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Adhesion strength characterization of PVDF/HA coating on cp Ti surface modified by laser beam irradiation

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ABSTRACT

Up to the moment, there is no standardized test for measuring the adhesion strength of polymeric coatings on titanium substrate modified by laser beam irradiation. The present work aimed to assess the adhesion strength of polyvinylidene fluoride (α-PVDF)/hydroxyapatite (HA) composite coating on commercially pure titanium (α-cp Ti) substrate surface modified by laser beam irradiation, using the three-point bending test. The preparation of coating was carried out by mixing α-PVDF pellets 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. Commercially pure titanium plates were coated with α-PVDF/HA composite film, in proportions of 100/00 (PVDF) and 60/40 (PVDF/HA) in weight. The Ti-PVDF/HA samples were subjected to the three-point bending test and analyzed by scanning electron microscopy. According to the results, PVDF and PVDF/HA coatings showed a good adhesion strength on α-cp Ti surface, since no detachment was observed.

1. Introduction

Commercially pure titanium (cp Ti) and its alloys are considered ideal as metallic biomaterials because they have shown better acceptability by human tissues than other metals under diverse circumstance [1]. In orthopedic and dental implantology, novel tools and techniques have been used to improve the regeneration of bone tissue. Numerous attempts have been made to enhance the osteoconductivity of titanium prostheses, including modifications in their surface properties and coating with calcium phosphate layers, for example, hydroxyapatite (HA) [2,3].

Many hydroxyapatite deposition techniques are described in the literature, such as ion sputtering, plasma spray, sol–gel, electroless, biomimetic processes and others. The coatings obtained by these methods exhibit good human body acceptance, however, they present poor 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. High interfacial coating/substrate adherence is required to avoid the implant failure [2–10].

Coating adhesion is considered a difficult subject which still needs to be deeply studied, since up to the moment there is no standardized test for measuring the adhesion strength of polymeric coatings on titanium substrate modified by laser beam irradiation. Further, the results depend upon the type of test used and, in general, they do not allow true adhesion quantification. An alternative method is the three-point bending test, where the coating is submitted to a complex stress state of tensile and compressive stresses, as illustrated in Fig. 1, and the adhesion strength is measured indirectly.

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 amongst fluorided polymers. As an example, PVDF composites and copolymers with ceramics (PZT, $BaTiO_3$, $CaCO_3$) are versatile in the attainment of thin and flexible films which make them technologically interesting [11–14]. In addition, laser beam irradiation has been demonstrated as a useful tool for modifying cp Ti surface in order to improve its surface roughness and specific area [15], contributing to a suitable coating physical adhesion.

Therefore, the present work aimed to assess the adhesion strength of α-PVDF/HA composite coating on α-cp Ti surface modified by laser beam irradiation, using the three-point bending test. Previous study has reported the suitable mechanical properties and biocompatibility of α-PVDF polymer and α-PVDF/HA composite for

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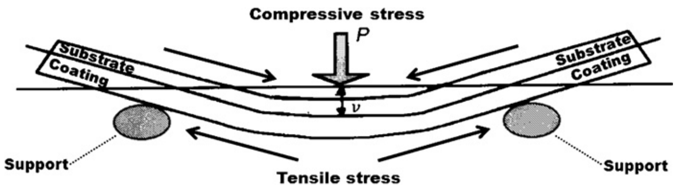

Fig. 1. Schematic illustration of the three-point bending test.

medical and dental applications [16]. Further, the applied method here has been shown to be an alternative for Ti implants surface modification by HA deposition [17].

2. Experimental details

Details about the preparation of Ti-PVDF/HA composites, including procedures and conditions of titanium superficial laser beam irradiation and the chosen α-PVDF/HA proportions in weight, have been reported in previous work, which indicated that the maximum HA amount incorporated in PVDF polymeric matrix is 40% in weight [17]. Thus, based on previous results, in the present study α-cp Ti plates (dimension: 25 mm × 5 mm × 2 mm) were used, which were modified by laser beam irradiation and coated with α-PVDF/HA composite film in proportions of 100/00 (PVDF) and 60/40 (PVDF/HA) in weight. For α-PVDF/HA composite film formation, the immersed samples in α-PVDF/HA emulsion were air-dried for 4 h in an oven set at 110 °C.

The adhesion strengths of PVDF and PVDF/HA composite coatings, with 0.07 ± 0.01 mm and 0.12 ± 0.02 mm in thickness, respectively, formed on titanium surface, were assessed by the three-point bending test. The maximum stress within elastic regime for cp Ti is approximately 500 MPa, above this value the material undergoes permanent deformation [18,19]. As an implant must not work under plastic regime condition, the three-point bending test for Ti-PVDF/HA samples was performed under elastic regime condition, applying a maximum force of 300 N, which generated a stress of 460 MPa. Such situation can be considered adequate, since no implant type will reach this state of stress.

The samples were also subjected to the three-point bending test under plastic regime condition, that is, with permanent deformation of metallic substrate. For this assay, no specific maximum force was established, which test criterion was the plastic deformation of material without rupturing it. Then, the maximum force recorded for each sample was different, however, with proximate values.

For the three-point bending test with 300 N maximum applied force, elastic regime condition, 7 cp Ti samples coated with PVDF polymer and 7 cp Ti samples coated with PVDF/HA composite were used. For the test under plastic regime condition, only one sample of each composition was utilized. In both test conditions, the assays were performed with force application speed of 0.5 mm/min in a MTS 810 universal testing machine.

After the three-point bending test, the surface analysis of PVDF/HA coatings by scanning electron microscopy (SEM) is important, since it desires to study the deformation effect on the metal-coating set. The analyses were performed in a high vacuum scanning electron microscope (LEO 440i). The 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, 100 pA and work distance of 25 mm; the images were recorded with 4000 times magnification in the force application region, where the samples underwent the maximum deflection, and also in the extremity region, where the samples were supported.

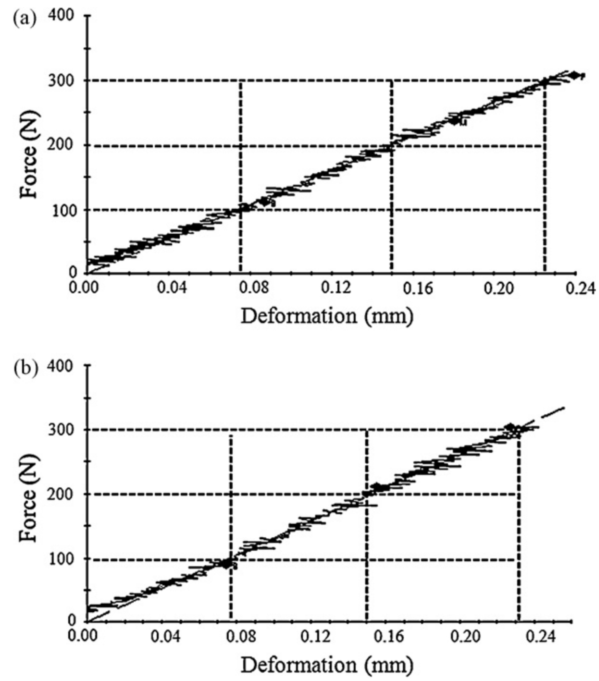

Fig. 2. Force–deformation curves of the three-point bending test with 300 N maximum applied force: (a) Ti-PVDF and (b) Ti-PVDF/HA.

3. Results and discussion

Fig. 2a and b presents the force–deformation curves of cp Ti samples coated with PVDF polymer and PVDF/HA composite, respectively, which three-point bending tests were performed with 300 N maximum applied force. Fig. 2 shows only one curve for each composition as illustration, since the assays were performed under elastic regime condition and the resulting curves did not show any significant variation. By drawing lines on the

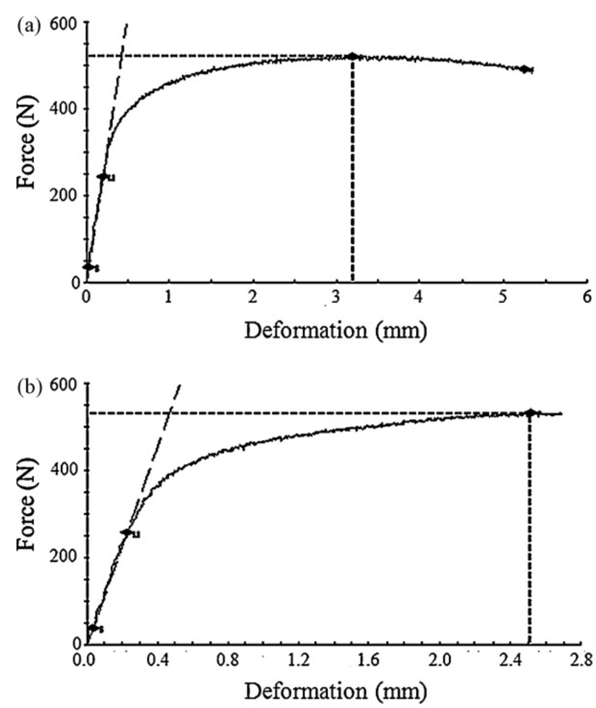

Fig. 3. Force–deformation curves of the three-point bending test under plastic regime condition: (a) Ti-PVDF and (b) Ti-PVDF/HA.

Table 1
Average results of the three-point bending test performed with 300 N maximum applied force, obtained for 7 samples of each Ti-PVDF/HA composition.

Sample	Maximum applied force (N)	Maximum applied stress (MPa)	Deformation (mm)
Ti-PVDF	306.6 ± 2.2	459.8 ± 3.4	~0.23
Ti-PVDF/HA	306.1 ± 2.7	459.2 ± 4.1	~0.23

Table 2
Results of the three-point bending test performed under plastic regime condition, obtained for one sample of each Ti-PVDF/HA composition.

Sample	Maximum applied force (N)	Maximum applied stress (MPa)	Deformation (mm)
Ti-PVDF	522	784	~3.2
Ti-PVDF/HA	534	800	~2.5

respective curves, it was observed that the deformation varied proportionally with the applied force variation for both Ti-PVDF/HA compositions. In addition, the linearity of curves confirmed the elastic behavior of Ti substrate. Table 1 shows the average values obtained for all samples, which maximum applied force generated a stress of approximately 460 MPa on the material, causing a deformation around ~0.23 mm. These parameters suggest that PVDF and PVDF/HA coatings were subjected to a tensile stress around 460 MPa.

Fig. 3a and b shows the force–deformation curve of only one sample of each Ti-PVDF/HA composition tested under plastic regime condition. In Fig. 3, it was observed that Ti-PVDF (Fig. 3a) and Ti-PVDF/HA (Fig. 3b) curves demonstrated similar behavior with a good linearity in the elastic region and plastic deformation above 333 N, which indicates suitable mechanical properties for biomedical applications [18,19]. Since only one sample was used in the assays, the average results were not possible to be determined. However, Table 2 presents the data obtained for each sample tested. As no specific maximum force was established for this test condition, the maximum applied force recorded for Ti-PVDF sample was 522 N, which generated a maximum applied stress of 784 MPa on the material, causing a deformation around 3.2 mm. For Ti-PVDF/HA sample, it was recorded a maximum applied force of 534 N with generated maximum stress of 800 MPa and a deformation of approximately 2.5 mm. Such results suggest that PVDF coating was subjected to a tensile stress of 784 MPa, while PVDF/HA coating to 800 MPa tensile stress. In addition, PVDF/HA-coated Ti substrate revealed to be more mechanically resistant than PVDF-coated Ti substrate, since Ti-PVDF/HA sample underwent lower deformation than Ti-PVDF sample.

Macrographic images of Ti-PVDF and Ti-PVDF/HA samples before and after the three-point bending test under elastic and plastic regime conditions are shown in Fig. 4. From Fig. 4b, c, e and f, it was observed that PVDF and PVDF/HA coatings were subjected to a tensile stress and kept adhered on the metallic surface in both test conditions. However, the PVDF/HA coating (Fig. 4f) presented cracks in one of the edges in the region with higher deformation, owing to the hydroxyapatite to make the PVDF film more brittle with lower mechanical strength and flexibility [15]. Further, in Fig. 4c and f, it was noted coating removal in the extremity areas, where the samples were supported.

SEM images of Ti-PVDF and Ti-PVDF/HA samples before and after the three-point bending test under elastic and plastic regime conditions are shown in Fig. 5. The globular structure of PVDF polymer with porous regions between the globes is noted in Fig. 5a. PVDF/HA composite, Fig. 5d, showed the HA phase partially filling the original porous spaces of pure PVDF. After testing with 300 N maximum applied force, Fig. 5b and e, it was observed that both PVDF and PVD/HA coatings underwent a slight deformation in the globular structure of polymeric matrix, however, the pore shape and size practically had no modification. In Fig. 5c, after testing under plastic regime condition with large PVDF-coated Ti substrate deformation, it was observed that the globular structure of PVDF coating underwent an intense elongation which led to a pore shape and size modification. From Fig. 5f, it can be seen that PVDF/HA coating presented cracking after testing under plastic regime condition although PVDF/HA-coated Ti substrate underwent a lower deformation, as shown in Fig. 4f. Moreover, it was not possible to note the globular structure of polymeric matrix, due to the high hydroxyapatite concentration in the analyzed area.

Fig. 6 presents the SEM images of the extremity region, where Ti-PVDF and Ti-PVDF/HA samples were supported. The images were

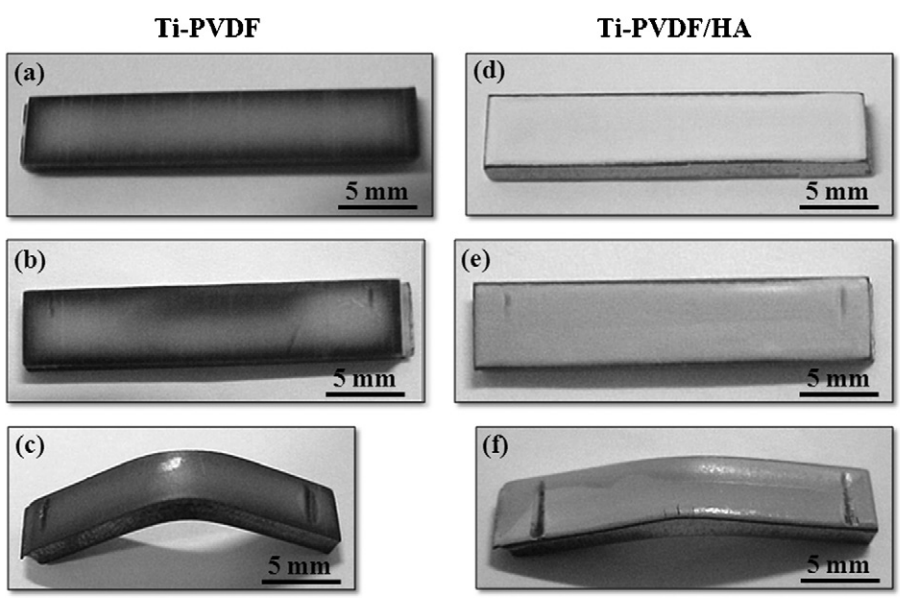

Fig. 4. Macrographic images of the samples before and after the three-point bending test: (a) Ti-PVDF sample before testing, (b) Ti-PVDF sample after testing with 300 N maximum applied force, (c) Ti-PVDF sample after testing under plastic regime condition, (d) Ti-PVDF/HA sample before testing, (e) Ti-PVDF/HA sample after testing with 300 N maximum applied force, (f) Ti-PVDF/HA sample after testing under plastic regime condition.

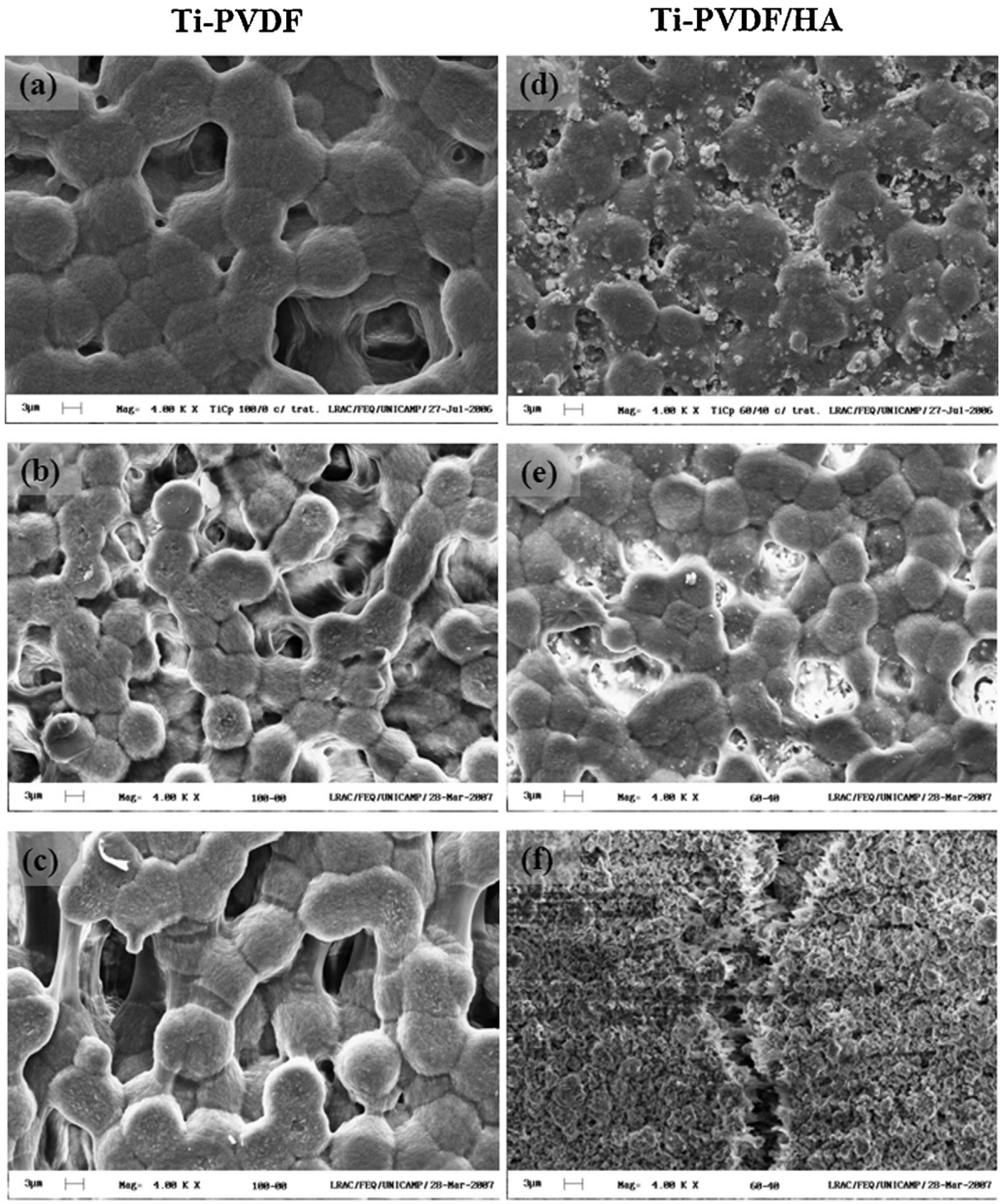

Fig. 5. SEM images with 4000 times magnification of the samples before and after the three-point bending test: (a) Ti-PVDF sample before testing, (b) Ti-PVDF sample after testing with 300 N maximum applied force, (c) Ti-PVDF sample after testing under plastic regime condition, (d) Ti-PVDF/HA sample before testing, (e) Ti-PVDF/HA sample after testing with 300 N maximum applied force, (f) Ti-PVDF/HA sample after testing under plastic regime condition.

recorded with 4000 times magnification after three-point bending test under elastic and plastic regime conditions. In Fig. 6a and c, it was observed that PVDF and PVDF/HA coatings were crushed after testing with 300 N maximum applied force and there was no detachment of the coatings from cp Ti surface. For samples tested under plastic regime condition, Fig. 6b and d, it was noted that PVDF and PVDF/HA coatings were practically pulled out from metallic surface, as shown in Fig. 4c and f.

After analyses we concluded that PVDF and PVDF/HA coatings showed good physical adhesion on cp Ti surface modified by laser beam irradiation, since under the maximum stresses studied in this work, only PVDF/HA coating presented cracks under 800 MPa maximum applied stress, without detaching from cp Ti surface. In addition, the three-point bending test revealed to be an alternative method capable of measuring indirectly the adhesion strength of polymeric coatings on metallic substrates.

In spite of the good obtained results, physical–chemical, mechanical and adhesion properties of PVDF/HA coating with different proportions in weight on Ti substrate will be studied, in order to analyze the changes in such properties with HA amount variation in the polymeric matrix and, if necessary, establish a more suitable PVDF/HA proportion.

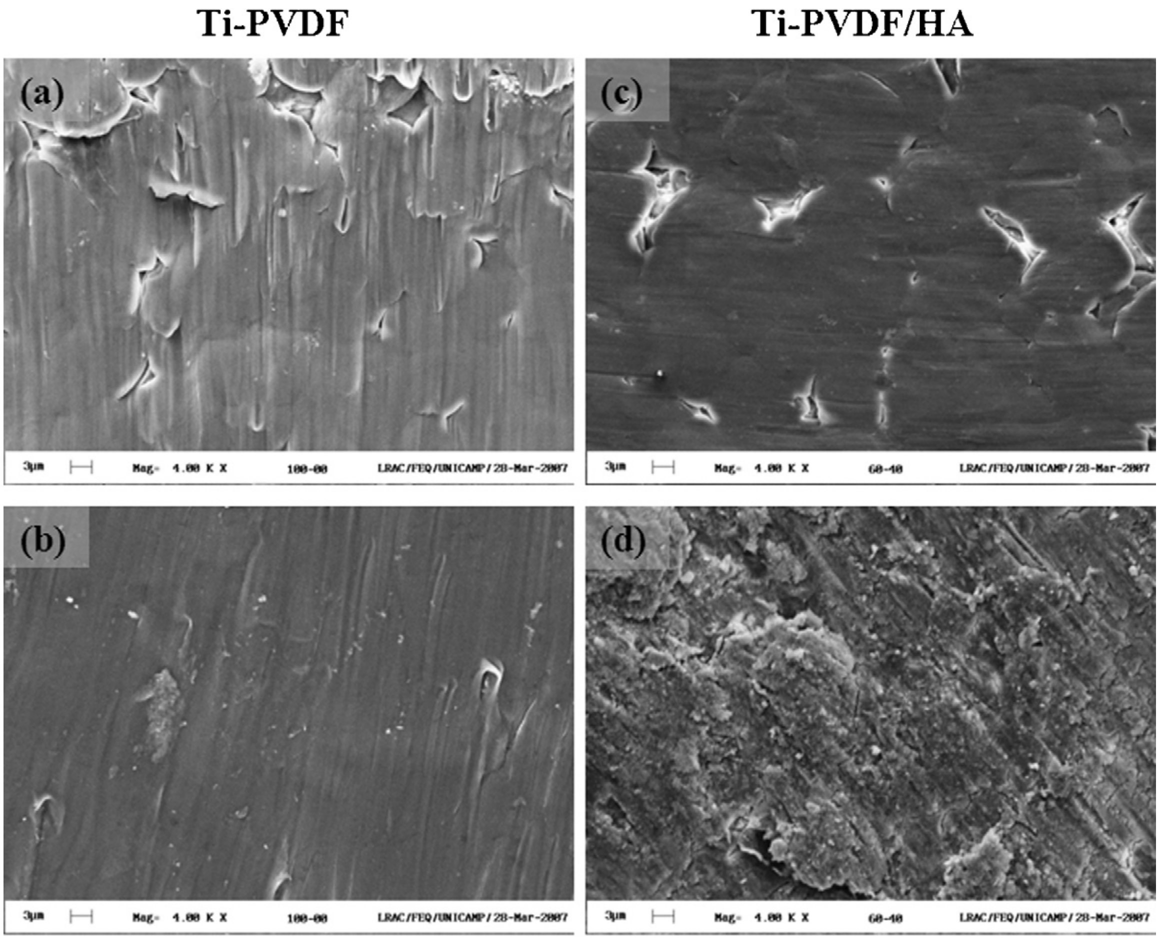

Fig. 6. SEM images with 4000 times magnification of the extremity region, where the samples were supported, after the three-point bending test: (a) Ti-PVDF sample after testing with 300 N maximum applied force, (b) Ti-PVDF sample after testing under plastic regime condition, (c) Ti-PVDF/HA sample after testing with 300 N maximum applied force, (d) Ti-PVDF/HA sample after testing under plastic regime condition.

4. Conclusions

Based on the obtained results, Ti-PVDF and Ti-PVDF/HA samples showed a good response to the tests, demonstrating suitable mechanical properties for biomedical applications. Under maximum applied force of 300 N, PVDF and PVDF/HA coatings were subjected to a tensile stress of approximately 460 MPa. For samples tested under plastic regime condition, PVDF coating was subjected to a tensile stress of approximately 784 MPa and PVDF/HA coating to 800 MPa. Although PVDF/HA coating has shown cracks under plastic regime condition, PVDF and PVDF/HA coatings presented good adhesion strength on cp Ti surface modified by laser beam irradiation, since no detachment was observed in both test conditions studied in the present work.

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