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Hydroxyapatite deposition study through polymeric process on commercially pure Ti surfaces modified by laser beam irradiation

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Abstract Many techniques have been used to coat metallic substrate with bioceramics. The aim of this study was to study the physical-chemical characteristics of polyvinylidene fluoride (α-PVDF)/hydroxyapatite (HA) composite coating, obtained by casting method, on commercially pure titanium (α-CP Ti) substrate surface modified by laser beam irradiation. The preparation of coating was done for mixing α-PVDF pellets shape dissolved in dimethylacetamide (DMA) with HA/DMA emulsion. The mixture was poured onto the α-CP Ti sample and left to dry in an oven. CP Ti plates were coated with α-PVDF/HA composite film, in proportions of 100/00 and 60/40 in weight, and characterized by particle size analysis, scanning electron microscopy, energy dispersive spectroscopy (EDS), X-ray diffractometry, thickness measurement and contact angle. Uniform coating with a small thickness variation along the coated surface was successfully obtained.

Introduction

Commercially pure titanium (CP Ti) and its alloys have been widely used as materials for dental and biomedical applications, owing to their excellent mechanical properties and biocompatibility [1]. There are, however, various problems related to metallic materials implantation in the human body due to corrosion, wear, and/or negative tissue reaction. Almost all metallic implants are encapsulated by dense fibrous tissue which prevents proper distribution of stresses and may cause loosening of the implant. Therefore, hydroxyapatite (HA) ceramic has been applied on CP Ti and Ti-alloys implants to increase the corrosion resistance, gain better biocompatibility and provide implant-bone tissue biological adhesion [2].

Many HA deposition techniques are described in literature, such as ion sputtering, plasma spray, sol–gel, electroless, biomimetic processes, and among others. Good human body acceptance is achieved by these methods, however, they present poor coatings quality with morphological variations and unsuitable uniformity (clusters and cracks formation). Another problem is related to the Ti/HA interface, which is directly affected by the difference of thermal expansion coefficient, interfering in the deposited layer adhesion [2–9].

In special, the polyvinylidene fluoride (PVDF) polymer has been widely employed in several applications because of its recognized good ferroelectric properties and biocompatibility and also due to be the cheapest among fluorided polymers. As an example, PVDF composites and copolymers with ceramics (PZT, $BaTiO_3$, and $CaCO_3$) have great technological interesting because of their versatility in the attainment of thin and flexible films [10–12]. In addition, laser beam irradiation has been demonstrated as a useful tool for surface modifying Ti CP in order to improve its surface roughness and specific area [13].

Therefore, the aim and the innovative character of this study was to study the possibility to coat α-CP Ti modified by laser beam irradiation utilizing the α-PVDF/HA

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composite. Since previous study has reported, by cytotoxicity assay (in vitro biocompatibility testing) and mechanical testing, that α-PVDF polymer and α-PVDF/HA composite exhibit biocompatibility and suitable mechanical properties to be used as biomaterials in medical and dental applications [14]. The investigated method here appears as an alternative for Ti implants surface modification by HA deposition.

Materials and methods

Preparation of Ti-PVDF/HA composites: casting method

The Ti-PVDF/HA composites were prepared by casting method. PVDF pellets' shape was dissolved in dimethylacetamide (DMA) in a 50-mL glass beaker under continuous agitation and a controlled temperature of 100 °C. A HA/DMA emulsion was then prepared by agitation without heating in another 50 mL glass beaker. After complete dissolution of PVDF, the HA/DMA emulsion was added, maintaining the temperature and agitation until the mixture attained the necessary viscosity, at which point it was poured onto a 60-mm glass Petri dish that contained the α-CP Ti sample (dimension: $15 \times 15 \times 2$ mm^3), which was completely submerged in the solution. The mixture was then oven-dried at 110 °C for 4 h to eliminate the DMA solvent. By this method, it was possible to obtain α-CP Ti plates coated on one side only with α-PVDF/HA composite film in proportions of 100/00 and 60/40 in weight.

In regard to the preparation of composites, it is necessary to make some observations: (i) details about procedures and conditions of α-CP Ti superficial laser beam irradiation can be verified in refs. [13, 15]; (ii) previous study showed that the maximum HA incorporated in PVDF polymeric matrix is about 40% [14]. In this study, we opted to use the proportions of 100/00 and 60/40 in weight in order to study α-PVDF polymer and α-PVDF/HA composite (maximum HA concentration) deposition on α-CP Ti modified by laser beam irradiation; (iii) oven-dried temperature and time were also based on previous study, where FTIR-ATR-spectroscopic analysis showed that this condition (100 °C and 4 h) is optimum to completely eliminate the DMA solvent [12].

Particle size analysis of the used HA

Particle size of the used HA was analyzed by a laser diffraction particle size analyzer (Mastersizer S/S-MAM 5005/Malvern) in order to compare the HA particles size with the pores size of PVDF polymer.

Scanning electron microscopy

The superficial morphology of Ti-PVDF/HA composite samples was analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) X-ray (LEO 440i). Samples were covered with a thin gold film under argon atmosphere, by sputtering process (Polaron SC7620 Sputter Coater), in order to make them conductive. The microscope was set at 10 kV and 100 ρA; the images were magnified 500 and 4000 times.

Energy dispersive spectroscopy

To analyze the chemical elements composition, the Ti-PVDF/HA samples were exposed to EDS X-ray of the largest possible surface area to obtain the most general representative spectrum for each sample.

X-ray diffractometry

Crystalline phases structure identification of Ti-PVDF/HA composite samples was obtained by X-ray diffractometry (XRD). Powder X-ray data were collected in the 2θ interval from 10 to 70°, in 5 s 0.01° steps, using a SIEMENS D5000 diffractometer with copper radiation monochromatized by a graphite crystal. The diffractometer was set at 40 kV and 30 mA.

Thickness measurement

The thickness of formed and adhered PVDF/HA composite film on the CP Ti plates surface was investigated by a Mitutoyo micrometer (0–25 mm, precision of 0.01 mm). Measurements were carried out on three points of each sample: central region and edges; the results correspond to the average of 24 measurements for each Ti-PVDF/HA composition.

Contact angle

Distilled water contact angle measurements were carried out on Ti-PVDF/HA composites surface by half-angle$^{\text{TM}}$ measuring method (sessile drop method), using a contact angle meter (TANTEC Cam-micro goniometer). The method is allowed to obtain direct measurement of the contact angle (θ); arbitrary tangent line errors are eliminated. This technique measures the half-θ angle, however, the device is graduated as $2 \times \theta$ and the contact angle measurement is direct [16].

The contact angle measurements were taken at room temperature in 75% relative air humidity, since the θ varies only slightly with temperature, according to Adam [17], who found no detectable variations in the water in several solid hydrocarbonates in an interval of 20–35 °C. To establish the balance of the forces involved, the contact angle reading was obtained 20 s after deposition of the drop on the surface of the samples. Each θ value corresponds to the average of four measurements, with a maximum deviation of ±2. The measurements were carried out on two samples surface of each Ti-PVDF/HA composition.

Results and discussion

Particle size analysis of the used HA

Figure 1 shows one of the distribution curves obtained by particle size analysis of the used HA. The values correspond to the average of five measurements. As it can be observed, the average diameter of particles is 10.64 μm under 28 vol.%. There is also a considerable amount of smaller particles than the average diameter, for instance, 25 vol.% is consisted of 5 μm particles size.

Scanning electron microscopy

Figure 2 shows SEM images of the morphology of PVDF and PVDF/HA-60/40 coatings. Note the PVDF polymer with a globular structure and porous regions between the globes, which average pores size is 12 ± 8 μm in diameter. In comparison with HA particles size (previous item), the used HA has a particle size amount smaller (>10.64 μm) than pores size of the polymeric matrix, the polymer porous spaces then can be filled by HA phase. Thus, the PVDF/HA-60/40 composite presents HA wrapped in the globules and homogeneously filling the inner part of the original porous spaces of the pure PVDF.

According to Sheldon [18], the filler phase (in this case HA) of a polymeric composite can act as a crystal-nucleating agent (or, in rare cases, as an anti-nucleant), affecting the size or the perfection of the polymer crystal. The presence of HA to the PVDF matrix appears to modify the polymer grain formation process, altering the size and morphology of the pores.

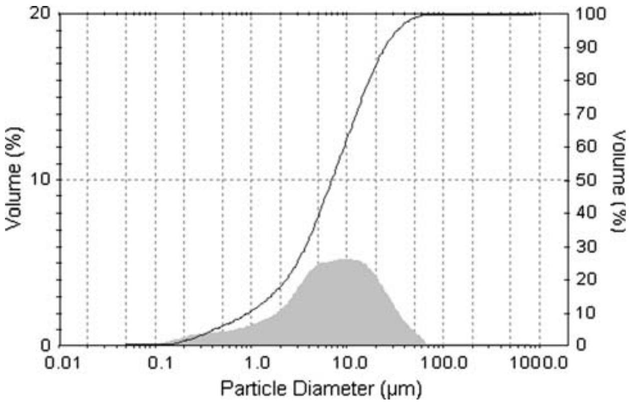

Fig. 1 Particle size distribution curve of the used HA

Energy dispersive spectroscopy

The EDS X-ray spectra in Fig. 3 show the main chemical elements of the PVDF and PVDF/HA-60/40 coatings. These elements were identified as carbon and fluorine originating from the PVDF structure, and as calcium (Ca) and phosphorus (P) originating from the incorporated HA.

A semi-quantitative ratio of the chemical elements can be calculated based on their peak intensities in the spectrum. According to Park [19], the Ca/P ratio of HA is usually 1.67, a slightly different ratio of 1.54 is observed in our study. This difference may indicate a chemical reaction between HA and PVDF during the synthesis. This issue can be clarified by X-ray diffraction and/or Fourier transform infrared techniques.

X-ray diffractometry

The successful incorporation of HA in the PVDF matrix was confirmed by XRD. Figure 4 shows the X-ray diffractograms: (a) Ti-PVDF/HA-60/40, (b) Ti-PVDF, and (c) pure HA. The crystalline phases were identified according to X-ray power diffraction patterns (PDF file) [20]: (d) PVDF, (e) Ti, and (f) HA.

According to Lovinger [21], PVDF presents Bragg peak positions at 2θ equal to 20, 27, and 40°. As the diffractogram in Fig. 4b demonstrates the XRD of Ti-PVDF sample presented characteristic diffraction patterns of Ti and PVDF, indicating that the polymer coating was successfully formed. A comparison of the HA diffraction patterns in Fig. 4f and the XRD of Ti-PVDF/HA-60/40 in Fig. 4a led us to conclude that the HA was incorporated in the PVDF. The PVDF diffraction patterns remain unchanged after the matrix was impregnated with HA, indicating that the PVDF polymeric structure was not modified during the synthesis of the composites.

Figure 4e shows the main Ti Bragg peak at 2θ equal to 40.22° and it is observed in Fig. 4a (Ti-PVDF/HA-60/40) and Fig. 4b (Ti-PVDF), such results are in according to Braga et al. [13]. The X-ray beam can reach the substrate, despite it is coated with polymeric composite film. Then, the Bragg peak detected by XRD technique is originating from CP Ti surface.

Thickness measurement

The thickness measurement results showed the PVDF polymer formed a coating on CP Ti surface of 0.07 ± 0.01 mm and the PVDF/HA-60/40 composite of

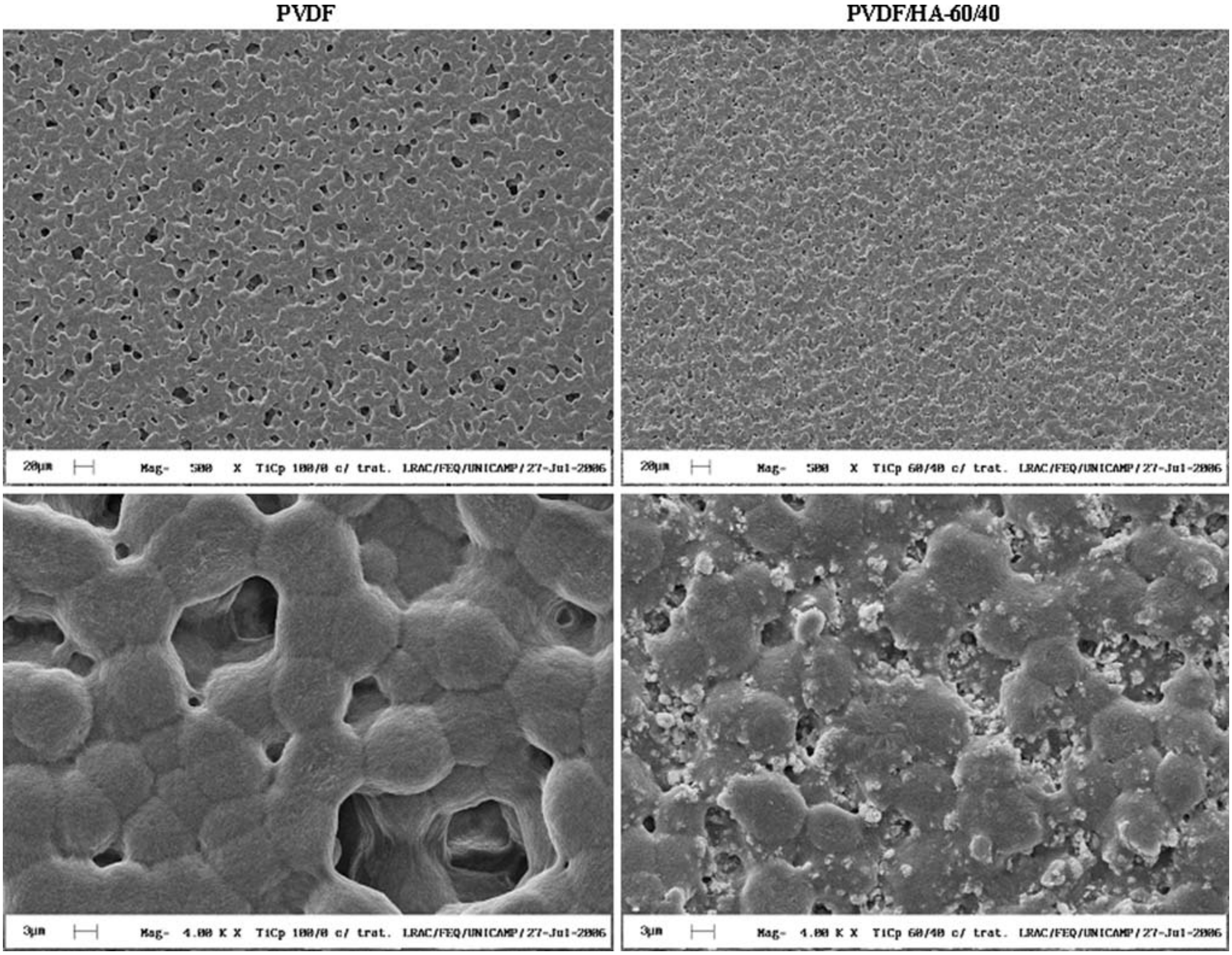

Fig. 2 SEM images of the PVDF and PVDF/HA coatings structure

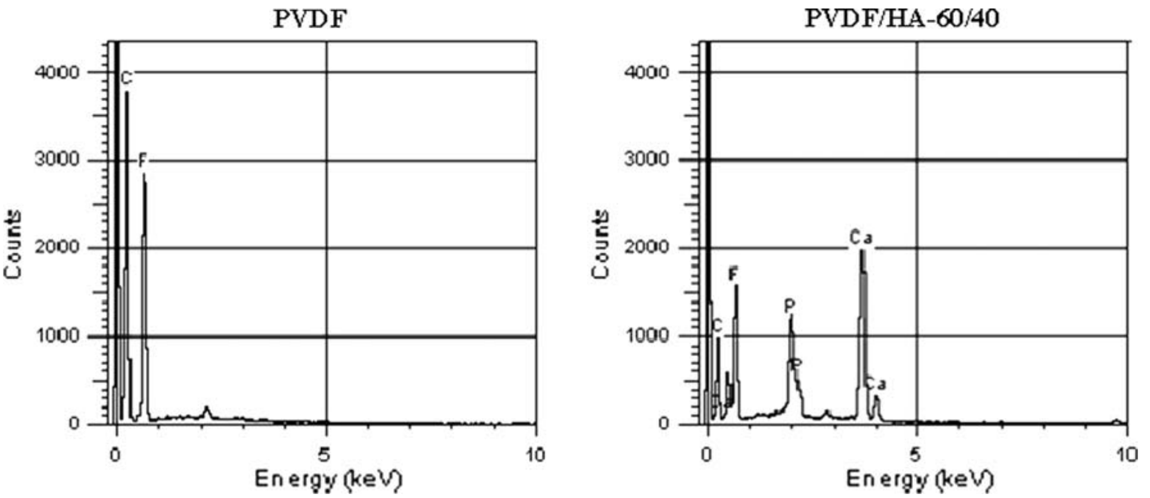

Fig. 3 EDS X-ray spectra of the PVDF and PVDF/HA coatings

0.12 ± 0.02 mm. This thickness difference could have occurred due to the mass variation of each material used in the composite composition; the mineral load causes a swelling in the polymer pores. However, the used method provided a uniform coating with a little thickness variation along the coated surface.

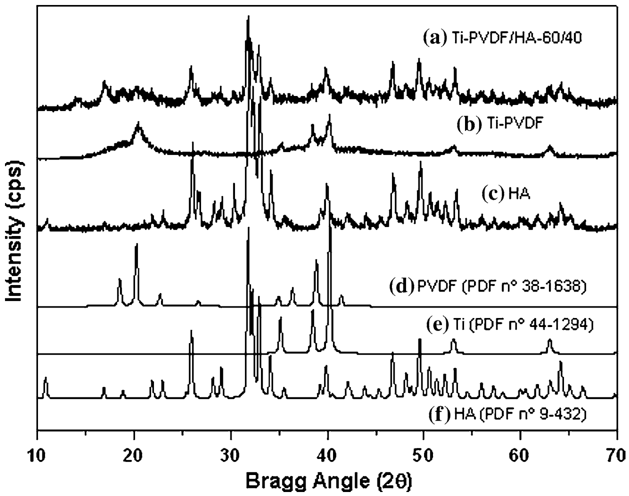

Fig. 4 X-ray diffractograms of the samples: (a) PVDF/HA-60/40 coating, (b) PVDF coating, and (c) pure HA. XRD patterns of the phases: (d) PVDF, (e) Ti, and (f) HA

Contact angle

Contact angle (θ) equal to 0° is an extreme situation of chemical affinity between surface and liquid and, therefore, the liquid material spreads completely on the solid surface. Contact angle equal to 180° is another extreme situation, where the liquid material presents no interaction with the solid surface. When θ is lower than 90° it is considered the surface is wet by liquid [22].

Table 1 shows the θ values and their respective standard deviations, using distillate water as a measuring liquid, of the Ti-PVDF and Ti-PVDF/HA-60/40 surfaces. It is observed that θ is practically the same for both compositions, since the device deviation is ±2°.

Previous study showed that θ of α-PVDF/HA composite films tended to increase with addition of increasing concentrations of HA in the polymeric matrix. However, in the compositions containing proportions of more than 60/40 the contact angle underwent a strong reduction due to saturation of the polymeric matrix by the mineral load, which caused the appearance of HA in the form of powder on the surface of the PVDF/HA films, increasing the wettability of material [14].

Table 1 Contact angle values (θ) of the Ti-PVDF and Ti-PVDF/HA-60/40 surfaces and their respective standard deviations

Composite	Contact angle (θ)				
	M_1 (°)	M_2 (°)	M_3 (°)	M_4 (°)	Average (°)
Ti-PVDF	98	98	99	98	98 ± 0.5
Ti-PVDF/HA-60/40	100	100	100	100	100 ± 0

M measurement

Conclusions

According to SEM, EDS, and XRD results, the used method is satisfactory to gain PVDF/HA composite coatings because it was observed that the bioceramic incorporation was homogeneous, the pores of polymeric matrix were filled and PVDF crystalline structure was not modified by incorporated HA.

The used method provided a uniform coating with a small thickness variation along the coated surface.

Contact angle data showed the hydrophobic characteristic of polymer predominated in the composite. This characteristic may represent an obstacle to the application of material in bone implants, since it is known that the greater the material's wettability the better its interaction with the body's tissues and liquids. However, a definitive conclusion concerning this property can only be reached by means of in vivo tests, which we plan to carry out in future studies.

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