Hydrophobic coatings for prevention of dental enamel erosion

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ABSTRACT

The protective effect of a hydrophobic surface against acid erosion was validated in the present work using octadecyltrichlorosilane (OTS) on hydroxyapatite films (HA) and on dental samples. The acid erosion was firstly evaluated on films made of HA and fluorapatite (HAF), and subsequently on films of HA coated by OTS. Our results have shown that the two first films were completely eroded during this evaluation and that no significant erosion was observed for the last film. Indeed, teeth coated with OTS showed no erosion at all after seven days of exposure to citric acid. The evaluation was based on QCM-D measurements, SEM images and water contact angle characterization. The results validate that a hydrophobic surface may be an effective tooth protector against acid erosion.

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1. Introduction

Hydrophobic surfaces are currently used as a protective barrier against acid exposure [1] essentially because materials with carbon–carbon and carbon–hydrogen bonds are naturally hydrophobic. The hydrophobic property is useful in several fields: such as textile, building construction, drug delivery and food [2–4], this property prevents water and gas microfiltration. Recently, this was used to protect the root canal using octadecyltrichlorosilane (OTS) [5].

A hydrophobic surface may also be useful in preventing dental erosion, which is the loss of dental hard tissue (enamel). This erosion is basically due to an acid attack which may be extrinsic or intrinsic in origin. Intrinsic erosion may be caused by gastric acid regurgitation or consequential medical or psychological problems (e.g. acid reflux, anorexia and bulimia) [6]. While extrinsic erosion may occur by exposure to acidic foods and drinks such as orange juice which contain citric acid and carbonated drinks that contain citric and phosphoric acids, or even wine whose pH is between 3.0 and 3.8 [7]. As a consequence, tooth structures undergo demineralization and remineralization processes, the teeth are "defending themselves" via a constant process of demineralization and remineralization through the ion exchange capacity with a surrounding of saliva which transfers inorganic salts

[8]. However, an increase in exposure to acid can surpass the natural protection capacity of the mouth, which initially results in erosion and then a carious cavity.

Tooth enamel is the hardest substance in the body of mammals, composed of calcium hydroxyapatite $Ca_{10}(PO_4)_6 (OH)_2$, 94%; 3–5% water and 1–2% organic material [9]. Hydroxyapatite begins to demineralize naturally below pH 5.5, so it is necessary to avoid reaching that pH, or alternatively, to make hydroxyapatite more resistant to acid dissolution. Once erosion has begun, there is no method that enables the regeneration of tooth structure; among other reasons, because the ameloblasts secreting tooth enamel disappear before teeth sprout. Several strategies have been utilized to prevent dental erosion including increasing saliva secretion, recommending diets rich in calcium, using laser irradiation to improve the resistance of enamel, and promoting strong teeth by fluoride exposure.

It is common knowledge that fluorides (NaF, Na_2PO_3F, NH_4HF_2, SnF_2, $Sn[ZrF_6]$) have an extraordinary ability to combine with hydroxyapatite, replace the hydroxyl ions (OH^-) and transform into fluorapatite (HAF), $Ca_{10}(PO_4)_6F_2$ [10]. Fluorapatite crystals have a high chemical stability, are less soluble in acid than HA (fluorapatite dissolves at pH lower than 4.5) and have an effect on the metabolism of bacterial plaque that prevents biofilm formation and partially inhibits acid production from the bacterial plaque [11,12]. Consequently, HAF is an excellent option to protect teeth against corrosion. Interestingly, fluorine at low concentration prevents tooth loss, while an excess produces diseases: prolonged intake (moderate or excessive) of fluorine for 30 or 40 years may cause

fluorosis (chronic intoxication), which although mainly affecting teeth and bony tissue and can also affect to a lesser extent the nervous system [13–16].

The main goal of the present work is to evaluate the protective effect of a hydrophobic surface against dental acid erosion. In this context we measured adsorption in situ of OTS on HA and acid erosion of OTS. Since fluoridation is the most widely used method to protect against dental acid erosion, fluorine adsorption on HA and acid erosion of fluorapatite were evaluated. The results presented below, HA coated with OTS showed no significant acid erosion, while the HA and FHA were completely eroded. These tests were also evaluated on teeth "in vitro", demonstrating the effectiveness of a hydrophobic surface as protection for dental enamel erosion.

2. Materials and methods

2.1. Materials

Diammonium hydrogen phosphate >98% (Sigma-Aldrich), calcium nitrate >99% (Sigma-Aldrich), ethanol >99.5% (Sigma-Aldrich), hydrogen peroxide 30% (Sigma-Aldrich), ammonium hydroxide 28–30% (Sigma-Aldrich), hydrochloric acid 36.5–38% (Sigma-Aldrich), buffer solution pH 4.0, 7.0, and 10.0 (Fluka), sodium fluoride >99% (Sigma-Aldrich), ethylenediaminetetraacetic acid (EDTA) >99% (J.T. Baker), sodium hypochlorite (J.T. Baker), sodium azide solution at concentration of >0.1% (Sigma-Aldrich), octadecyltrichlorosilane (OTS) >90% (Sigma-Aldrich), chloroform >99.5% (Sigma-Aldrich), hexadecane 99% (Sigma-Aldrich), citric acid ≥99.5% (Sigma-Aldrich), Milli-Q quality distilled water. All reagents were used without further purification.

2.2. Hydroxyapatite and fluorapatite synthesis

Hydroxyapatite was prepared by a homogeneous precipitation method using double decomposition to obtain Ca/P molar ratio 10:6 (~1.67) [17–19]. A solution of ammonium phosphate $(NH_4)_2HPO_4$ 1.5 M and a solution of calcium nitrate $Ca(NO_3)_2$ $4H_2O$ 2.5 M were prepared separately and then $(NH_4)_2HPO_4$ solution was added drop by drop $Ca(NO_3)_2 \cdot 4H_2O$ solution under stirring conditions. A solution of ammonium hydroxide (NH_4OH) was added to improve gelation and the subsequent formation of an apatite structure. The initial pH value of 3 was therefore adjusted to 9 while mixing [20]. We assume that the chemical reaction that takes place in the synthesis of HA was:

$$10Ca(NO_3)_2 \cdot 4H_2O + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 43H_2O.$$
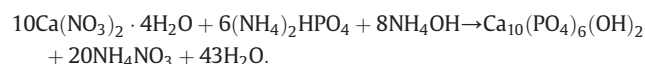
The resulting precipitate was filtered and washed several times with distilled water until the supernatant reached a neutral pH. The final suspension was intermittently stirred at room temperature for 7 days at 25 °C. Finally the material obtained was dried at 80 °C, annealed at 800 °C for 2 h and crushed with an agate mortar.

Fluorapatite was obtained by the adsorption of fluoride ions on HA. The adsorption process was carried out for 24 h, using NaF solutions previously prepared and stored in PVC bottles to prevent contamination by the dissolution of silicates and fluoride ion adsorption on glass. These solutions were prepared at different concentrations of ion fluoride ($[F^-]$ = 19, 38, 57, 76 and 95 ppm) in deionized water as solvent. HCl or NH_4OH was used to adjust the acidity to pH = 9 before the adsorption process.

2.3. Electrodeposition (EDP) of hydroxyapatite on gold sensors

The gold sensor (Q-Sense) surface was cleaned by immersion in 5:1:1 mixture of Milli-Q quality distilled water and, H_2O_2 (30%) and NH_3 (25%) for 10 min at 70 °C, then washed with deionized water and dried with nitrogen gas. The cleaning procedure was completed by 10 min UV/ozone irradiation. The layer of HA was deposited by means of electrodeposition (EDP) using the gold QCM sensor as cathode and applying 70 V/cm^2 DC voltage for 60 min. The electrolyte was 1% (w/V) of HA suspension in ethanol. The ultrasonic treatment (28 kHz, 100 W) for 1 min in ethanol was conducted to remove the surplus HA from the deposited layer on the cathode, thereby obtaining an HA sensor [21]. Subsequently, the HA sensor was immersed into an OTS solution prepared at different concentrations (1, 3, 6, 10, 23 and 35 mM) with chloroform and hexadecane (volume ratio 4:1) as solvent and stored under vacuum. Another HA sensor was immersed into a fluor solution, previously prepared to obtain fluorapatite.

2.4. Atomic Force Microscope (AFM) analysis

Atomic Force Microscope (Bruker, Dimension Edge) was used to evaluate the morphology and surface roughness of the HA electrodeposited on the gold QCM sensor. AFM images were obtained operating in tapping mode, the measurements were performed using a cantilever and tip (Model SCM-PIT) at a scan rate of 0.3 Hz, and a scan size of 3 μm × 3 μm. The root mean square (R_{rms}) of the surface roughness was calculated from the roughness profiles.

2.5. Static water contact angle measurement

The effect of HA electrodeposition on a gold QCM sensor and the gold QCM sensor after OTS adsorption were evaluated for water affinity with the water contact angle. The contact angle was measured by placing 10 μl of distilled water on the surface of the substrates and measured at room temperature using a goniometer (RAMÉ-HART, model 100-00-115, serial number 2017), images and angle were processed with DROPimage standard software.

2.6. fourier transform infrared spectroscopy (FTIR) analysis

FTIR was used to identify functional groups, especially the presence of OH^-, F^- and PO_4^{3-}. Infrared spectroscopy analysis was performed using a spectrometer Nicolet Nexus 470 FTIR (Nicolet, Madison, WI, USA). The interferograms, covering a spectral range of 4000–525 cm^{-1} at a resolution of 2 cm^{-1} with 80 scans, were collected at room temperature. The processing and analysis of the spectra band regions were performed with the OMNIC E.S.P.5.1 software (Nicolet).

2.7. Scanning electron microscopy (SEM) characterization

The surface morphology of samples was characterized using a scanning electron microscope (JEOL JSM-820). In order to quantify the chemical composition of samples, energy-dispersive X-ray spectroscopy (EDS) mode in SEM was used to carry out an elemental analysis.

2.8. Monitoring fluor and OTS adsorption on HA and acid erosion

QCM-D microbalance (Q-Sense E1) was employed to study OTS and fluor adsorption on HA, and to evaluate acid erosion. OTS and HA adsorption on HA was carried out for all solutions ([OTS] = 1, 3, 6, 10, 23 and 35 mM) and ($[F^-]$ = 19, 38, 57, 76 and 95 ppm) previously prepared. Acid erosion of previously electrodeposited HA was evaluated with exposure of citric acid solution (pH = 4.3). Erosion was concluded when no further change was detected in the sensor. This process was repeated for HAF and HA coated by OTS. All solutions were injected into the QCM-D chamber at a flow rate of 15 μL · min^{-1}. The resonance frequency (Δf) and dissipation (ΔD) were detected simultaneously driving the QCM quartz crystal at a fundamental frequency (f_0) of 5 MHz and 25 °C.