

Alternative Biomedical Materials for Prosthetics: Ti-6Al-7Nb and Nylon 6

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Received: July 18th, 2017

Accepted: September 18th, 2017

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ABSTRACT

This research deals with the study and characterization of two materials with different chemical nature, a metallic alloy (Ti-6Al-7Nb) and an FDM 3D-printed thermoplastic polymer (Nylon 6), applying techniques such as metallographic analysis, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction for the titanium alloy; and Fourier transform infrared spectroscopy and differential scanning calorimetry for the analysis of the Nylon polymer. Among the most relevant results for the titanium alloy stands the presence of two phases in the crystal structure: a primary phase α immersed in a duplex matrix ($\alpha+\beta$), with a lower fraction of β crystals. The X-ray analysis showed the existence of Ti and TiO in the sample. For the polymeric sample, it was possible to identify the basic structure with infrared analysis, confirming that the sample is from a Nylon 6 filament. Also, the calorimetric analysis made possible the identification and comparison of the melting temperature for both raw and processed samples.

RESUMEN

Esta investigación trata con el estudio y caracterización de dos materiales con diferente naturaleza química, una aleación metálica (Ti-6Al-7Nb) y un polímero termoplástico impreso en 3D por FDM (Nylon 6), aplicando técnicas como análisis metalográfico, microscopía electrónica de barrido, espectroscopía de energía dispersiva y difracción de rayos-X para la aleación de titanio; y espectroscopía infrarroja por transformada de Fourier y calorimetría diferencial de barrido para el análisis del polímero Nylon. Entre los resultados más relevantes para la aleación de titanio alloy, se encuentra la presencia de dos fases en la estructura cristalina: una fase primaria α inmersa en una matriz duplex ($\alpha+\beta$), con una fracción menor de cristales de β . El análisis de rayos-X mostró la existencia de Ti y TiO en la muestra. Para la muestra polimérica, fue posible identificar la estructura básica con el análisis infrarrojo, confirmando que la muestra proviene de un filamento de Nylon 6. Adicionalmente, el análisis calorimétrico hizo posible la identificación y comparación de la temperatura de fusión tanto para la muestra virgen como para la procesada.

Keywords:

Titanium alloy, Nylon, Characterization, SEM, XRD, FTIR, DSC.

Palabras clave:

Aleación de Titanio, Nylon, caracterización, SEM, XRD, FTIR, DSC.

1. Introduction

Ti-6Al-7Nb is a relatively new titanium alloy. The mechanical properties of Ti-6Al-7Nb alloy are very similar to Ti-6Al-4V alloy, which has been used as a biomaterial for many years. The major difference between the alloys is the replacement of Vanadium with Niobium [1]. This is because Vanadium is released as cytotoxic ions with time, while Niobium ions do not exhibit this behavior, and in turn are considered as vital for cellular functions [2].

Based on the phase analysis by metallography, scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and other material characterization techniques such as X-ray diffraction (XRD), it is possible to identify structures and crystalline compounds in metallic alloys [3].

In addition, ASTM E 92-82 standard [4] defines the Vickers microhardness test as an indentation method, in which, by the use of a calibrated machine with a pyramidal square based indenter, a predetermined load is applied against the material test surface. The measure of the resulting size of the indentation after removing the load, is proportional to the resistance of the material to plastic deformation. The Vickers microhardness test can provide a correlation of the atomic structure with the mechanical properties [4].

The polyamides were the first engineering thermoplastics produced specifically by design as a plastic, and are the largest family in both production volume and number of applications [5].

Fused Deposition Modeling (FDM) 3D printing technology has been used for prototyping and end-use products and parts, applying high performance thermoplastics [6]. Nylon is one of most used polymers for FDM technology, presenting a low cost custom design alternative. Materials characterization techniques such as Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) can be performed to detect if the thermoplastic polymer properties are affected by temperature during 3D printing.

The purpose of this study is to document the characterization of new materials that could be used to manufacture prosthetics by additive manufac-

turing techniques, in order to aid in creating design criteria to make process optimization decisions in the future application of these technologies.

2. Experimental Procedure

The characterization study of titanium alloy Ti-6Al-7Nb and the polymer Nylon 6 were performed by different techniques. The diagram in Fig. 1 shows the experimental strategy of this study.

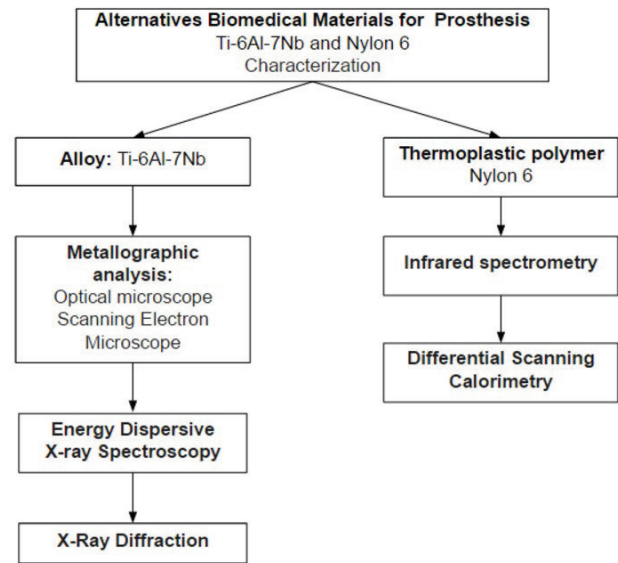


Fig.1. Experimental Strategy.

2.1 Metallic alloy sample: Ti-6Al-7Nb

The sample preparation for the metallographic analysis was performed at the Center for Materials Research and Extension (CIEMTEC, School of Materials Science and Engineering, Costa Rica Institute of Technology). Samples were mounted on thermoplastic resin and polished using SiC paper. Buffing was carried out with 1 μm particle size alumina suspension to a mirror-like surface, and finally chemical etching was performed to reveal microstructures for observation under the optical microscope. The chemical solution for etching was: 11% HF_(ac), 59% C₃H₆O_{3(ac)}, 24.6% H₂SO_{4(ac)}, 3.6% C₂H₆OS_(ac) and 1.8% C₃H₈O₃.

A Mitutoyo HM-101 hardness tester located in the Center for Materials Research and Extension (CIEMTEC, School of Materials Science and Engi-

neering, Costa Rica Institute of Technology) was used to measure the Vickers microhardness. The load of 200 g was applied for 15 s. A total of 10 measurements were carried out on the surface of the as-polished sample.

The grain size and phase characteristics of the alloy were also analyzed in a Hitachi TM-1000 scanning electron microscope (Institutional Microscopy Laboratory, Costa Rica Institute of Technology). The SEM was operated with an electron acceleration voltage of 15 KV. Also, the EDS spectrometer was used to analyze the concentration of the elements present in the alloy. The XRD analysis was performed with the PANalytical Empyrean X-ray diffractometer located in the Center for Materials Research and Extension (CIEMTEC, School of Materials Science and Engineering, Costa Rica Institute of Technology). A copper target with $\lambda = 1.54 \text{ \AA}$ $K\alpha_1$ radiation was used, using a voltage of 45.0 KV and current of 40.0 mA. A divergence slit of $\frac{1}{2}^\circ$ and anti-scatter slit of 1° were used, respectively. The sample was scanned with the goniometer range of $2\theta = 30^\circ\text{-}80^\circ$.

2.2 Thermoplastic polymer sample: Nylon 6

For the FTIR spectroscopy, a section of Nylon filament was cut and placed in the ATR holder of a Nicolet 6700 FTIR spectrometer located at the National Nanotechnology Laboratory (LANOTEC-CeNAT). HR Hummel Polymer and Additives Library was used to identify the polymer structure.

The thermal analysis was performed with the DSC equipment TA Q200 located at the National Nanotechnology Laboratory (LANOTEC-CeNAT), with a heat only calibration method, on a range from 100 to 250 °C. The temperature accuracy was of ± 0.1 °C. The initial sample weight was 4.5 mg with air as the sample reference. The samples for the DSC analysis were extracted from a Nylon filament (raw material) and from a 3D printed part with the same material (processed material).

3. Results and Discussion

3.1 Ti-6Al-7Nb

Optical Microscopy and SEM

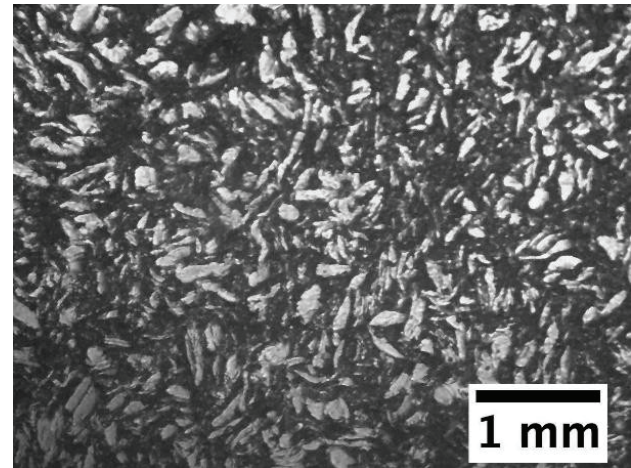


Fig. 2. Metallography of Ti-6Al-7Nb: Optical Micrograph 400x.

Fig. 2 shows the microstructure of Ti-6Al-7Nb; which reveals the presence of two phases. As it is known, the duplex type structure ($\alpha+\beta$) is characteristic for this alloy composition [1]. The dark contrast corresponds to an $\alpha+\beta$ matrix and the bright grains correspond to the primary alpha phase (α). The α phase has a hexagonal close-packed crystal structure (HCP), while the β phase exhibits a crystalline arrangement in the body centered cubic (BCC) structure [7].

Fig. 3 shows a SEM image from a region within the one shown in Fig. 2. It shows the matrix phases ($\alpha+\beta$) in higher magnification, with the β particles in bright contrast, surrounding the α component of the matrix. The primary α grains have darker contrast but with different hues (some darker than others), this is due to the different orientations of the crystals. These areas are rich in aluminum (Al), because the Al stabilizes the alpha phase. Additionally, the grains of the β phase which are immersed in the matrix are rich in niobium (Nb) because Nb stabilizes the beta phase [7].

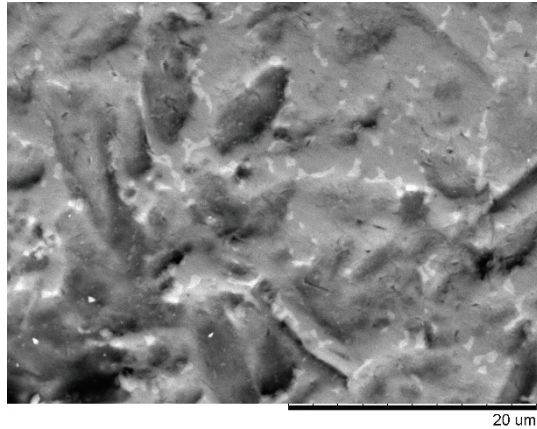


Fig. 3. Metallography of Ti-6Al-7Nb: SEM image 4000x.

Energy Dispersive Spectroscopy analysis

EDS was used to determine the chemical composition from the phases shown in the image of Fig. 3. The results in Fig. 4 show that two characteristic elements (Ti and Al) from the alloy Ti-6Al-7Nb were detected. The larger mass percentage corresponds to Ti since it is the main component. However, since EDS detects the chemical composition in the near surface, some other elements were detected, mainly C and O, and are included in the calculation of the total fraction. Thus, the fraction of Ti is much lower than expected. Nonetheless the ratio of Al to Ti is consistent with the alloy composition. C is detected from the conductive tape that holds the sample in the instrument, as well as from surface contamination, so it can be neglected from the composition of the alloy itself.

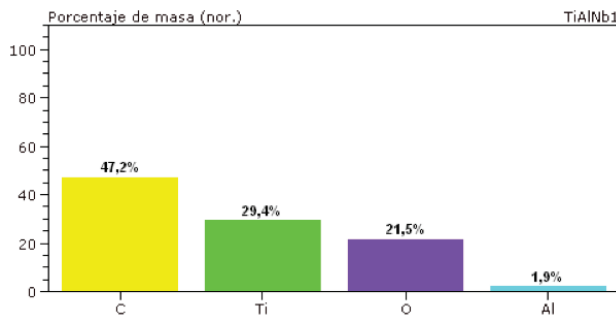


Fig. 4. Chemical composition of Ti-6Al-7Nb (mass percentage) obtained from EDS analysis

In the case of O, the high fraction is possibly due to the titanium oxides than are generated in the surface, which gives Ti its high corrosion resistance, as it acts as a passivation layer [7]. Since Nb is only

present in the fine β phase, it was difficult to detect by EDS due to the small size of the particles, as shown in Fig. 3.

XRD analysis

The diffraction pattern of the Ti-6Al-7Nb sample shown in Fig. 5 confirmed the presence of the hexagonal compact crystalline structure of α -Ti phase, which has three main peaks (in order of intensity) at $2\theta = 40.416^\circ$ (101 plane) $2\theta = 38.439^\circ$ (002 plane) and $2\theta = 63.204^\circ$ (110 plane). All other peaks corresponding to α -Ti are shown in Fig. 5 with their respective Miller indices $2\theta = 35.308^\circ$ (100), $2\theta = 53.212^\circ$ (102), $2\theta = 70.785^\circ$ (103), $2\theta = 76.084^\circ$ (112). As mentioned in the previous section, Ti-6Al-7Nb presents two phases ($\alpha+\beta$); however, the diffraction pattern corresponding to the β peaks overlap with the peaks of the α phase, so it cannot be isolated by XRD. The positions corresponding to the β phase are indicated in Fig. 5. In addition, characteristic diffraction peaks of titanium oxide (TiO), with monoclinic crystal structure were detected, with the three main peaks in order of intensity $2\theta = 42.694^\circ$ (121), $2\theta = 40.486^\circ$ (400) and $2\theta = 63.464^\circ$ (511). TiO presence was expected because the passivation layer is present in the surface of the sample, and is consistent with the high O content detected by EDS.

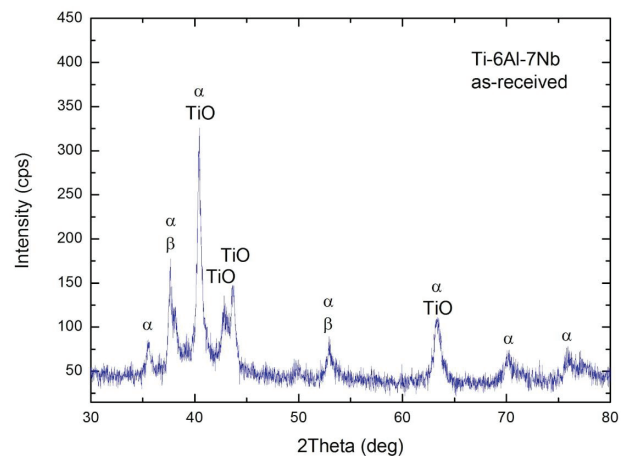


Fig. 5. Ti-6Al-7Nb XRD profile

Vickers Hardness Test

Table 1 shows results of the microhardness measurements carried out in different regions of the sample. The average hardness value is ~ 292 HV,

which is consistent with the reported value in the literature of 270-290 HV for the wrought Ti-6Al-7Nb [7]. Additionally, variations in the magnitudes of microhardness are observed, which accounts for a standard deviation of ~ 10 HV. This is due to the presence of two phases, whereby, some indentations include higher proportion of either primary or ($\alpha+\beta$) phase.

Table 1. Vickers microhardness measurements of Ti-6Al-7Nb

Measurement	HV (± 0.1)
1	297.6
2	296.0
3	286.2
4	283.0
5	287.8
6	306.2
7	279.9
8	299.3
9	304.5
10	279.9
Average	292.04
Standard deviation	9.91

3.2 Nylon 6

FTIR Spectroscopy

The FTIR spectroscopy analysis allowed to identify the basic structures present in the chemical configuration of Nylon 6, and to carry out a correlation with the structures of the HR Hummel Polymer and Additives database. The FTIR spectrum of the sample analyzed is represented in Fig. 7, and the similarity correlation is shown in Fig. 8. The vibrational frequencies represented in the spectrometry result, gave information to confirm the basic molecular structure of Nylon 6, and therefore confirm the polymer provided by the supplier of the

filament. Characteristic bands of C (O) NH appear around 3296, 1634 and 1540 cm^{-1} in the spectrum [8].

Table 2 shows the results of the similarity correlation of the infrared spectrum obtained from the Nylon sample. Comparison with the HR Hummel Polymer and Additives Library, confirmed that the supplier of the filament possibly provides Nylon 6, with 72.47% of similarity with the polymer Poly(amide 6,6:amide 6) from the database. Other results with similar correlation indices all correlate to commercial or ideal structures of Nylon 6 or Nylon 6,6.

Differential Scanning Calorimeter DSC

A sample was analyzed before and after an FDM 3D printing in order to compare how the melting process affected its thermal properties. The DSC curve comparison between the raw sample and the processed sample is shown in Fig. 9. The results show that the composition of the sample probably was not affected, since the response of the material is very similar when it is heated to the melting temperature. The melting temperature (T_m), is ~ 196 °C for the raw filament, which is important to characterize the optimal process specifications for FDM 3D printing. In terms of the FDM process parameters provided by the supplier of the filament, the material should be heated up to 220 °C, and has a consistent material flow at 275 °C, so it is clear the process is well within specification. Fig. 9 also shows there is a slight increase in the T_m to ~ 202 °C after the process, possibly due to thermal memory imprinted by the FDM process.

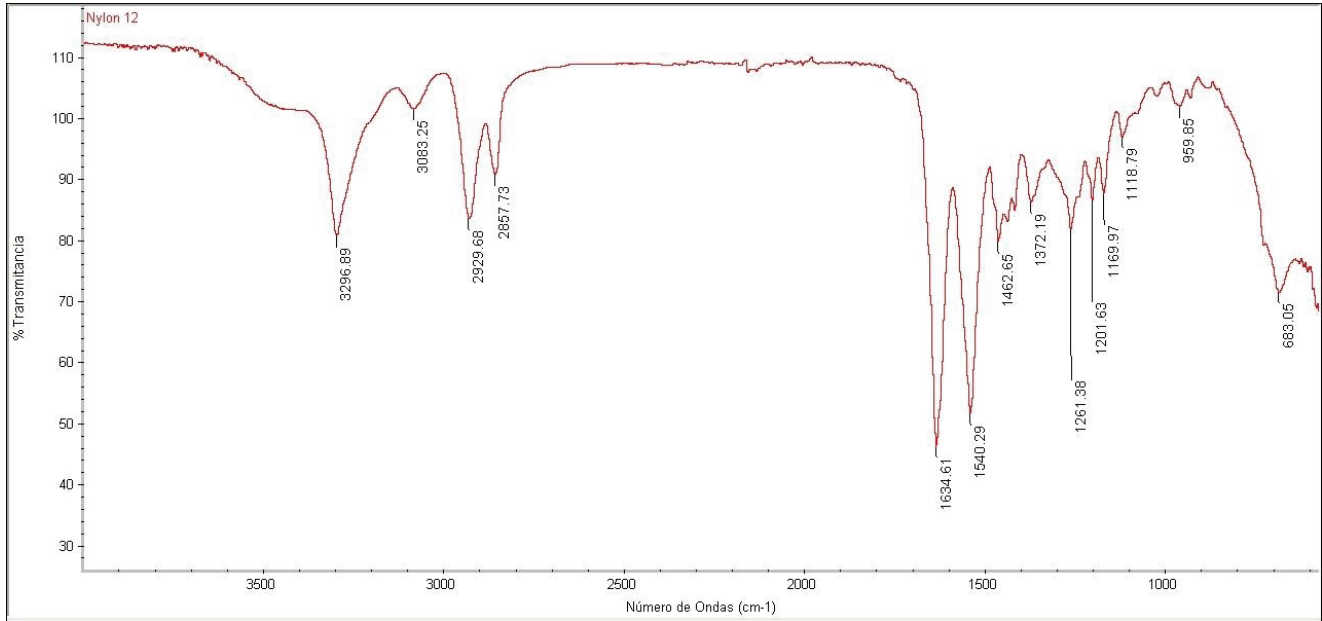


Fig. 7. FTIR spectrum obtained from the Nylon sample.

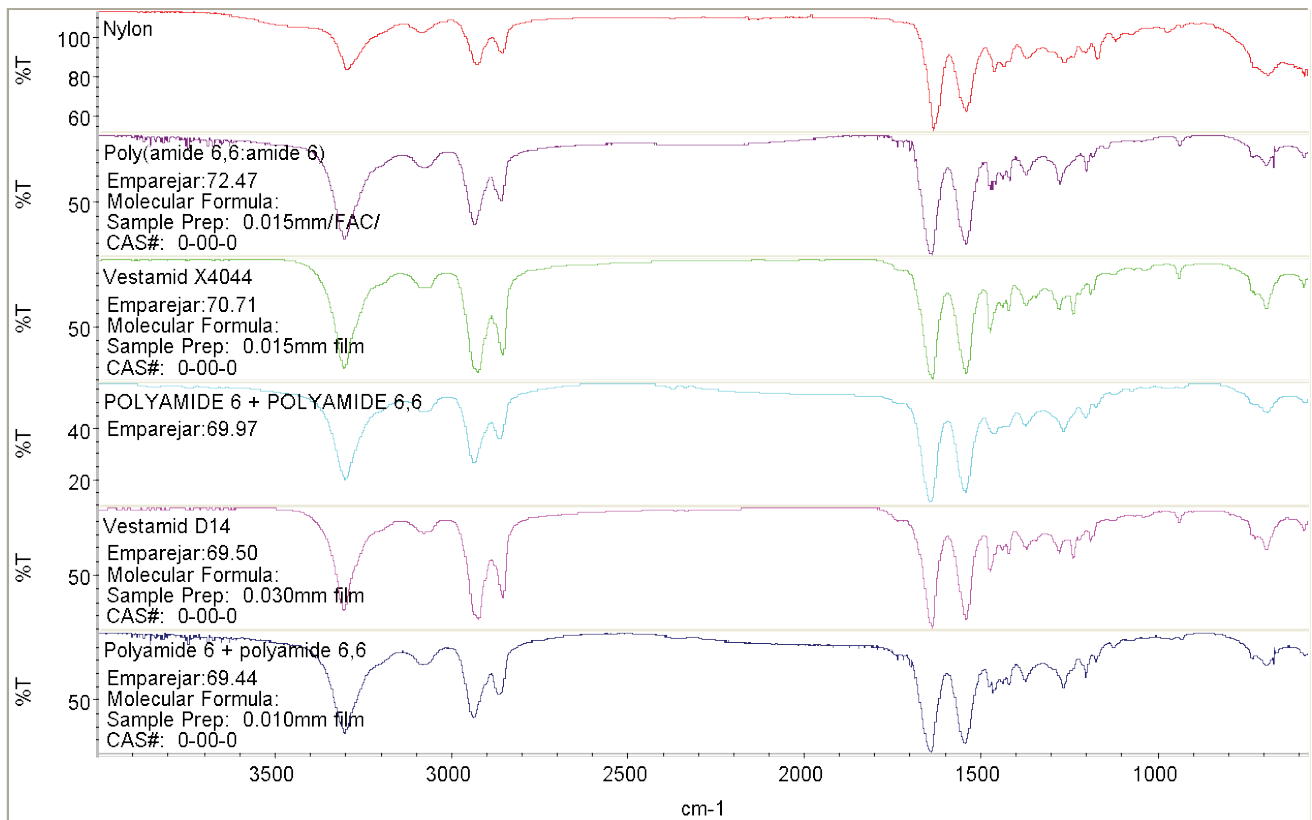


Fig. 8. Similarity correlations of FTIR spectrum obtained for Nylon sample with the HR Hummel Polymer and Additives library.

Table 2. Similarity correlation of FTIR spectrum obtained for Nylon sample.

Index	Similarity %	Compound Name	Library
290	72.47	Poly(amide 6,6:amide 6)	HR Hummel Polymer and Additives
1025	70.71	Vestamid X4044	HR Hummel Polymer and Additives
28	69.97	POLYAMIDE 6 + POLYAMIDE 6,6	HR Hummel Polymer and Additives
1024	69.50	Vestamid D14	HR Hummel Polymer and Additives
286	69.44	Polyamide 6 + polyamide 6,6	HR Hummel Polymer and Additives

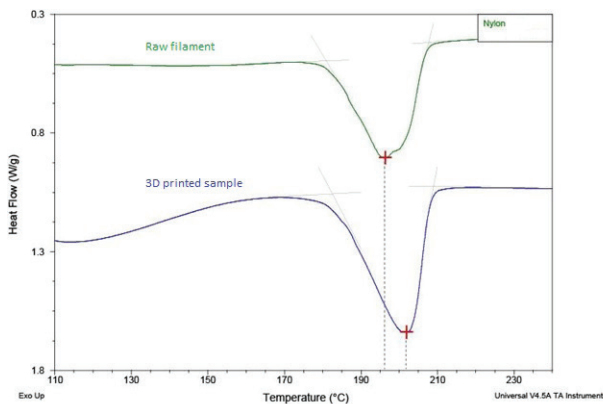


Fig. 9. Nylon 6 DSC curves before and after 3D printing.

4. Conclusions

The metallographic analyses provided information about the microstructures in the Ti-6Al-7Nb alloy. Two phases were identified: an α primary phase with grains immersed in an $\alpha+\beta$ matrix. SEM was used to identify the morphology of the β phase in the matrix, as fine particles with a low fraction with respect to α phase.

By the EDS analysis high concentration of Ti and O were detected, which corresponds to the passivation layer of the Ti-6Al-7Nb alloy. Al, but not Nb, was detected since it is present in the α phase, which has a larger fraction with respect to β , which is rich in Nb.

From the XRD analysis of Ti-6Al-7Nb, Ti (HCP) structure corresponding to the α phase, and TiO (monoclinic) structure corresponding to the passivation layer of the alloy, were identified as the main crystal structures. The characteristic peaks of β phase overlapped with the peaks of the α phase.

Using FTIR analysis it was possible to identify the polymer as Nylon 6, confirming that it has a Polyamide 6 basic molecular structure. This information was useful in a subsequent DSC analysis, in which it was possible to compare the melting point of the sample before and after an FDM manufacturing technology, and also to compare it with the specifications provided by the supplier of the filament.

Acknowledgements

The authors are grateful to Felipe Orozco from the National Nanotechnology Laboratory (LANOTEC-CeNAT), to Esteban Rodríguez from the Center for Research and Extension in Materials (CIEMTEC) of the Costa Rica Institute of Technology, and to Luis Alvarado Marchena from the Institutional Microscopy Laboratory of the Costa Rica Institute of Technology, for their assistance and guidance in carrying out the analyses.

5. References

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