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Surface modification tailors the characteristics of biomimetic coatings nucleated on starch-based polymers

A. L. OLIVEIRA, C. ELVIRA, R. L. REIS*
Department of Polymer Engineering, University of Minho, School of Engineering, Campus de Gualtar, 4719, Braga, Portugal
E-mail: rgreis@fe.up.pt

B. VÁZQUEZ, J. SAN ROMÁN,
CSIC, Institute of Polymer Science and Technology, Juan de la Cierva, 3, 28006 Madrid, Spain

**also with Department of Metallurgical and Materials Science Engineering, Faculty of Engineering, University of Porto, Rua dos Bragas, 4099 Porto Codex, Portugal*

This work describes the influence of surface pretreatments over the nucleation and growth of an apatite layer, formed by a biomimetic process, on which a bioactive glass is used as a precursor of the calcium-phosphate (Ca-P) formation on the materials surface. SEVA-C, a corn starch-based biodegradable blend, was used as substrate. The surfaces were pretreated during various periods by: (i) physical methods, namely ultraviolet radiation (u.v.), and over exposure to ethylene oxide sterilization (EtO); and (ii) chemical methods, namely potassium hydroxide (KOH) and acetic anhydride $(CH_3CO)_2$ etchings. The surface modifications, performed before the production of the biomimetic coatings, resulted in a faster formation of Ca-P nuclei during the first stages of SBF immersion, particularly in the case of the KOH etching. In this case, it was possible to observe a decrease in the average surface roughness, as measured by laser profilometry, and an increase of the hydrophilicity of the material, which was evident from a clear increment in the water-uptake ability and quantified by contact angle measurements. With this treatment it was possible not only to reduce the induction period for the formation of a well defined and dense apatite-like layer, as observed by scanning electron microscopy (SEM), but also to improve the adhesion of the Ca-P layer to the substrate, as confirmed by the adhesion strength tests. For all the studied pre-treatments, the composition of the films, analyzed by energy dispersive spectroscopy (EDS) and identified by thin-film X-ray diffraction (TF-XRD), seems to be very similar to that of human bone apatites.

1. Introduction

Biodegradable polymers are nowadays becoming more and more important in the biomaterials field. Applications include, among others, bone fixation and replacement [1–3], tissue engineering scaffolds [4] and carriers for the release of drugs or bioactive agents [5, 6]. The development of new biodegradable polymeric systems may be quite useful, especially in temporary applications for the repair and regeneration of healing tissues. Starch-based polymers are well-known biodegradable materials [7] that may constitute a good alternative to the currently used bioresorbable biomaterials [8]. These polymers exhibit a range of properties [2, 7, 8] that can allow their use as biomaterials. When considering a particular material as being adequate for bone replacement it must be mechanical and biologically compatible with bone [9]. It is well known that the bulk structures of materials govern their mechanical properties. On the other hand, their surface chemistry and structure largely controls the biological responses to biomaterials and other medical devices. The rationale for surface modification is therefore straightforward: to retain the key physical properties of a biomaterial, while modifying only its outermost surface in order to influence the biointeraction.

In vivo, it may be advantageous for an orthopaedic implant to exhibit a bone-bonding behavior [1]. This can be achieved by nucleating and growing a calcium phosphate (Ca-P) coating on its surface by means of a biomimetic treatment [1, 10, 11]. To do this on a degradable polymer is not a very easy task, as the surface of the substrate (and pH around it) is continuously changing. Nevertheless, biomimetic coatings on the surface of starch-based polymers have been successfully produced in previous works [1, 3].

This study presents a preliminary report describing the influence of surface pretreatments: (i) over the induction period of the apatite layer formation by a biomimetic process; (ii) on the substrate/Ca-P coating adhesive strength. A biodegradable blend of starch with poly (ethylene vinyl alcohol) (SEVA-C) was selected for this study.

2. Materials and methods

A biodegradable blend of corn starch with poly(ethylene vinyl alcohol) (SEVA-C, Mater-Bi 1128RR, Novamont, Novara, Italy) was used as substrate. Further information on the properties of this type of polymer and its potential for biomedical applications may be found elsewhere [1–3, 6–8].

The material was injection molded on a Klockner Desma FM-20, using a nozzle temperature of 170 °C, in order to produce standard ASTM tensile dumb-bell samples with a cross-section of $2 \times 4\,mm^2$. For Fourier transform infrared spectroscopy (FTIR) analysis thin films were prepared by a hot compression technique, in a Grasby–Specac press, at 150 °C and by applying a pressure of 400 Pa.

For the biomimetic assays a bioactive glass in the system MgO—CaO.P_2O_5—SiO_2 (BGE1), kindly supplied by University of Aveiro, Portugal, was used as a precursor of the calcium phosphate (Ca-P) nucleation. The preparation of this bioactive glass was in accordance with previously published routes [12, 13]. Table I presents the composition of the bioactive glass used to nucleate the coatings. The methodology used to produce these biomimetic coatings has been published before [1]. This procedure is briefly described in Section 2.6 of the present paper.

2.1. Surface modifications

In previous work SEVA-C has demonstrated to be quite a hydrophilic substrate [1]. The presence of OH groups on the surface seems to facilitate the connection with an apatite layer, nucleated by a biomimetic treatment [1]. This fact justifies the present efforts of trying to increase the number of OH groups, as well as of incorporating chemical groups which facilitate ions complexation at the material surface, modifying properties such as water-uptake ability.

In this work the samples were pre-treated during various periods by (i) physical and (ii) chemical methods:

(i) the samples were exposed to:

- UV radiation, for various periods (from 0 to 180 min), in a Hanovia Uvitron irradiation system, with a 100 W high-pressure mercury lamp (wavelength ranging from 254 to 365 nm).
- Ethylene oxide (EtO) sterilization (one or two consecutive cycles). The sterilization cycles were performed in an industrial autoclave at 45 ± 1 °C, in an atmosphere with 88% CO_2, 12% EtO and 50% humidity. Each cycle lasted 25 h.

(ii) the samples were soaked in 20 ml of:

- potassium hydroxide (KOH), 3 *M*;
- acetic anhydride (Ac_2O), $(CH_3CO)_2O$ (98%, commercial, without further purification).

All the treatments were carried out from 0 to 24 h, at room temperature (23 ± 1 °C). After each treatment the samples were washed using ultrasound in distilled water, and then dried at room temperature, in a controlled atmosphere (23 °C; 55% RH).

TABLE I Bioactive glass composition (BGE_1 wt %) [12, 13]

Compounds	E_1 glass (wt %)
$3CaO\cdot P_2O_5$	52.75
SiO_2	30.00
MgO	17.25

2.2. FTIR analysis

The substrates were analyzed by FTIR in a Perkin Elmer System 1600 FTIR with an attenuated total reflectance (ATR) device, from SPECAC, aiming at detecting any type of chemical modification on the sample's chemical structure.

2.3. Laser profilometry

Surface roughness was assessed by laser profilometry technique, in a Perches Mars Perthometer PRK, with an optical sound "Focodyn". Five measurements were carried out for each sample. The parameters used for comparing the surface roughness of the untreated and treated surfaces were R_a (arithmetical mean roughness), R_Z (mean peak-to-valley height) and R_{max} (maximum roughness depth). R_a is the arithmetical average value of all departures and of the profile from the mean line throughout the sampling length. R_z is the average of the single peak-to-valley heights of five adjoining sampling lengths [14].

2.4. Water-uptake ability

Water-uptake studies are of great importance for a biodegradable material, because when implanted, it will inevitably be in the presence of body fluids that will diffuse into the bulk of the polymer as degradation is taking place. For water-uptake measurements all the samples were weighted before being immersed on distilled water (at room temperature) and then each 2 h, during the first 12 h of immersion. After that period, the weights started to be registered each 24 h, until the end of the experiment time (15 days). The samples were carefully removed from the water-containing flasks and immediately weighted for the determination of the wet weights as function of the immersion time. Water-uptake is given by

$$\text{Water absorbed} = [(m_i - m_f)/m_i] \times 100 \quad (1)$$

Where m_i is the initial weight of the sample, and m_f is the sample weight after a given time of immersion.

2.5. Contact angle measurements

The contact angle measurements were obtained by the sessile drop method using a G10 model with an image processor G1041 model, from Kruss. Duplicate measurements were recorded for each drop (one on each side of the sessile drop) and the average between these two values was considered. Thirty average values have been recorded, the first after 5 s of the drop deposition (settling time) and then one measurement was recorded every 3 s. The final contact angle values are averages of the results obtained as a function of the surface pretreatment time, from a set of at least four experiments. Distilled water and methylene iodide were used as tests liquids. The obtained results from both liquids were used to calculate the surface tension (γ) according to a method proposed by Owens and Went [15]. According to this method the surface tension (γ) of each phase can be resolved into a polar (γ^p) and disperse part (γ^d). The test liquid (l) placed on the solid surface (s) has polar (γ_l^p) and disperse (γ_l^d) parts that are known, and are presented in Table II.

Using these two test liquids the resulting values of the surface tension were calculated by this method which is particularly useful for the determination the surface energy of low energy surfaces (polymers).

2.6. Ca-P film formation

To produce the so called biomimetic coatings the substrates were submitted to a procedure previously described by Kokubo and co-workers [10, 11] and adapted by Reis *et al.* [1]. The samples were: (i) involved in a dispersion of a bioactive glass (BGE1) and then soaked in a simulated body fluid (SBF) with an ion concentration nearly equal to human blood plasma (Table III) in order to form apatite nuclei; (ii) soaked in another solution with ion concentrations 1.5 × SBF for making apatite nuclei to grow. The studied times were an incubation period of 7 days and a growing period up to 15 days.

TABLE II Polar (γ_l^p) and disperse (γ_l^d) components of water and methylene iodide

	γ_l	γ_l^d	γ_l^p
Water	72.8	21.8	51.0
Methylene iodide	50.8	50.8	0.0

2.7. SEM, EDS and TF-XRD

The morphological characterization was carried out by SEM observations, in a Jeol JSM 7301 F. All the samples were coated with a thin film of carbon by ion sputtering, prior to any observation. The electron beam energy was 15 KeV in all cases. A half-quantitative characterization, using well established calibration subroutines, of the atomic concentrations of the Ca-P coatings was performed by EDS, in a Noran Instruments spectrometer with a Voyager software. The amounts of Ca, P, Mg, K and Na were quantified. From these results Ca/P ratios were calculated. Considering the possibility of Mg^{2+}, Na^+ and K^+, being present in the SBF, substituting the Ca^{2+} in the crystalline network of the apatite, the following relation was also calculated: $(Ca + Na + Mg + K)/P$. Thin-film XRD spectra were also acquired in a Rigaku equipment at 60 kV at 30 mA, in order to identify the cystalline phases present in the several Ca-P layers.

2.8. Coating adhesion

An adhesion test was carried out in order to quantify the effectiveness of several modifications on improving the adhesion of the biomimetic coating. The adhesion strength was measured by means of a pull-off test that was performed in an Instron 4505 universal testing machine. A pair of brass jigs were attached to the coated surface of the polymers by means of double-face type tape adhesives with 5 mm diameter. The crosshead speed was 1 mm min^{-1}.

3. Results

3.1. FTIR analysis

The FTIR (ATR) spectra showed differences between non-treated SEVA-C blends and samples treated with KOH and $(CH_3CO)_2O$. No remarkable changes were observed for the u.v. and sterilization methods. Table IV shows the assignment of the most characteristic FTIR signals of SEVA-C treated and non-treated samples. The most important changes were observed on the region

TABLE III Ion concentration of SBF and the human blood plasma [11]

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5
Human plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

TABLE IV Most significant FTIR (ATR) band position for SEVA-C blends: SEVA-C treated with KOH and SEVA-C treated with $(CH_3CO)_2O$

Sample	Peak assignment (cm^{-1})			
	—OH stretch	C—H stretch	C=O stretch	C—O stretch
SEVA-C	3500–3100 broad	2920–2850 two bands	1700, 1664 weak band	1110, 1020 weak
SEVA-C (KOH treatment)	3500–3100 medium (several peaks)	2950–2880 two bands	1680 weak	1150, 1075, 1025 (3 bands) intense
SEVA-C (Ac_2O treatment)	3500–3100 weak	2940–2860 two bands	1640 broad	1108, 1048 intense

from 3500 to 3100 cm^{-1} assigned to the OH stretching vibration of the starch and vinyl alcohol hydroxy groups, on which non-treated SEVA-C exhibits a broad band intensity which is reduced when treated with KOH and Ac_2O. Two signals appeared for the —CH- and —CH_2- groups stretching vibrations of the three samples. On the other hand, in the carbonyl stretching region, signals can be observed, which have been attributed by several authors [16, 17] to the appearance of these groups as a consequence of a small and partial degradation of starch when processed at high temperatures giving rise to complex products [18]. In this region, a broad signal at 1640 cm^{-1} was observed when SEVA-C was treated with Ac_2O indicating a partial acetylation of the hydroxy group. This fact is also confirmed by the —OH stretch signals intensity decrease, as well as by the increased intensity of the bands appearing at 1108 and 1048 cm^{-1}, assigned to the C—O stretching vibration of the —O—CO—CH_3 groups. SEVA-C samples treated with KOH also exhibited three very intense bands at 1150, 1075, 1025 cm^{-1} which are assigned to C—O streching vibrations. The decrease of —OH signal intensity and the appearance of the third band in the 1100 cm^{-1} region suggests that hydroxyl groups of SEVA-C are forming molecular complexes by hydrogen bonding interactions with KOH; the formation of partial alkoxide (—O^-K^+) is also possible, as described in the literature [19].

3.2. Laser profilometry

Fig. 1 presents the R_a, R_z and R_{max} values for the untreated, u.v. radiated, EtO sterilized, $(CH_3CO)_2O$ etched and KOH etched samples. For the non-treated samples the roughness profile is not homogeneous, as the surface is being scanned in zones where there are peaks/valleys with dimensions out of the normal range (exceptional peaks/valleys). In fact, R_a values do not approach R_z, meaning that R_{max} was affected by the presence of exceptional peaks/valleys.

The roughness values measured in the u.v.-treated surfaces indicate that there are some significant changes in R_{max} with u.v. exposure time, but R_a and R_z values remain constant. After 5 min of u.v. exposure R_{max} has diminished significantly, remaining constant after 15 days. Therefore, the surface has become more homogeneous once the exceptional peaks and valleys are near the average roughness. EtO sterilization does not seem to have a very pronounced effect over the roughness of the material. For the $(CH_3CO)_2O$ and the KOH treatment the R_{max} has suffered an accentuated decrease starting for the lesser treatment times. These two treatments have etched preferentially the salient peaks, that have become nearer the average peaks/valleys, creating a smoother surface.

3.3. Water-uptake ability

Fig. 2 shows a typical water-uptake versus time graph for SEVA-C and SEVA-C treated by the previously described procedures. The hydration degree of SEVA-C blends, after 50 h is about 25% due to its hydrophilic nature, mainly as a result of the starch and vinyl alcohol hydroxy groups, as has been previously described [20].

The u.v. exposure treatment does not exhibit remarkable differences on the SEVA-C water-uptake behavior. Sterilized SEVA-C samples show a faster water-uptake during the first hours of the experiment when a second consecutive sterilization cycle was performed, which is probably due to a loss of

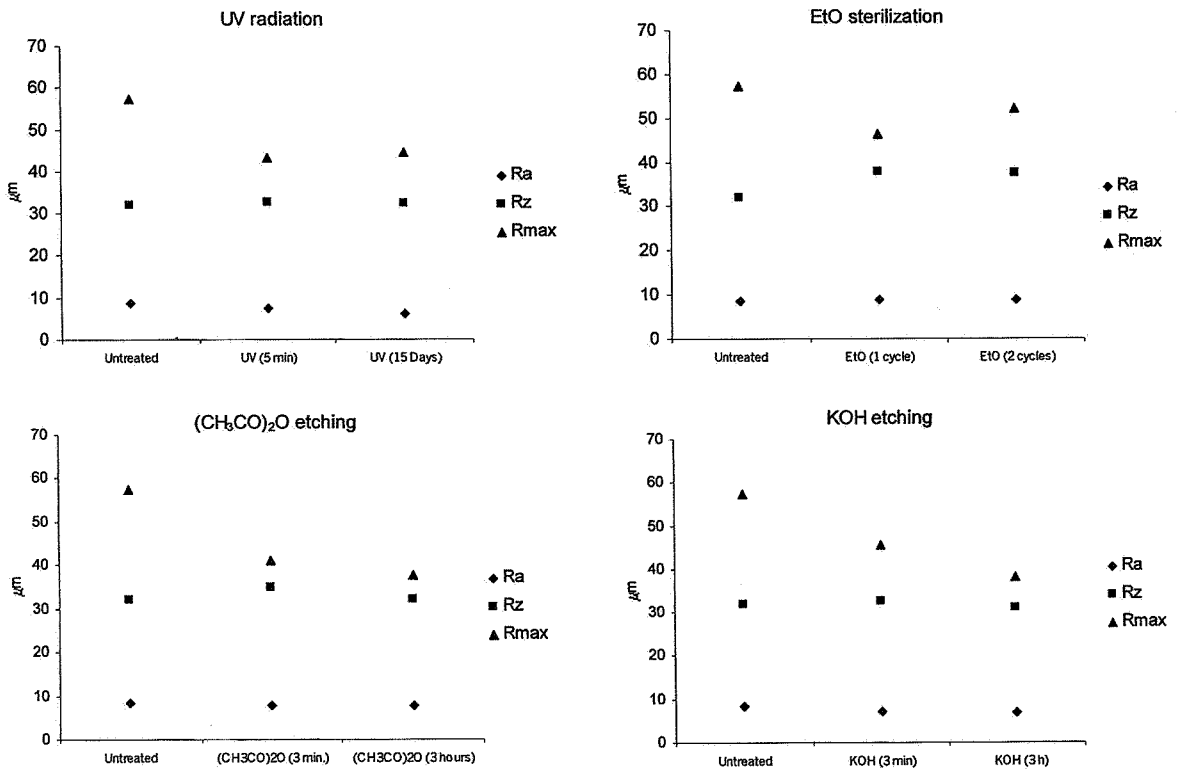


Figure 1 Laser profilometry of the surface of SEVA-C treated samples (u.v., sterilization, Ac_2O and KOH treatments).

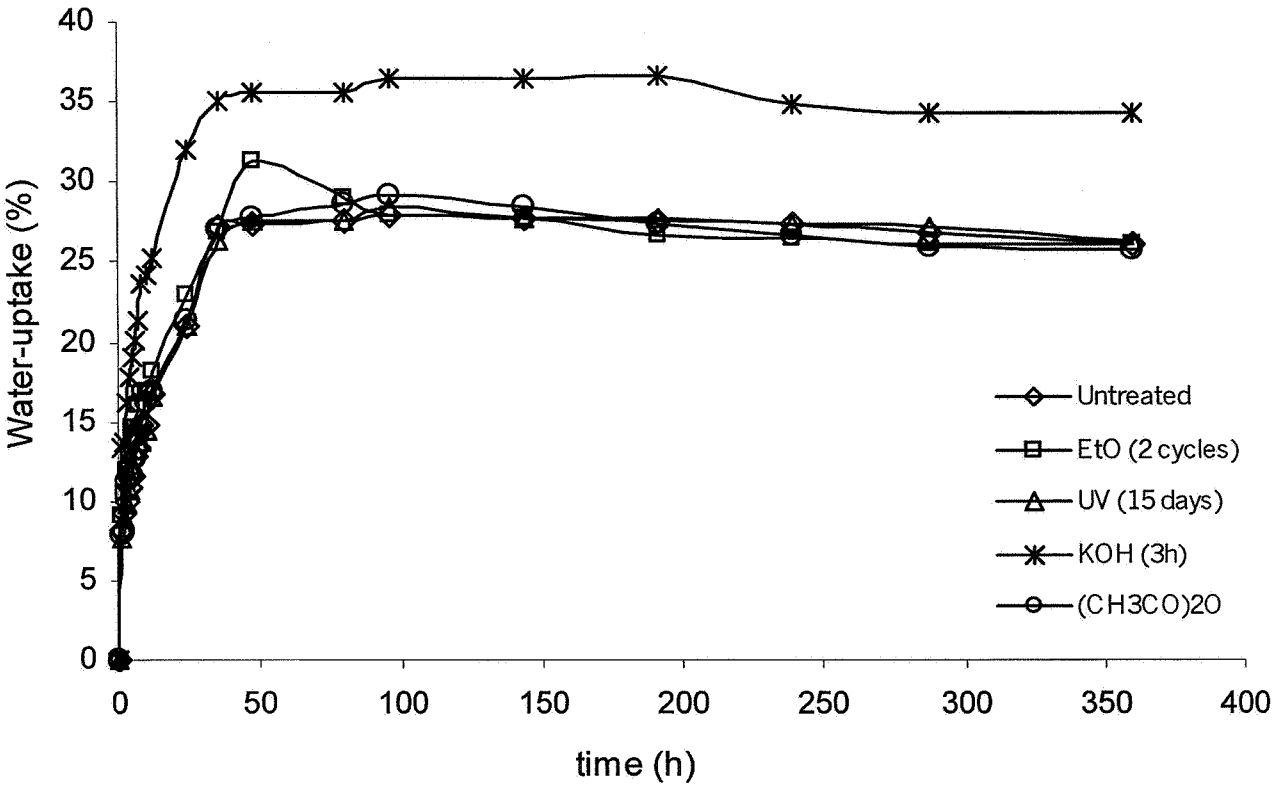


Figure 2 Water-uptake (%) versus time for treated and non-treated SEVA-C samples.

crystallinity of the material, as found by Raman spectroscopy in a previous work [20]. It can be concluded that sterilized samples after 15 days of immersion do not show notable variations in the equilibrium hydration degree in comparison to untreated SEVA-C. The hydration degree of Ac_2O-treated samples is also similar to untreated SEVA-C. The most significant differences were obtained with KOH treated SEVA-C samples, which after 50 h of immersion achieved its equilibrium hydration degree above 35%. The increased hydrophilicity after this treatment can be justified by the molecular hydroxy-KOH hydrogen bonding complexes, which are easily solvated by water molecules.

3.4. Contact angle measurements

Understanding the surface behavior of a biomaterial in contact with hydrated media is of great importance to predict interactions of a certain material with the surrounding tissues, when applied in a particular biomedical application. These parameters are determined, in general, by means of wetting experiments, the sessile drop technique being the most usual [22]. In this work, this technique was applied, in air and at room temperature, to determine the water contact angle and surface energy of the modified surfaces. The contribution of the dispersion and polar interactions to the surface energy was calculated by considering that the intermolecular attraction which causes surface energy, γ, results from a variety of intermolecular forces according to an additive rule. Most of these forces are functions of the specific chemical nature of a particular material, and the surface energy can be compiled as γ^p (polar interactions), taking into consideration that the dispersion forces (γ^d) are always present in all systems, independently of their chemical nature. Thus, surface energy and contact angle of a liquid on a solid were calculated using the Fowkes [21] and Young–Dupre [22] equations, with liquids of different polarity such as water and methylene iodide [23].

Fig. 3 and Table V present the results concerning the average water contact angle (θ) and average surface tension (γ_s) of the treated surfaces. Ultraviolet treatment does not show any significant changes, neither in contact angle nor in the polar contribution, whereas dispersive and total surface energy remains approximately constant. Sterilization treatment shows an increase in the contact angle values for one and two cycles, while the total surface energy remains approximately constant. On the other hand, a small decrease (12.8 to $\approx 11\,mN\,m^{-1}$) in the polar contribution to the surface energy was observed over all treatment times for $(CH_3CO)_2O$ treated samples, with an increase in the contact angle during short treatment times, as a consequence of partial incorporation of acetyl groups (which have a smaller polarity to the hydroxy ones) to SEVA-C blends. For longer periods of time, the total surface energy remains constant with respect to untreated samples. KOH treatment of SEVA-C samples did modify the surface parameters, such as contact angle polar and total surface energy. As the KOH treatment time increases an increment in total surface energy, as a consequence of the increase of the polar contribution (12.8 to $33.8\,mN\,m^{-1}$ after 1440 s) was observed. Values changed, from $45.1\,mN\,m^{-1}$ for non-treated SEVA-C to $66.7\,mN\,m^{-1}$ after 1440 s of KOH treatment. These significant changes in the polar contribution to the total surface energy can be attributed to molecular complex formation, as described above.

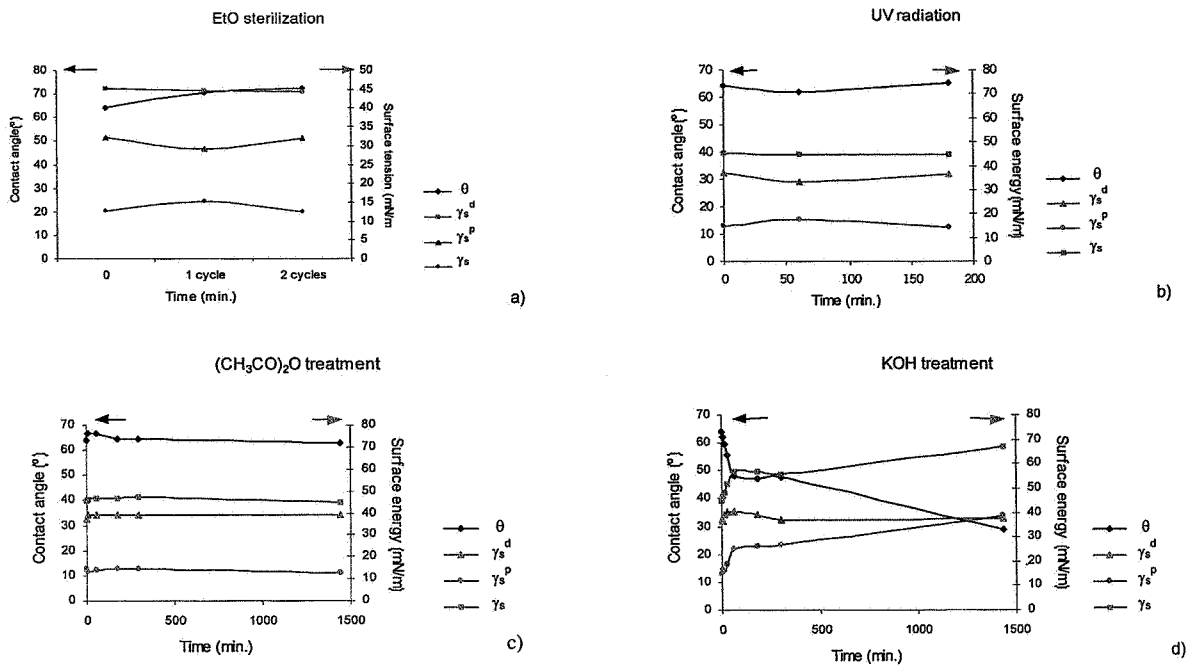


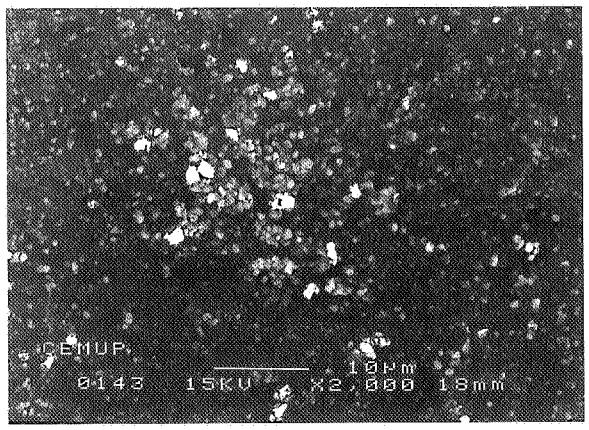
Figure 3 Contact angle measurement diagrams of treated SEVA-C blends and their respective total surface energy (dispersive and polar components), as a function of treatment time.

3.5. SEM, EDS and TF-XRD

The study of the influence of surface pretreatments over the induction and growing periods of a biomimetic coating was the main aim of this work. Fig. 4 presents SEM photographs focusing on the first 6 and 12 h of SBF immersion, where the effect of the surface modifications was manifestly evident. This figure clearly presents an example of effective pretreatments such as u.v. radiation and KOH etched substrates. In Fig. 5 the Ca/P and (Ca + Mg + Na + K)/P ratios for the first 4 days of SBF immersion are plotted.

Fig. 4a and b show the surface of untreated SEVA-C after the first 6 and 12 h of SBF immersion. The u.v.-treated surface presented in Fig. 4c shows that after 6 h of SBF immersion it seems that a greater number of apatite nuclei exist on the surface of SEVA-C, when compared with the untreated substrate. After 12 h of SBF immersion (Fig. 4d) the difference is already clear in the quantity of formed nuclei that are more uniformly distributed. The Ca/P ratio for the apatite formed on a u.v. radiation-treated surface after 6 h of nucleation is 1.23 (Fig. 5a). This value is smaller than the stoichiometric relation of a hydroxyapatite (1.67). However, it is near the characteristic value for brushite, which is a very well known apatite inductor [3]. For greater times of SBF immersion, Ca/P ratios tend to increase and then to stabilize, reaching a value of around 1.7 after 4 days. TF-XRD data obtained for these samples clearly match the standard XRD hydroxyapatite pattern (JCPDS 09-432 standard file), although a more amorphous nature of the *film* is also evident. In Fig. 5b it is possible to observe that the inclusion on the calculation of the Ca/P ratios of Mg, Na and K elements does affect the "Ca/P ratio", mostly in the first 24 h ("Ca/P" = 3). The composition of the apatites formed on the u.v. radiation-modified substrates is similar to that found on an untreated substrate. After 15 days of SBF immersion a ratio of 1.77 was calculated. Again, TF-XRD data confirm that Ca-P films are mainly apatite-like.

KOH treatment has been demonstrated to be the most effective in inducing the formation of an apatite layer in the SEVA-C substrate. In fact, Fig. 4e shows that after only 6 h of SBF immersion it is already possible to observe a clear apatite-like layer formed on the SEVA-C surface, which for an untreated sample only could be observed after 7 days immersion in SBF. This layer presents a singular morphology, which can be related to the large quantities of Mg detected by EDS on the coating. In fact, on Fig. 5 it is possible to observe that considering the elements Ca, Mg, Na and K, the Ca/P ratio for the KOH treatment suffers a great increment in the first hours, Mg being the major element responsible for this result. After 12 h of immersion this "needle type" structure is still visible, and only disappears after 24 h, which matches with the decrease in Mg (Fig. 4f and g). It seems that Mg may play a role on apatite nucleation. This should be confirmed in future studies. The Ca/P ratio also drops to characteristic values. This result is supported by the effectiveness of this treatment in increasing the surface hydrophilicity, detected by contact angle measurements, that lead to an increase of the polar energy component of the surface which has favorable sites for salt ions complexation and for the apatite nucleation. On the order hand, the water-uptake ability was improved, allowing the material to absorb higher quantities of Ca^{2+} and PO_4^{3-} ions from the SBF solution when immersed. As a consequence, the Ca^{2+} and PO_4^{3-} ion concentration in the surface would probably rise, leading to the formation of nucleating sites for the biomimetic coating formation. This phenomenon has already been reported for *PEO/PBT* copolymers [24], being related to a chelation effect. The Ca/P ratio of the calcium phosphates obtained in the biomimetic coatings, after 15 days of SBF immersion



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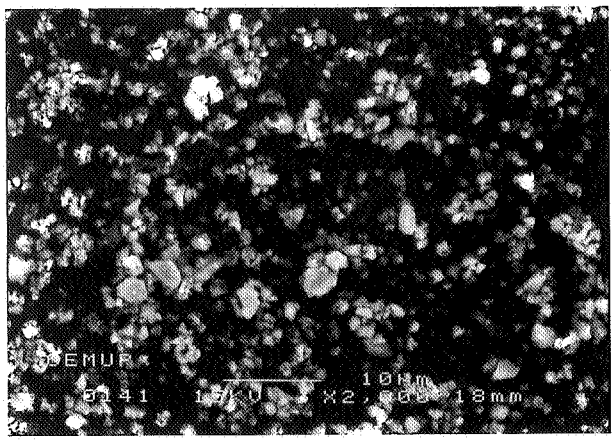

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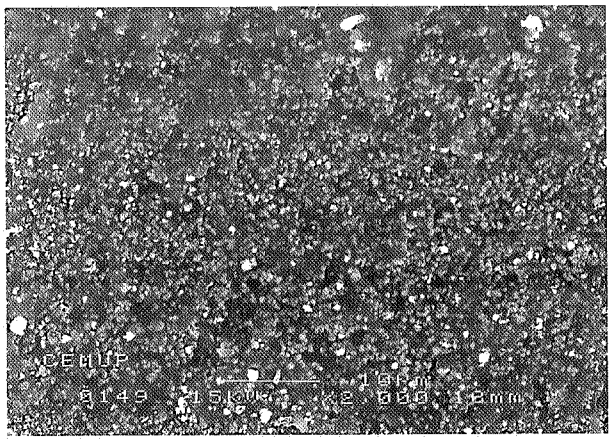

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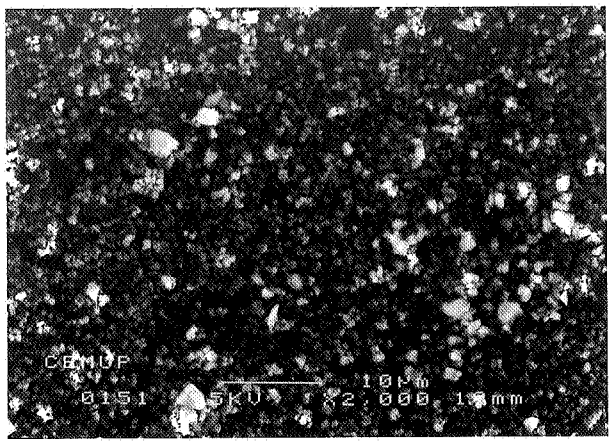

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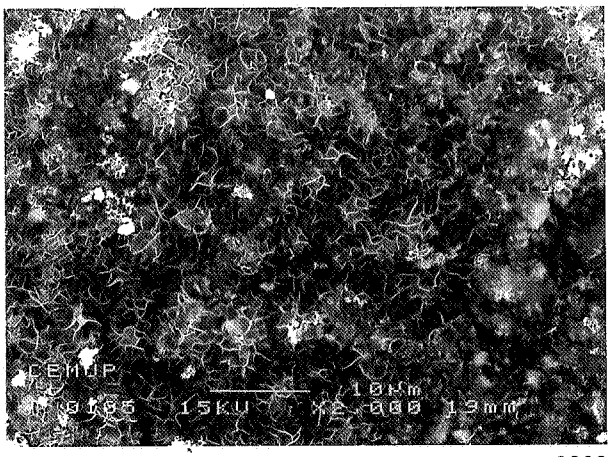

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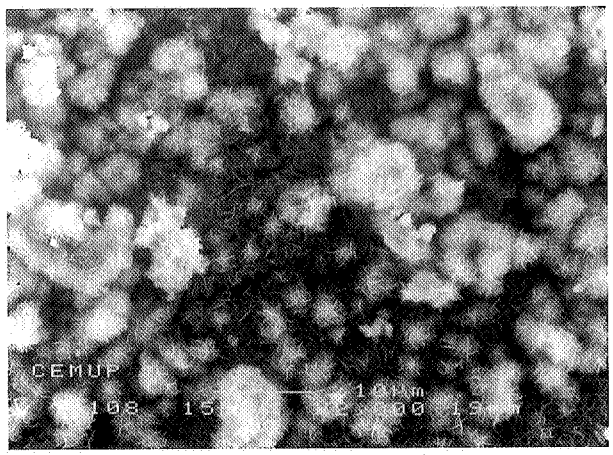

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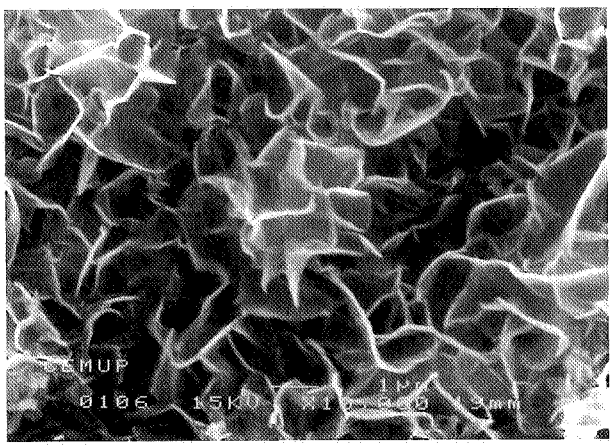

(g) × 10000

Figure 4 SEVA-C SEM photographs of (a) non-treated (6 h), (b) non-treated (12 h), (c) u.v.-treated (6 h), (d) u.v.-treated (12 h), (e) KOH-treated (6 h), (f) and (g) KOH-treated (12 h): ( ) corresponds to immersion time (hours) in SBF solution.

TABLE V Water contact angle and surface energy measurements of SEVA-C untreated and after surface treatments, as a function of time

Treatment	Time	Water contact angle θ (°)	γ_s (mN m^{-1})	γ_s^d (mN m^{-1})	γ_s^p (mN m^{-1})
SEVA-C untreated	0	64.1	45.1	32.3	12.8
EtO sterilization	1 cycle	70.7	44.5	29.2	15.3
	2 cycles	72.4	44.4	32	12.4
u.v. radiation	60 min	62.0	44.5	29.2	15.3
	180 min	65.4	44.4	32	12.4
	5 min	66.7	45.7	34.1	11.7
$(CH_3CO)_2O$ treatment	60 min	66.7	46.5	34.4	12.0
	180 min	64.7	46.7	34.2	12.5
	300 min	64.6	47.0	34.3	12.6
	1440 min	62.9	44.8	33.9	10.9
	5 min	62.2	46.5	32.0	14.5
	15 min	59.7	48.4	34.3	14.1
	30 min	55.7	51.7	35.2	16.4
KOH treatment	60 min	48.1	56.9	35.4	21.6
	180 min	47.1	56.7	34.1	22.6
	300 min	47.8	55.4	32.1	23.3
	1440 min	28.6	66.7	32.8	33.8

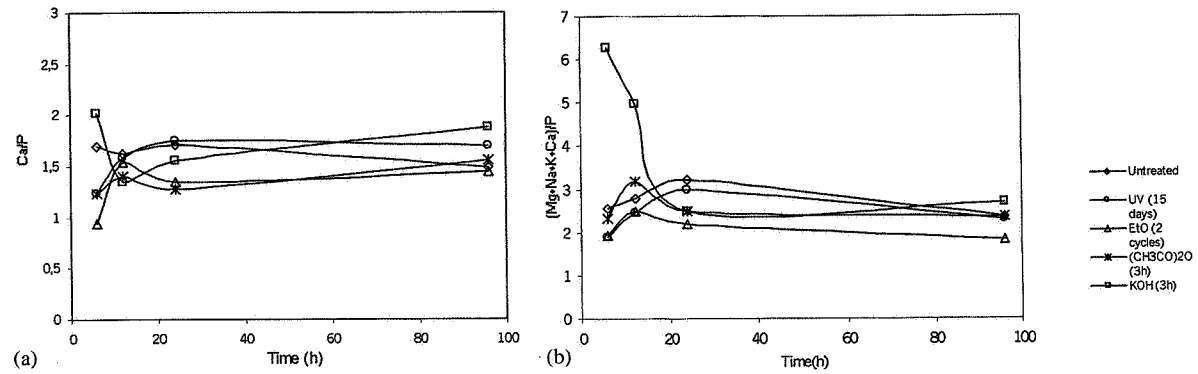

Figure 5 Evolution of the (a) Ca/P and (b) (Ca + Mg + Na + K)/P ratios of the apatites formed on the treated and non-treated SEVA-C substrates.

were very close to the value attributed to hydroxyapatite (1.67), which is the main mineral phase in human bone.

3.6. Coating adhesion

The adhesion of the biomimetic coatings to the different SEVA-C substrates was very good in the 37 to 47 MPa range. The presence of OH groups on the substrate seems to facilitate connection with the apatite layer. Similar results were obtained by other authors [25] studying polyvinyl alcohol (PVA) polymers. The water-uptake ability of PVA generated a higher adhesive strength of the Ca-P when compared with other polymeric substrates. In fact, it seems that a fairly strong bond could be formed between the polar groups of the polymer and the calcium ion of the apatite layer. Fig. 6 shows the preliminary results of a pull-off test, carried out in order to quantify the effect of u.v. radiation and KOH etching pretreatments on the adhesive strength of the Ca-P coatings to the substrates. These coatings were formed after 15 days of SBF immersion. In spite of the results scattering, it is possible to affirm that the adhesion of the biomimetic coating to the substrates pretreated with KOH was considerably enhanced. This treatment, besides diminishing the induction period for apatite nucleation, resulted in the formation of a thicker apatite coating with a higher adhesive strength.

4. Conclusions

The surface modifications performed on the SEVA-C substrates, before biomimetic coating, resulted in a faster formation of more Ca-P nuclei during the first stages of SBF immersion, particularly in the case of the KOH etching. With this treatment it was possible not only to reduce the induction period for the formation of a well defined apatite-like layer but also to improve the adhesion of the layer to the substrate. The Ca/P ratio of the calcium phosphates obtained in the biomimetic coatings, after 15 days of SBF immersion, were very

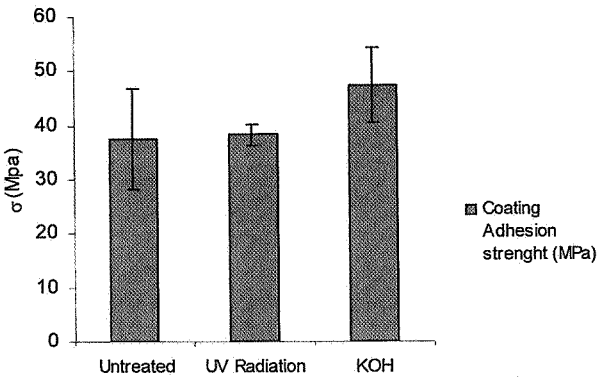

Figure 6 Adhesion strength of the Ca/P coatings nucleating on the surface of the treated and non-treated SEVA-C substrates.

close to the value attributed to hydroxyapatite. The production of biomimetic coatings prior to implantation, on biodegradable polymers, can allow for the development of bone-bonding starch-based biodegradable implants.

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