Surface and mechanical properties of a nanostructured citrate hydroxyapatite coating on pure titanium

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ABSTRACT

The presence of a biomimetic HAP coating on titanium surface, which reduces the structural stiffness, is essential to improve implants biocompatibility and osteointegration. In this study, new citrate-HAP (cHAP) coatings were produced by a simple hydrothermal method on pure titanium (Ti) surface, without requiring any additional pretreatment on this metal surface. The formed cHAP coatings consisting of nanorod-like hydroxyapatite particles, conferred nanoroughness and wettability able to endow improved biological responses. Indeed, the presence of citrate species in the precipitate medium seems to be responsible for controlling the morphology of the new coatings. The presence of citrate groups on the surface of cHAP coatings, identified by chemical composition analysis, due to their implication in bone metabolism can additionally bring an add-value for bone implant applications.

From a mechanical point of view, the Finite Element algorithm showing that cHAP coatings tend to decrease the mechanical stress at pure Ti, further favors these new coatings applicability.

Overall, the simple and expedite strategy used to developed new biomimetic coatings of citrate-HAP resulted in improved physicochemical, morphological and mechanical properties of Ti, which can endeavor improved implantable materials in bone healing surgical procedures.

1. Introduction

Titanium (Ti) and its alloys are widely used as metallic biomaterials in dental and orthopedic implants owing to their high strength-to-weight ratio, excellent biocompatibility, and corrosion resistance (Albrektsson et al., 2008; Geetha et al., 2009). Ideal implants should possess enhanced adhesion to human tissues and improved corrosion resistance, to prevent implant failure due to a lack of bioactivity and loosening (Xu et al., 2017). These properties can be enhanced by chemical modifications on the surface or by the deposition of bioactive coatings (Rodrigues et al., 2013; Sousa and Barbosa, 1993; Zhang et al., 2019).

To improve bone integration between implants and bone tissue, bioactive hydroxyapatite coatings have been produced by various deposition methods such as electrodeposition (Dinh et al., 2016), sol-gel coating (Wen et al., 2007; Xu et al., 2006), plasma spraying (Liu et al., 2004; Ong et al., 2004), laser deposition (Kurella and Dahotre, 2005; Kwaśniewski et al., 2015) and hydrothermal (Feng et al., 2016; Hamada et al., 2002; Kwaśniewski et al., 2015; Lorenzetti et al., 2014; Pazos et al., 2010; Suchanek et al., 2015; Yang et al., 2015). From these, the hydrothermal method (HT) stands out for its simplicity, by being relatively inexpensive, environment-friendly, and versatile enough to produce homogeneous coatings on complex-shaped substrates for biomedical applications (Ren et al., 2020; Suchanek et al., 2015). As such, hydrothermal methods have been preferentially used to produce HAP particles with tailored morphology for biomedical applications (Santos et al., 2012, 2015), particularly due to the possibility to obtain coatings with a chemical composition and crystallinity similar to that of mineral bone.

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tissues (Suchanek et al., 2015; Yang et al., 2015).

Indeed, the structural similarity of hydroxyapatite [HAP; Ca₅(PO₄)₂(OH)] with that of hard tissues, i.e. bone, makes of HAP the elected coating to accelerate bone growth around the implant, while offering the possibility of acting as a barrier to prevent the release of toxic Ti ions, which can possibly cause toxic and/or allergic effects (Ducheyne et al., 1984; Paoz et al., 2010; Rettig et al., 2017), as well as the formation of fibrous tissue between the implant and living bone. Not only the chemical composition of the surface will affect the biological response to the coatings, but as well the surface morphology, topography and wettability, which will additionally play an essential role in the mechanical performance of the biomaterial (Kokubo and Yamaguchi, 2016). Despite the increasing attention of HAP coatings produced by HT, the surface properties of these layers have received little attention, and the importance of surface properties on the mechanical performance has seldom been reported in the literature (Fathyunes et al., 2019; Fomin et al., 2017; Saber-Samandari et al., 2018). For instance, it was stated that HAP precipitated non-uniformly on unmodified titanium surface, with the formation of separated needle-like aggregates (Fujishiro et al., 1995). To overcome this problem, Suchanek et al. (2015) produced HAP coatings with HT, using a two-step approach: first, the Ti surface was treated with a mixture of acid solution, to increase the adhesion, and subsequently HT was performed. Feng et al. (2016) coated Ti substrate with HAP via a combined biomimetic/HT. The biomimetic mineralization was applied to provide a seeding layer, which was considered a prerequisite to facilitate the subsequent hydrothermal growth, while HT was used to promote the nucleation and growth of highly crystalline nano-prism-like HAP (Feng et al., 2016). In all the above-mentioned studies, EDTA (ethylenediamine tetraacetic acid) was used as a chelating agent. An interesting alternative chelating agent is citrate, which can contribute to tailoring the morphology of HAP nanoparticles (Santos et al., 2012, 2015), and due to its important key role, to favor bone metabolism (Hu et al., 2010; Ma et al., 2018). During the degradation of biomaterials, trapped citrates can enter into human mesenchymal stem cells via plasma membrane, leading to a osteogenic differentiation, and subsequently, to an increase in the production of bone-related extracellular matrix (Ma et al., 2019). Additionally to citrates, the presence of inorganic phosphate during biomaterials’ degradation can play a concerted role in regulating human mesenchymal stem cells energy metabolism, facilitating bone regeneration (Ma et al., 2019). Within this line of thought, the development of HAP coatings that can harbor citrate in their composition, will be of an undoubtedly value for Ti-based implant materials targeting bone applications, a research yet to be explored.

Finding the perfect balance between biological and mechanical properties is a challenge in the design of implants, which is of extreme importance for both orthopedic (Dohan Ehrenfest et al., 2010) and dental (Chiapasco et al., 2009) materials. The success of an implant strongly depends on an effective transmission of stresses and strains to the bone and surrounding tissues. The stress and strain distributions in an implanted material are influenced by several factors, such as bone-implant surface, quality and quantity of surrounding bone tissues, dimensions and geometry of the piece, as well as the type of loading exerted in the bone-implant segment (Bicudo et al., 2016).

Numerical models, particularly finite element (FE), are extensively used in medicine, and specifically in dentistry to simulate and predict the mechanical behavior of the implanted pieces (Bicudo et al., 2016; Huan et al., 2018; Rettig et al., 2017). While there is a large number of works on numerical modelling with emphasis on removal torque, extraction force, shear strength and cyclic behavior of implants (Bicudo et al., 2016; Rettig et al., 2017), the literature on bending tests is relatively scarce. Bones and implants along their lifetime are widely subjected to different types of loadings, including bending conditions (Xu et al., 2017).

As such, the present work studies the effect of the HT parameters on the surface properties and mechanical behavior of citrate-hydroxyapatite (cHAP) coatings, including the effect of coatings on strain and stress fields, which are evaluated through experimental bending tests and FE analysis.

2. Materials and methods

2.1. Materials

Commercially pure titanium (Ti) was supplied in the form of rods (CP-Ti, Goodfellow). Disks with a diameter of 16 mm were cut to specimens of 2 mm thickness. These Ti specimens were polished by using SiC abrasive papers of 800 and 1000 grit, after which the polished Ti was cleaned with water and acetone and immediately placed inside the autoclave.

2.2. Hydrothermal deposition of the coatings

For the hydrothermal (HT) synthesis, a 0.6 M solution of citric acid (C₆H₈O₇·H₂O, 99.5%) was prepared with distilled water. The pH of this solution was adjusted with ammonium solution (NH₄OH, 25%) until pH 8.0. Afterwards, 0.2 M solution of calcium nitrate ((Ca(NO₃)₂·4H₂O, 99%) and 0.2 M solution of ammonium hydrogen phosphate ((NH₄)₃HPO₄) were added. Finally, the solution was immediately put into a Teflon vessel. The polished Ti samples, were introduced in the solution and inserted in the autoclave. The sealed autoclave was set up to 180 °C for 3 h, 6 h or 24 h; according to the HT treatment samples were named as cHAP_3h, cHAP_6h or cHAP_24h, respectively.

2.3. Surface characterization of the coatings

Coatings thickness and morphology were examined using a scanning electron microscope (FE-SEM JEOL 7001F) equipped with energy-dispersive X-ray spectroscopy (EDX), which enabled to assess the chemical compositions of samples. Observation of the samples was performed at 20 kV.

Atomic force microscopy (AFM) analyses were performed using a Vecco™ DI CP-II AFM. The images were acquired in contact-mode, using a standard commercial Bruker silicon MP31 (CN = 0.9 N/m) tip. The roughness was evaluated by Ra, the arithmetic mean of the area between the roughness profile and its mean line, and calculated using the WSxM 5.0 Develop 4.0 software on areas of 5 × 5 μm².

To identify the functional groups, attenuated total reflectance (FTIR-ATR) spectra were acquired using a Nicolet (Thermo Electron) spectrometer. Coatings were placed on the ATR diamond crystal, and spectra were obtained in the range of 4000 to 500 cm⁻¹ resulting from an average of 128 scans collected with a resolution of 8 cm⁻¹.

The surface wettability of cHAP coatings was evaluated by measuring the static contact angles of water employing the sessile drop method. Images were acquired using a video camera (JAI CV-A50) attached to a microscope (Wild M32). The image acquisition and analyses were performed 30 s after the droplet deposition using the ADSA-P software (Axisymmetric Drop Shape Analysis-Profile). All measurements were done at room temperature.

Further chemical characterization of a cHAP coating was made by X-ray Photoelectron Spectroscopy, XPS using a XSAM800 dual anode spectrometer from Kratos and the Al Kα radiation (hν = 1486.6 eV) was selected. Spectrometer operation conditions, TOA, pressure and temperature of analysis were as described in Perreira et al. (2010). Spectra were collected with a step of 0.1 eV, using the software Vision 2 for Windows, Version 2.2.9 from KRATOS. Data processing was performed by using XPSpeak 4.1, with the curve fitting been made using by using Shirley backgrounds and Gaussian-Lorentzian curves. The shift due to charge accumulation was corrected using as reference the binding energy (BE) of aliphatic C 1s contamination set to 285 eV (Hantsche, 1993). Quantification was made with the corrected using the equipment library sensitivity factors (SF) of: 0.278 for C 1s, 0.78 for O 1s, 1.833 for Ca 2p, 2.001 for Ti 2p and for...
2.4. Mechanical characterization

To evaluate mechanical responses, experimental tests were conducted on bare Ti and on cHAP coated specimens. A finite element (FE) model was developed to assess stress, \( \sigma \) and strain, \( \varepsilon \) distributions, and then numerical and experimental results were compared. The stress \( \sigma_{VM} \) presented in the numerical simulations is the von Mises equivalent stress, which is computed using equation (1) and correlates the components (xyz) of the stress tensor with the uniaxial tension stress (Budynas et al., 2015).

\[
\sigma_{VM} = \sqrt{\left(\sigma_x - \sigma_y\right)^2 + \left(\sigma_y - \sigma_z\right)^2 + \left(\sigma_z - \sigma_x\right)^2 + 6\left(\tau_{xy}^2 + \tau_{yz}^2 + \tau_{xz}^2\right)}
\] (1)

Biaxial bending tests were often performed on the untreated and treated discs based on the procedure of ASTM F394-78, used for ceramic...
materials (Spazzin et al., 2016). The discs were centrally placed on a ring support with a 16 mm diameter and loaded axially with a cylindrical punch with a flat end and with a diameter of 1.9 mm (Fig. 1). Tests were conducted in an Instron 5566 device with a load cell of 10 kN. The punch advanced at a rate of 2.5 mm/min until reaching the maximum load of 50N. The load was determined for the specimen to remain in the linear elastic regime. Three specimens were tested: two were comprised of pure Ti, while the other one was coated with CHAP on its upper surface.

Strain measurements were performed in the center of each disk using 350 Ω strain gauges. The strain gauges were placed in a half-bridge configuration with a dummy strain gauge for temperature correction.

The FE model was developed in software Siemens NX, version 1859. The domain was comprised of a support, a disk specimen with or without a coating. Due to the existence of two symmetry planes, only one-quarter of the initial geometry was considered. The simplification of the geometry was followed by the enforcement of symmetry boundary conditions. The applied load was also reduced to 12.5N, since the maximum load of 50N that was applied to the entire geometry. Both the Ti disk specimen and the aluminium cylindrical support were modelled using quadratic hexahedral (CHEXA20) elements. The coating, on the other hand, due to its comparatively low thickness (0.1 μm), was modelled with cubic (CQUAD8) elements. The Young's modulus of the materials of the support (aluminium), disk (titanium) and coating (HAP) were taken, respectively as 70, 100 and 150 GPa, while the Poisson’s ratio value was assumed to be 0.3 (Ashby, 2017; Avila et al., 2018; Saber-Samandari and Gross, 2009; Zamiri and De, 2011). The values of the mechanical properties of the metallic materials, such as aluminium and titanium, which are well established and widely used materials, were obtained from the literature (Ashby, 2017; Avila et al., 2018). As hydroxyapatite is a newer material in comparison with the metals mentioned, its mechanical properties were found in adequate literature (Saber-Samandari and Gross, 2009; Zamiri and De, 2011).

3. Results and discussion

3.1. Characteristics of citrate-HAP coatings

The present study focused on the surface morphology, roughness, wettability and chemical composition of nanostructured citrate-hydroxyapatite (cHAP) coatings deposited on commercially pure Ti, without any surface pretreatment, using two different hydrothermal conditions.

Fig. 2a and b) shows SEM images of citrate-HAP surfaces after HT for 6 and 24 h. The development of uniform coatings with nanometric rods with well-defined geometry was visible in the top-view SEM images (Fig. 2 a-b).

The morphological differences were further assessed by the characterization of the surfaces’ topography by AFM (Fig. 2c and d). Scratches due to mechanical polishing were visible in both surfaces (Fig. 2c and d (small arrows)), suggesting that a relatively thin coating is formed. After 3h, small islands (Fig. S1a), and after 6h or 24h of HT, nanotopographical features could be observed, with the HAP nanoparticles grown on pure Ti (Fig. 2c and d). The size of the HAP particles varied from 50 to 100 nm in width and approximately 150 nm in length in all coatings (Fig. S1a, Fig. 2c and 2d), and an arithmetic average roughness (Ra) of 12.6 and 13.9 nm was depicted for cHAP_6h and cHAP_12h, respectively. As such, no relevant morphological differences were depicted on these cHAP coatings surface, and hence on the nanoparticles, formed along the HT time.

Considering that surface roughness and topography can severely affect surface wettability, the water contact angle of citrate-HAP coatings was determined (inset of Fig. 2c and d). While the uncoated Ti surface exhibited hydrophilicity (contact angle $\sim$65°; Fig. S1b), the presence of homogenous cHAP coatings resulted in lower contact angles, of $\sim$61° ± 8° and $\sim$55° ± 4° for cHAP_6h and cHAP_24h, respectively. Since the surface roughness was similar for both coatings with the HT time, this wettability result suggests that the chemical environment of the surface of these coatings maybe also similar.

To characterize the thickness of the HAP coatings, the cross-sectional micrographs of cHAP_6h and cHAP_24h were analyzed. Fig. 2e and f) allowed estimating thicknesses of approximately 0.25 and 1.0 μm, for cHAP_6h and cHAP_24h, respectively.

Overall, only the thickness of the coating increased with the HT time, with the morphology and roughness of the coatings being unaltered along the HT time, suggesting that the same nanostructures are the basis of these coatings formation.

The surface topography and roughness are well known to be essential factors in osteointegration and interface stability (Avcu et al., 2018). Surfaces with nanoroughness are reported to induce spontaneous cell differentiation and can modulate the response of osteoblast (Ferraris et al., 2016; Kerativitayanan et al., 2015), together with the general agreement that surfaces, specifically for bone regeneration applications, should have contact angles between 35 and 80° (Avcu et al., 2018), suggest that the newly developed cHAP coatings are suitable for bone regeneration applications.

The recognized presence of citrate species, essential in bone
metabolism (Hu et al., 2010; Ma et al., 2019), lead to the investigation of the presence of this compound on cHAP coatings. To assess the presence of organic bondings associated to of citrate species, FTIR-ATR was used (Fig. 3 a). The most intense bands in the range of 960–1100 cm⁻¹ observed on citrate-HAP coatings can be attributed to the asymmetric stretching vibration mode of phosphate groups. As expected, the intensity of these bands was similar along the HT time. Another visible and small band observed at 630 cm⁻¹ can be attributed to the bending mode of the OH groups of HAP. This is a band that can be assigned to crystalline hydroxyapatite (Costa-Rodrigues et al., 2014; Santos et al., 2017). The weak band with a maximum at 1570 cm⁻¹, observed in both citrate-HAP coatings, is reported to be associated with carboxylate groups (COO⁻), which result from the coordination of citrate species to the HAP surface (Santos et al., 2015). The presence of this band confirms the incorporation of citrate species in both cHAP coatings, anticipating an increase in biocompatibility that was easily achieved by the incorporation of this small organic molecule during HT. To the authors’ best knowledge, this is the first report of citrate species incorporated on calcium phosphate coatings on Ti.

To further characterize the cHAP coatings, X-ray spectroscopy (EDS) studies were performed. This analysis confirmed the presence of calcium (Ca), phosphorus (P) and oxygen (O) on both coatings where a homogenous distribution of Ca, P and O on the surface is clearly visible in Fig. 3 b). The atomic ratios of calcium to phosphorus (Ca/P) increased with the synthesis time, i.e., changed from 1.42 to 1.56, for HAP_6h and HAP_24h, respectively. The Ca/P molar ratios of the coating are lower than the Ca/P molar ratio of stoichiometric hydroxyapatite (Ca/P = 1.67) (Yu et al., 2019), which make of cHAP_6h and cHAP_24h non-stoichiometric HAP coatings. Deviations from stoichiometry occur when the apatite contains HPO₄²⁻ in place of PO₄³⁻, or when carboxylates replace phosphate groups (Yu et al., 2019). It is quite evident that both situations can occur since, phosphate could have been replaced by carboxylate groups from citrate, and phosphate anions could suffer hydroxylation during cHAP formation.

Fig. 4. XPS high resolution survey scan of (a) Ti 2p (b) C 1S (c), P 2p and (d) Ca 2p regions (dots) and respective fitting peaks (lines) of the cHAP_24h coating.

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Based on these data, and by knowing that citrate species are similar in both cHAP coatings (Fig. 3 a), one can suggest that by increasing the time of HT, hydroxylation of phosphate ions decreased (Fig. 3 a), making of cHAP_24h, the coating that better aligns to the chemical properties of bone.

To further explore the chemistry of the best coating, cHAP_24h, X-ray photoelectron spectroscopy (XPS) technique was used, where the relative species oxidation states of cHAP_24h coating formed on Ti could be depicted (Fig. 4). Fig. 4 a) shows the Ti 2p region displaying 3 doublets, with a spin-orbit split of 5.6 eV. The main components of each doublet are centered at 453.7 ± 0.1, 455.2 ± 0.1 and 458.1 ± 0.1 eV. The first and the third ones are, undoubtedly, assignable to Ti$^{0}$ and Ti$^{4+}$, respectively. The second one is a mixture of Ti$^{2+}$ and Ti$^{3+}$ (Naumkin et al., 2000). The main component of Ti 2p corresponds to Ti$^{4+}$, which can be related to a native TiO$_{2}$ layer. This is not surprising since the standard reduction potentials for the species Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$ to Ti$^{0}$ are, −1.63, −1.37, and −0.88 V, respectively. This data shows how thermodynamically favorable are the oxidations state of Ti to Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$.

In Fig. 4 b) the C 1s region is shown. The fitted peaks are centered at 285.0 eV (set as a reference for the charge shift estimation), 286.6 ± 0.1 and 288.7 ± 0.1 eV corresponding, respectively to C 1s photoelectrons from carbon bonded to other carbon and/or hydrogen atoms, carbon singly bonded to oxygen and carbon in a carboxylate/carboxylic group, these being related with the presence of citrate species on the surface of this coating, as previously suggested by FTIR-ATR for both cHAP coatings (Fig. 3 e).

The quantitative treatment of Ca 1s and P 2p spectra (Fig. 4c and d) allows to obtain an atomic ratio of Ca/P = 1.56, compatible with a nonstoichiometric hydroxyapatite, corroborating the Ca/P ratio obtained by the previous EDS analysis.

The functionalization of Ti surface and its alloys with a bioactive coating requires a two-step procedure (Feng et al., 2016; Kokubo and Yamaguchi, 2016; Suchanek et al., 2015). The first step, is typically associated with the formation of a TiO$_{2}$ layer on titanium surface to generate nucleation sites, followed by a second step, which usually involves incubation in simulated body fluid solutions or calcium phosphate rich solutions for the synthesis and growth of the apatite coating (Feng et al., 2016; Kokubo and Yamaguchi, 2016; Suchanek et al., 2015). Recently, K. Kapat and co-workers (Kapat et al., 2018) demonstrated the possibility to precipitate HAP on Ti6Al4V by a single step using HT procedure and an aqueous solution of sodium tripolyphosphate and calcium hydroxide. At an initial pH of 7.93, the authors (Kapat et al., 2018) were unable to precipitate HAP, just when reaching pH values close to 13 the precipitation of HAP occurred.

The pioneer work on citrate-HAP coating, using a low alkaline pH, can be related with the previous knowledge of free HAP nanoparticles precipitating in the presence of citrate species. The evidence provided by the literature, does not allow to draw definitive conclusions on the mechanism of citrate-hydroxyapatite coating formation; however, is quite evident that the presence of citrate as a chelating molecule, reduces the “free” calcium in the precipitant medium and helps to tailor the hydroxyapatite particles morphologies by selectively binding to specific crystallographic faces of the HAP (Santos et al., 2015).

<table>
<thead>
<tr>
<th>Specimen thickness (mm)</th>
<th>Ti</th>
<th>Ti with coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ - Exp.</td>
<td>26.3 $\times$ 10$^{-5}$</td>
<td>6.53 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$\varepsilon$ - Num. (min)</td>
<td>19.2 $\times$ 10$^{-5}$</td>
<td>2.67 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$\varepsilon$ - Num. (max)</td>
<td>100 $\times$ 10$^{-5}$</td>
<td>11.6 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>$\varepsilon$ - Num. (avg.)</td>
<td>37.6 $\times$ 10$^{-5}$</td>
<td>4.76 $\times$ 10$^{-5}$</td>
</tr>
</tbody>
</table>

Fig. 5. (a) Finite element model for the circular specimen, (b) numerical and experimental results for the tested specimens at maximum load (P = 50N).
Whatsoever, the presence of Ti, and consequently of a native TiO$_2$ film, will be a key factor contributing for this coating formation. There is a variety of surface reactions that can occur between the titanium oxide native films and citrate/calcium/phosphate solution during the coating formation. According to the literature at pH ~8, 50% of the hydroxy-related species at titanium oxide surface are neutral and the other 50% are negative (Textor et al., 2001). For that reason, a hydroxylation/hydration and formation of surface charge can occur, as well as the adsorption of cations and/or anions onto the surface, which can be hypothesized to promote and stabilize HAP nucleus towards the formation of a HAP layer.

According to the obtained results, and having in mind that the titanium oxide layer has negative species on its surface, in the first stage of HT process a competition between phosphate groups and citrate complexed with calcium (Ca-Citrate) for adsorption sites at the titanium oxide surface occurs. As phosphate ions or Ca-citrate accumulate, the surface charge changes. Along the coating formation, while the temperature is increasing, the stability of Ca-citrate complexes can change, leading to the release of the complexed calcium ions. This phenomenon will lead to the nucleation and growth of the citrate-HAP coatings.

In the context of biomaterials, the presence of citrate species can have a dual role in this system: one, in the control of the coating morphology, and another, to make the surface chemically closer to that of bone tissue (Hu et al., 2010).

Overall, our work confirms the formation and growth of citrate-HAP coatings on pure Ti, by a single step procedure, without requiring any additional pretreatment. The formation of such coatings occurred for short-time periods of HT (6h), with longer procedures (24h) resulting in thicker coatings. Despite the similar morphological features attained when varying the time of HT treatment, a Ca/P ratio closer to that of bone tissue was attained for longer HT procedures.

### 3.2. Mechanical properties of the HAP coatings

After the successful synthesis of citrate-HAP coatings on Ti, a step forward in the mechanical characterization of HAP was performed. Both experimental and numerical simulations were performed to evaluate the effect of the coating on the bending properties of Ti. Thus, it was verified if the numerical models follow the same trends as the experimental model with respect to the thickness and presence of coatings. Fig. 5 exhibits the developed FE model. The thickness of the coating was taken to be of 0.1 μm, in accordance with the values obtained in SEM observations, presented in Fig. 2e) and f).

In thin plate theory, the stresses and strains are inversely...
proportional to the cube of the thickness (Reddy, 2006). Even though in this case the used thicknesses were not low enough to apply thin plate theory, a non-linear relation was found between the stresses and strains with the specimen thicknesses, although not as pronounced as is verified in thin plates. Since the coated specimen has a thickness of 2.5 mm and the pure Ti(1) specimen has a thickness of 1 mm, the pure Ti(2) specimen, with a thickness of 2.74 mm, was tested and simulated as well.

After testing the disk specimens, the experimental and numerically computed strain values were compared. A rectangular patch was defined on the center of the disk with the same dimensions as the strain gauge. The maximum, minimum, and average strain values were computed in local averaging of values. The corresponding stress distribution is presented in Fig. 6a for the pure Ti specimen with a 2.74 mm thickness and in Fig. 6b and c for coated Ti and cHAP, respectively.

The presence of a coating over the Ti substrate provided a reduction in the stress in the substrate, as can be observed in Fig. 6b. For almost the same thickness of the substrate and the same applied load, the maximum von Mises stress $\sigma_{VM}$ at the center of the specimen, in pure Ti, is of 13.16 MPa. When a coating was present, the stress in the substrate decreased to 7.18 MPa, while the coating supported a much higher stress of $\sigma_{VM} = 33.33$ MPa. Thus, the cHAP coating enabled a reduction in stress of the substrate. The deformation, or strain, was not affected by the existence of the cHAP coating, exhibiting almost the same values for uncoated and coated Ti. The comparison of the stress fields of pure titanium (Fig. 6a) with the one of coated Ti (Fig. 6b and c) showed that a larger area is affected in the case of the uncoated sample. These findings indicate that the existence of a cHAP coating plays an important role in the stress distribution on the substrate, leading to lower stress transfer to the substrate. Similarly, Darwich et al. (Darwich et al., 2020) found a reduction in the stress of polycrystalline coated Ti–6Al–4V alloy pieces in comparison with the bare ones.

4. Conclusions

Nanostructured citrate-HAP coatings were successfully synthesized on pure titanium by the hydrothermal method in one step. The results suggest that the pure titanium exposed for 6 h to a calcium/citrate/phosphate solution showed remarkable citrate-HAP coating formation on its surface without any pre-treatment. The presence of citrates in the precipitate medium seems to be responsible for the attained cHAP coatings morphology.

A longer synthesis time was crucial for the development of a citrate-HAP coating with physicochemical characteristics closer to that of bone tissue.

Experimental and numerical simulations of bending tests indicated that the presence of the coating enabled a reduction of stress in pure titanium. The present results showed that it was possible to produce a nanostructured cHAP coating, with an improved biomimetic composition, without the loss of structural integrity. These findings demonstrate that cHAP coatings, easily synthesized by HT with the addition of citrate, have potential to improve the performance of Ti in dental and/or orthopedic implant applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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Appendix A. Supplementary data

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