TEOS solutions formed a strong interface PDMS/HAp, this enhanced the tensile strength of the composite.

Keywords: composite, silicone, hydroxyapatite, mechanical properties, biocompatibility.

INTRODUCTION

Silicone rubber (SR) has been widely used in clinic as implant for a long time. It is well known that SR posses good biocompatibility and physiological inertness. Its well workable property promises

a great convenience in clinical applications. However, SR is not able to bond organically with tissues owing to its inertness. In some cases inflammation and foreign-body reaction occur after the implantation.⁽¹⁾ In recent years, many serious attempts have been made to improve the biocompatibility of SR.⁽²⁾ It has been demonstrated that these modifications can improve significantly the biological properties of SR. But so far these techniques have not been so successful in enhancing the bioactivity of SR.⁽³⁾

Bioceramics have excellent biological performance that can encourage new bone formation by self-degradation under the microenvironment of the organism to produce a pore-like structure, facilitating adherence to tissues and growth of peripheral tissues.⁽⁴⁾ In this regard, hydroxyapatite (HAp) is the preferred calcium phosphate because the primary constituent of bone comprises inorganic crystallites similar to HAp. It can form a bonding with bone tissues and possesses excellent biocompatibility. However, in contrast to SR, HAp demonstrates poor processing properties due to its brittleness.⁽⁵⁾ At present, either HAp or SR can be utilized as plastic material in clinic, but neither is ideal. Naturally, it would be desirable for us to combine the advantages of HAp and SR and to form a new material system.⁽⁴⁾

In recent years, a number of studies have focused on improving the mechanical, physicochemical and biological properties of polymers such as SR and chitosan scaffolds through incorporation of bioactive inorganic substances such as calcium phosphate, especially HAp [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], to achieve porous tissue ingrowth and high mechanical strength.⁽⁶⁾ The resulting composite can be viewed as representing a new class of nanostructured biomaterial. It has the potential to exhibit excellent physical and biological properties, with the SR providing the desired fine mechanical properties and HAp acting synergistically to promote bioactivity. The compounding of SR with HAp will provide bioactive sites that are bioresorbable and favorable to tissue ingrowth.⁽⁷⁾

Consequently, one can expect that SR/HAp composites can be made with improved mechanical and biological properties. In this study, HAp powder was prepared by the precipitation method, its surface was modified with tetraethyl orthosilicate (TEOS) solutions and the mechanical properties and biocompatibility of SR/HAp-TEOS composites was assessed.

MATERIALS AND METHODS

1. Hydroxyapatite synthesis and surface modification

In order to obtain hydroxyapatite (HAp) via the precipitation reaction, an aqueous solution of Ca(OH)_2 (95% Synth) was placed in a balloon and heated up to 90 °C, while continuously stirred, an aqueous solution of H_3PO_4 (85% Nuclear) was dropped. The system was continuously stirred for 24 h at 90 °C, the obtained precipitate was then washed with ethylic alcohol (98% Vetec), filtered and dried. The powder was calcined at 800 °C for 2 h. The materials used to obtain the α -tricalcium phosphate via the combustion reaction were $\text{Na(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99% Vetec), $(\text{NH}_4)_2\text{HPO}_4$ (99% Vetec) and urea (99% Vetec) as fuel. The material was washed with ethylic alcohol and then dried. The powder was calcined at 1200 °C for 4 h, followed by a rapid cooling to room temperature.

For the surface modification of the calcium phosphates, an aqueous solution of ethylic alcohol at 25% (wt/wt) was prepared, to whom tetraethyl orthosilicate (TEOS) (98% Sigma-Aldrich) was added in order to obtain 5 % (wt/wt) and 10 % (wt/wt) TEOS solutions, the pH was adjusted to 4.0 with acetic acid (99% Synth). The solutions were stirred for 30 min at 50 °C to allow hydrolysis, then, 5 % (wt/wt) of the calcium phosphates were added, the systems were agitated once again for 30 min at 50 °C. Finally, the modified calcium phosphate were washed with ethanol (95% Vetec) and dried.

2. Composite preparation and characterization

In order to prepare the composites, 10 % (v/v), 20 % (v/v) or 30 % (v/v) of modified or unmodified HAp was incorporated into the poly(dimethylsiloxane) (PDMS) NE-140 (Wenda Co.) in a open two-roll mixer. Afterwards, 0.8 % (wt/wt) of the curing agent, dicumil peroxide (98% Aldrich), was added to the system, then, the composites were placed between metal plates and pressed to obtain ~ 3 mm thick samples, which were cured at 185 °C for 35 min.

The phase composition of the obtained composite was characterized by scanning electron microscopy (SEM) (JEOL JSM 5800) coupled with a energy disperse spectroscopy (EDS) equipment and by X-ray diffraction (XRD) (Phillips X'Pert MPD, $K_\alpha = 1.5418 \text{ \AA}$). In order to evaluate the tensile properties of the composite, tensile tests were made in a universal testing

machine (Instron 3369), following the standard method ASTM D412. Measurements were at room temperature with samples 10 mm wide, 33 mm long, and 3 mm thick, the rate of elongation was 30 mm/min. The Shore A hardness of the composite was evaluated (Mitutuyo ID-S1012M) following the standard method ASTM D2240, measurements were based on the initial indentation of 6 mm thick samples and were at room temperature. To assess the *in vitro* bioactivity of the composite, samples were soaking in simulated body fluid (SBF) for up to 7 days, afterward, the physic-chemical modifications of the sample surface were characterized by XRD and MEV.

RESULTS

SEM micrographs of HAp powders modified with 5 %(wt/wt) and 10 %(wt/wt) TEOS solutions are showed in Fig. 1, along with the related EDS spectra. The EDS spectra, in both conditions, show the peak corresponding to silicon. This result could indicate the presence of a silane layer in the particles surface, formed during the surface modification of the powders with the TEOS solutions.

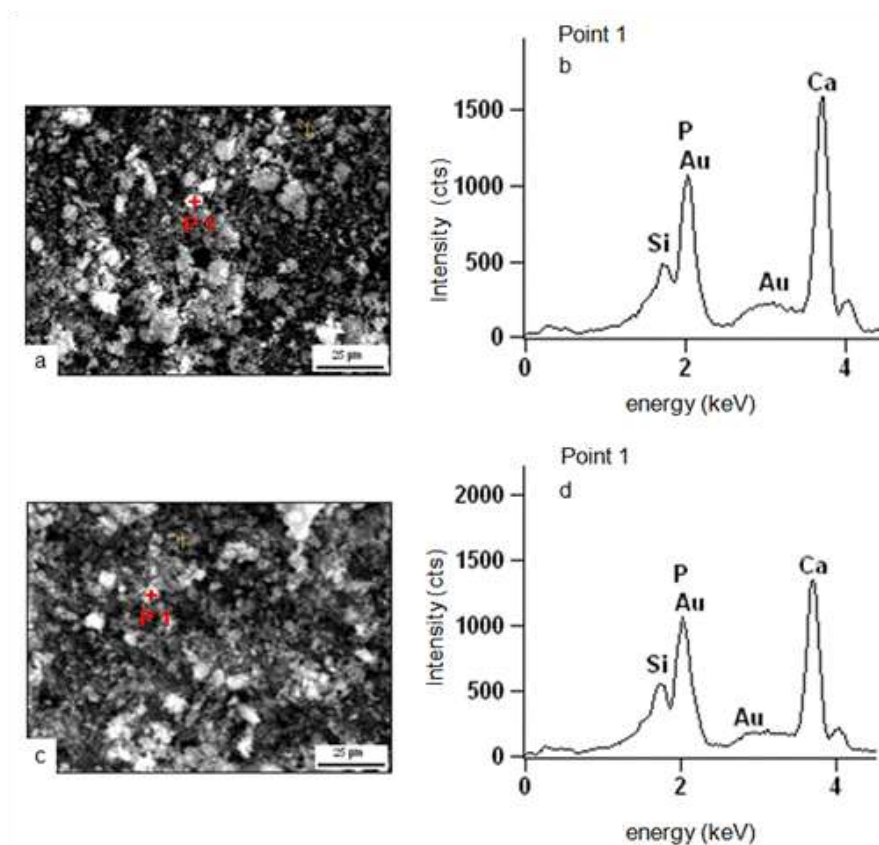


Figure 1. SEM micrographs of hydroxyapatite powders modified with (a) 5 %(wt/wt) and (c) 10 %(wt/wt) TEOS solutions, along with related EDS spectra, (b) and (d), respectively.

Fig. 2 shows SEM surface micrographs of the PDMS/20%(v/v)HAp composite, made with HAp treated with 0, 5 and 10 %(wt/wt) TEOS solutions. This results show that the dispersion and distribution state of the particles in the silicone matrix were homogeneous, regardless the surface treatment applied to the fillers.

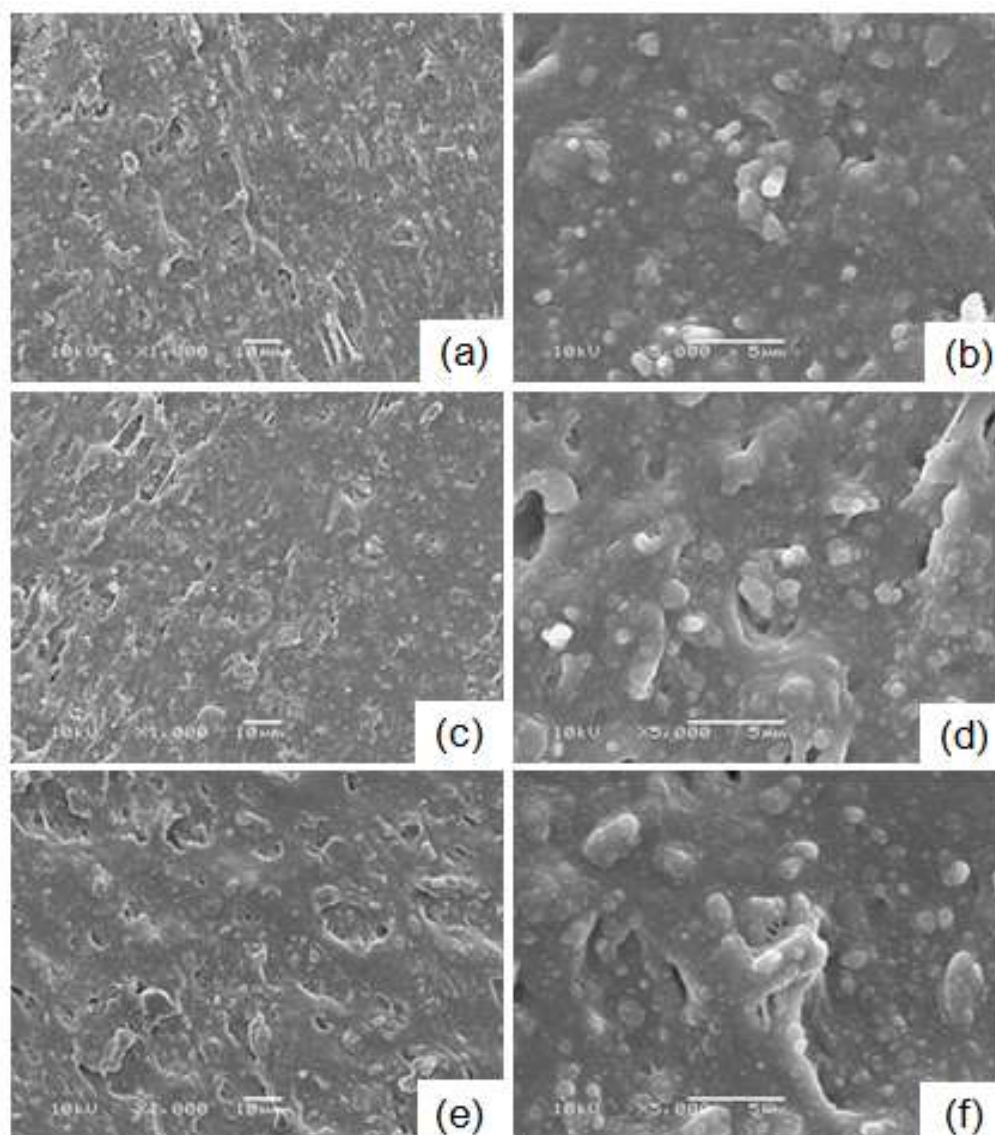


Figura 2 . SEM surface micrographs of composites made with 20 %(v/v) of HAp modified with 0, 5 and 10 %(wt/wt) TEOS solutions. (a), (b) HAp 0 %, (c), (d) HAp 5 %, (e), (f) HAp 10 %.

Figure 3 shows XRD diffractograms of the composites made with modified and unmodified HAp. In both cases, the patterns show the main peaks corresponding to HAp (JCPDS 9-0432) and a broad peak, located between 10 – 15 °, related to the amorphous poly(dimethylsiloxane) morphology. Therefore, the integrity of the calcium phosphate phase remained intact after both, the surface modification and incorporation to the elastomeric matrix processes, during the composite elaboration. The tensile strength of PDMS and composites are presented in Fig. 4.

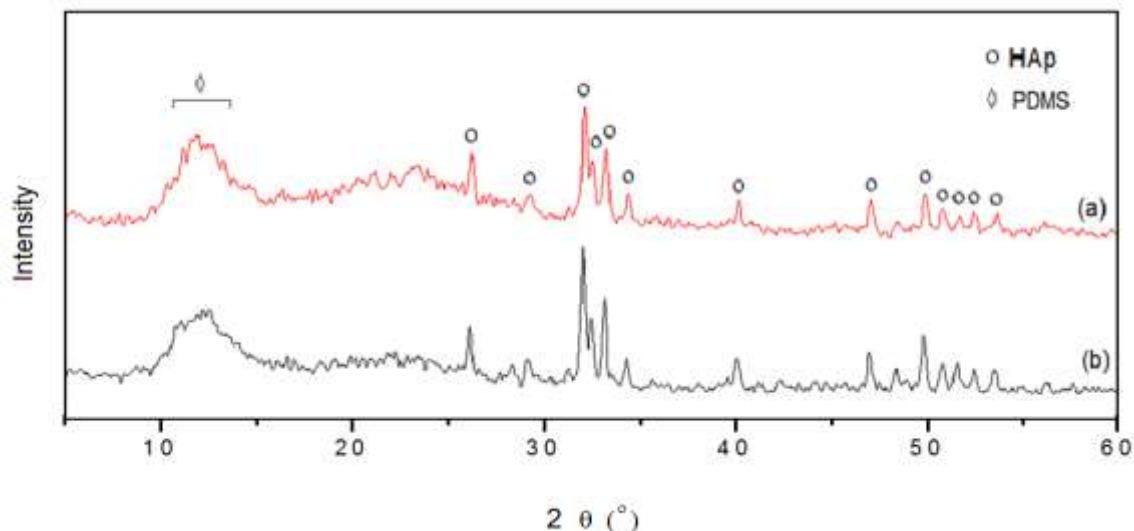


Figure 3. XRD diffractograms of the composites made by the incorporation of 20 %(v/v) of hydroxyapatite, (a) unmodified and (b) modified with a 10 %(wt/wt) TEOS solution.

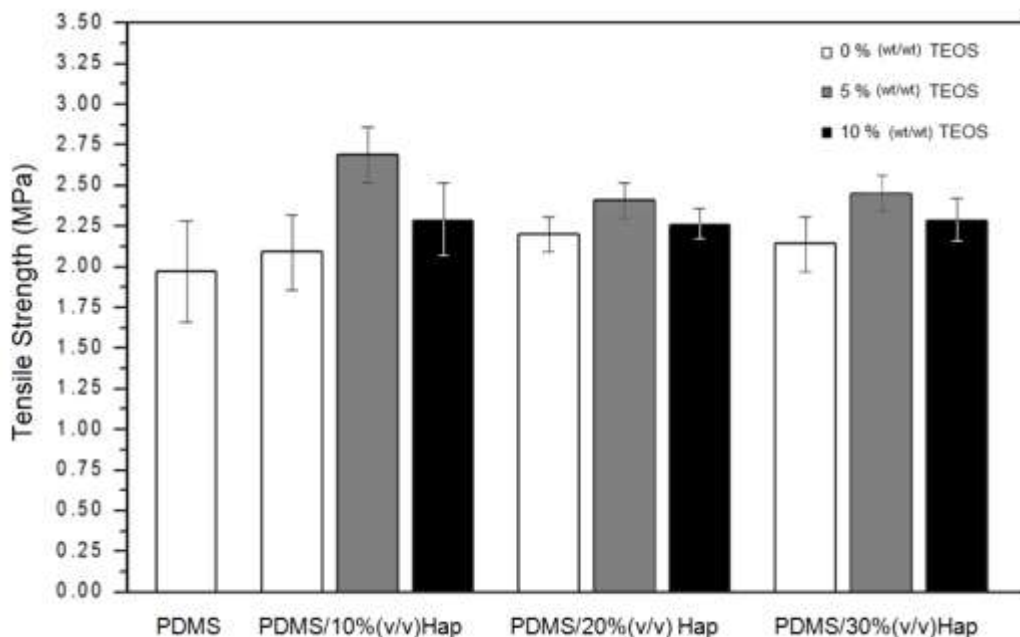


Figure 4. Tensile strength of PDMS and PDMS/10,20,30 %(v/v)Hap composites, modified with 0, 5 and 10 %(wt/wt) TEOS solutions.

The incorporation of unmodified HAp into the PDMS matrix led to slightly higher values of average tensile strength, as the volume fraction of HAp added was increased. The composite PDMS/10%(v/v)HAp-0%(wt/wt)TEOS showed a 6 % increase in the average tensile strength, once compare to the pure PDMS. The composites made with modified HAp showed higher values of tensile strength than those made with unmodified HAp, regardless the volume fraction of calcium phosphate added. Higher values of tensile strength were achieved with HAp treated by a 5 %(wt/wt) TEOS solution, once compared to HAp treated with a 10 %(wt/wt) TEOS solution.

The composite PDMS/10%(v/v)HAp-5(wt/wt)TEOS showed a 37 % increase in the tensile strength, once compared to the pure PDMS. Therefore, the surface modification strengthened the interfacial bond between the matrix and the fillers. This allowed loading to be more efficiently transferred, leading to the composite reinforcement.⁽⁸⁾

The mechanical properties, also got by means of the tensile test, are presented in Tab. 1. It is possible to observe that the values of elastic modulus increased monotonically as the volume fraction of unmodified HAp added was increased. On the other hand, the composites made with modified HAp showed higher values of elastic modulus, once compared to the composites made with unmodified HAp, regardless the volume fraction of calcium phosphate added. Higher values of elastic modulus were achieved with HAp treated by the 5 %(wt/wt) TEOS solution, once compared to the fillers treated by the 10 %(wt/wt) TEOS solution.

Table 1. Mechanical properties of PDMS and 10, 20 and 30 %(v/v) HAp composites, modified with 0, 5 and 10 %(wt/wt) TEOS solutions.

Sample	Deformation (%)	Elastic Modulus (MPa)
PDMS	525,28 ± 36,97	0,63 ± 0,07
PDMS/10 %(v/v) HAp-0 % TEOS	533,80 ± 90,73	1,11 ± 0,32
PDMS/10 %(v/v) HAp-5 % TEOS	163,98 ± 19,39	3,66 ± 0,60
PDMS/10 %(v/v) HAp-10 % TEOS	170,28 ± 14,29	2,77 ± 0,25
PDMS/20 %(v/v) HAp-0 % TEOS	365, 58 ± 65,62	1,58 ± 0,32
PDMS/20 %(v/v) HAp-5 % TEOS	139,62 ± 10,95	3,37 ± 0,62
PDMS/20 %(v/v) HAp-10 % TEOS	73,44 ± 3,45	2,29 ± 0,22
PDMS/30 %(v/v) HAp-0 % TEOS	200,05 ± 47,41	2,66 ± 0,18
PDMS/30 %(v/v) HAp-5 % TEOS	113,43 ± 17,16	5,39 ± 0,30
PDMS/30 %(v/v) HAp-10 % TEOS	33,18 ± 6,62	5,30 ± 0,35

Knowing that the composite tensile strength and elastic modulus depend on the matrix/filler interface, these features are a measure of the interfacial strength. When the interfacial adhesion is strengthened, by means of a coupling agent, in this particular case, reactive silane, polymer chains surrounding the particles may bond to the particle surface and form a layer of immobilized polymer chains. Thus, the tensile strength and elastic modulus of the composite made with modified filler increase, once compared to the composite made with unmodified filler, as a result of the interface strengthening and increased stiffness.⁽⁹⁾

Higher volume fractions of HAp added to PDMS led to lower values of deformation, once compared to the values of pure PDMS. This behavior was intensified with the filler surface modification. Higher TEOS concentrations led to lower values of deformation, for a constant volume fraction of HAp. This feature could be a result of polymer chain bonding to the filler surface, as previously described.

Fig. 5 shows SEM surface fracture micrographs of the composites made with modified and unmodified HAp. Fig. 5(a), related to the composite made with unmodified HAp, shows a particle detached from the matrix. The process of particle filler detaching from the matrix after the composite deformation is known as debonding. The debonding normally occurs due to the lack of adhesion between the matrix and the filler. Whereas, the particle is unable to support any loading and the composite tensile strength is reduced with the addition of any further amount of filler (8). The Fig. 5(b) and (c) are related, respectively, to the composites made with HAp modified with 5 and 10 %(wt/wt) TEOS solutions.

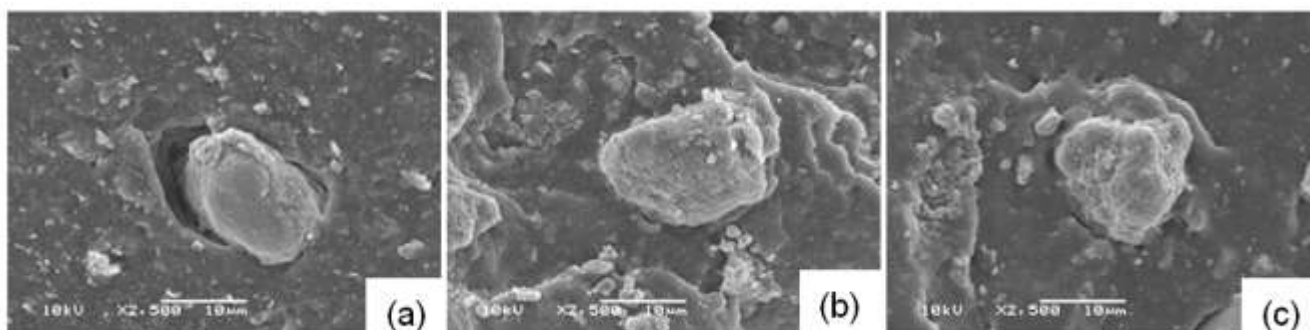


Figure 5. SEM surface fracture micrographs of 20 %(v/v) HAp composites, modified with (a) 0 %(wt/wt), (b) 5 %(wt/wt) and (c) 10 %(wt/wt) TEOS solutions.

It's possible to observe that the particles remained well embedded in the matrix after the deformation, this as result of the matrix/filler interface strengthening, achieved with the surface modification using TEOS solutions. Tab. 2 shows Shore A hardness values of PDMS and composites. It can be seen that the addition of unmodified HAp particles increased monotonically the PDMS hardness. On the other hand, the particles surface modification led to higher values of hardness, once compared with the values of the unmodified particles. This behavior is also evidence of the matrix/filler interface strengthening.

Fig. 6 and 7 show SEM surface micrographs of the composites made with HAp, treated with 0 %(wt/wt) and 10 %(wt/wt) TEOS solutions, samples were soaked in SBF for up to 7 days. After 7 days of soaking a homogeneous layer of HAp like crystals can be seen at the samples surface, regardless the surface treatment applied to the fillers.

Table 2. Shore A hardness values of 10, 20 and 30 %(v/v) HAp composites, modified with 0, 5 and 10 %(wt/wt) TEOS solutions.

Sample	Shore A Hardness
PDMS	31 ± 1
PDMS/10 %(v/v) HAp-0 % TEOS	38 ± 1
PDMS/10 %(v/v) HAp-5 % TEOS	56 ± 1
PDMS/10 %(v/v) HAp-10 % TEOS	50 ± 1
PDMS/20 %(v/v) HAp-0 % TEOS	46 ± 1
PDMS/20 %(v/v) HAp-5 % TEOS	55 ± 1
PDMS/20 %(v/v) HAp-10 % TEOS	50 ± 1
PDMS/30 %(v/v) HAp-0 % TEOS	52 ± 1
PDMS/30 %(v/v) HAp-5 % TEOS	66 ± 1
PDMS/30 %(v/v) HAp-10 % TEOS	66 ± 1

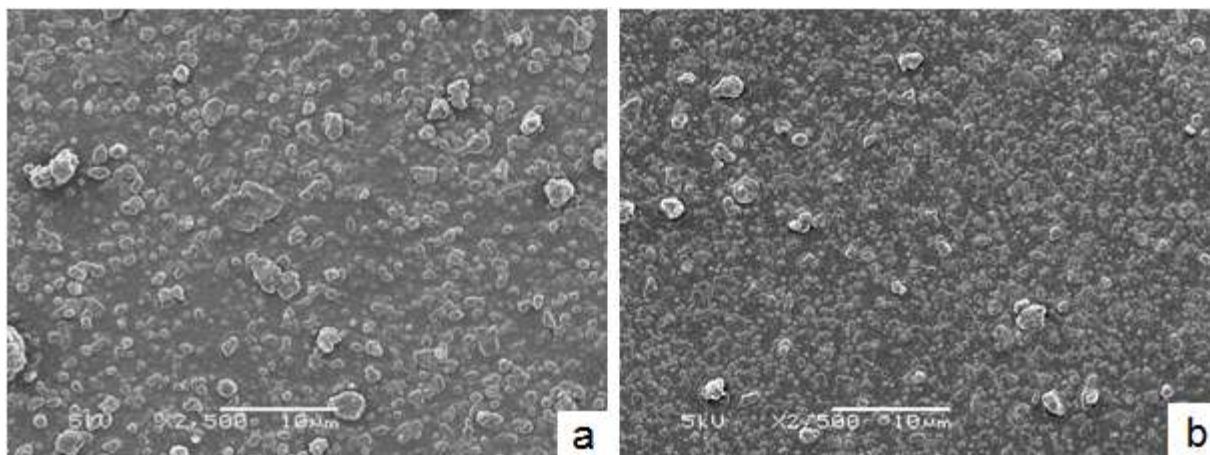


Figure 6. SEM external surface micrographs of the composites after 3 days of immersion in SBF. (a) PDMS/20%(v/v)HAp-0%TEOS, (b) PDMS/20%(v/v)HAp-10%TEOS.

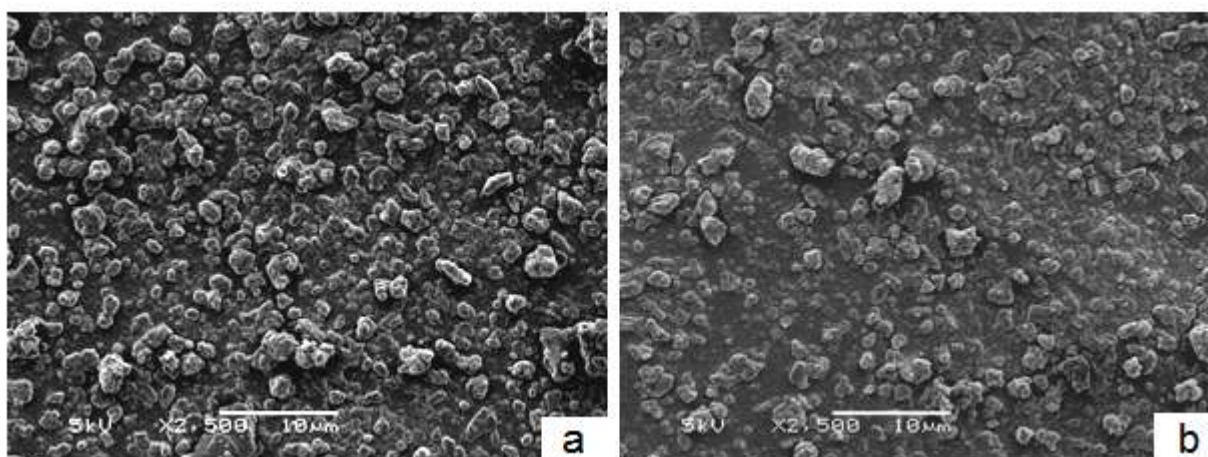


Figure 7. SEM external surface micrographs of the composites after 7 days of immersion in SBF. (a) PDMS/20%(v/v)HAp-0%TEOS, (b) PDMS/20%(v/v)HAp-10%TEOS.

Fig. 8 and 9 show XRD surface diffractograms of the composites made with HAp, treated with 0 %(wt/wt) and 10 %(wt/wt) TEOS solutions, samples were soaked in SBF for up to 7 days. From these results, it's possible to see that the chemical composition of the composites remained unchanged after 7 days of soaking, regardless the surface treatment applied to the fillers. The XDR technique applied didn't allow the differentiation between the HAp from the composite and the HAp precipitated from the SBF. Due to this limitation, it was not possible to detect any variation in the chemical composition at the composites surface.

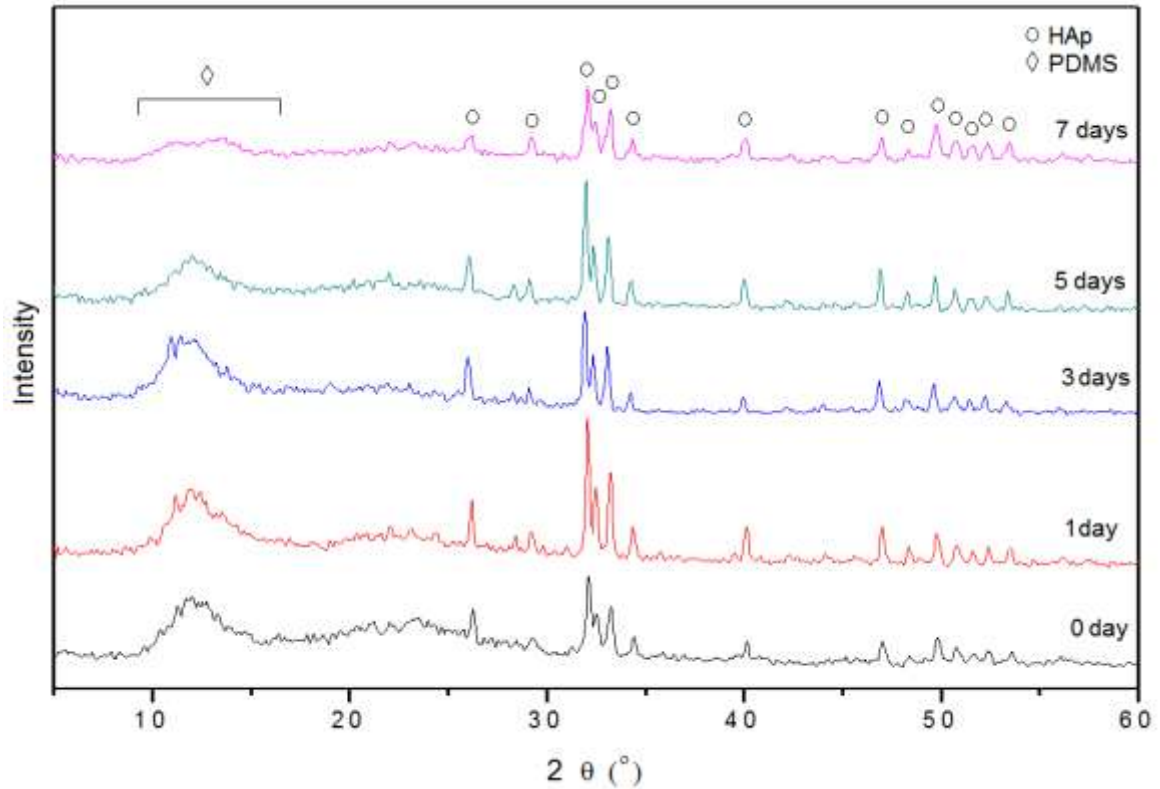


Figure 8. XRD surface diffractograms of the PDMS/20%(v/v) HAp-0 %TEOS composite, with 0 – 7 days of soaking in SBF.

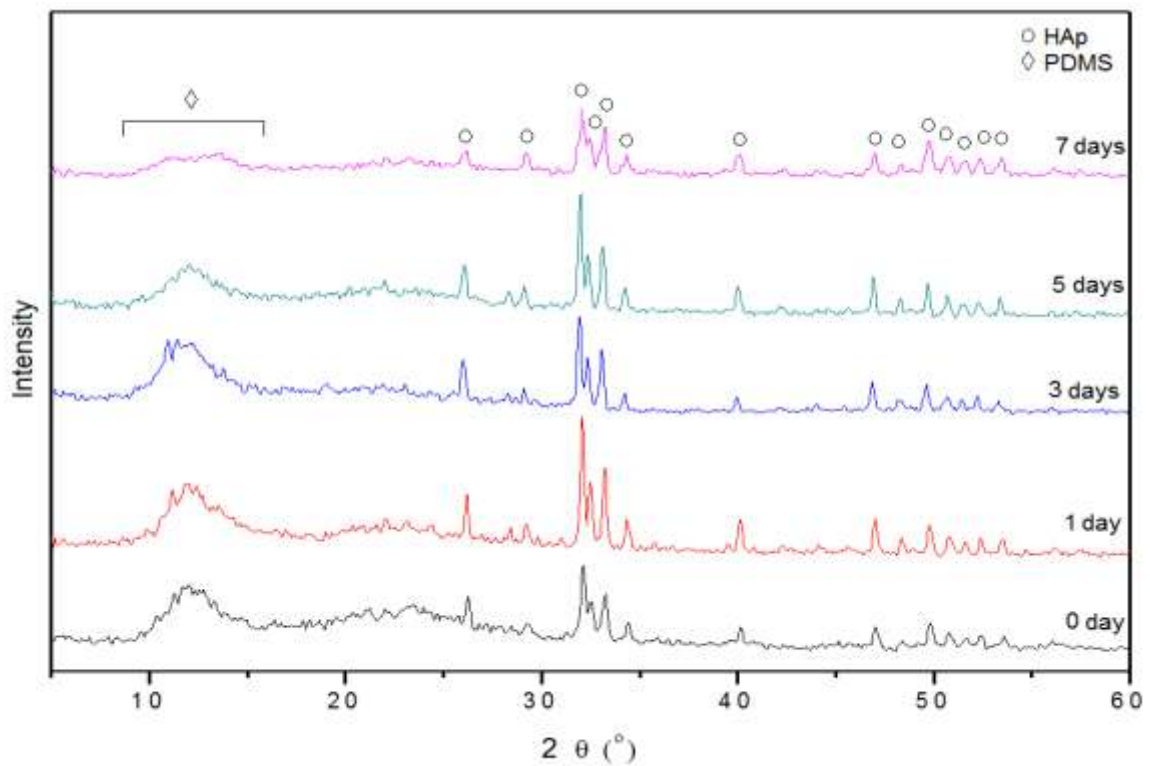


Figure 9. XRD surface diffractograms of the PDMS/20%(v/v)HAp-10%TEOS composite, with 0 – 7 days of soaking in SBF.

CONCLUSIONS

Hydroxyapatite was synthesized by the precipitation method and its surface was modified using TEOS solutions. The EDS spectra showed evidence of a silane layer formed in the HAp surface after the surface modification. The integrity of the filler phase remained intact after both, the surface modification and incorporation to the elastomeric matrix processes, during the composite elaboration. The modified HAp was added to an elastomeric matrix of PDMS in order to make composites, tensile measurements showed that the composite PDMS/10%(v/v)HAp-5(wt/wt)TEOS achieved a 37 % increase in the tensile strength, once compared to the pure PDMS. Composites made with modified HAp showed higher values of elastic modulus, once compared to the composites made with unmodified HAp. The surface modification strengthened the interfacial bond between the matrix and the fillers. SEM fracture micrographs showed that the particles remained well embedded in the matrix after deformation. The *in vitro* bioactivity essay showed that after 7 days of soaking in SBF a homogeneous layer of HAp like crystals can be seen at the samples surface, this result suggests that the composite will demonstrate an excellent biocompatibility once implanted *in vivo*.

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