**Revista de Ciencias Tecnológicas (RECIT). Universidad Autónoma de Baja California ISSN 2594-1925**
**Volumen 4 (4): 388-398. Octubre-Diciembre 2021. https://doi.org/10.37636/recit.v44388398**

# Polylactic acid/multi walled carbon nanotubes (PLA/MWCNT) nanocomposite for 3D printing of medical devices

## *Nanocomposito ácido poliláctico-nanotubos de carbono multi pared (PLA/MWCNT) para la impresión 3D de dispositivos médicos*

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**Received:** November 22 2021 **Accepted:** November 25 2021 **Published:** December 8 2021

**Abstract. -** *In recent years, the composite nanomaterials area has had a great development impact in health sciences. Biomaterials depict as one of the most promising since they are compatible with additive manufacturing (AM) techniques. It is also possible to use them to mold specific medical parts. Composite nanomaterials have shown good biocompatibility and low toxicity to have benefits equal to or greater than metals (i.e., Co-Cr alloy). The purpose of this study is to develop a nanocomposite biomaterial (PLA/$MWCNT_f$) from Polylactic Acid (PLA) and functionalized Multi Walled Carbon Nanotubes ($MWCNT_f$) to evidence its potential application in 3D printing of orthopedic fixation devices. PLA/$MWCNT_f$ nanocomposite was prepared by solution blending technique, incorporating a proportion of 0.5 wt% of $MWCNT_f$ to the PLA matrix. TGA analysis of the PLA/$MWCNT_f$ was used to determine the thermal stability, a slight increase was found compared to the PLA. FTIR spectroscopy confirmed the presence of carboxylic acid groups in the $MWCNT_f$ which improves good incorporation of the nanotubes in the PLA matrix. Additionally, Raman spectroscopy, SEM, and AFM micrographs were used to verify $MWCNT_f$ reached the PLA surface homogeneously. Additive manufacturing preparation was done by extrusion molding of PLA/$MWCNT_f$ as well as its 3D printing.*

**Keywords:** Polylactic acid (PLA); Multi walled carbon nanotubes (MWCNT); 3D printing; Biomaterials; Nanocomposites.

**Resumen. -** *En los últimos años el área de los nanomateriales compuestos ha tenido un gran impacto en el desarrollo de las ciencias de la salud. Los biomateriales se describen como uno de los más prometedores, ya que son compatibles con las técnicas de manufactura aditiva (AM). También es posible utilizarlos para moldear piezas médicas específicas. Los nanomateriales compuestos han demostrado una buena biocompatibilidad y baja toxicidad para tener beneficios iguales o superiores a los de los metales (p. ej. aleación de Co-Cr). El propósito de este estudio es desarrollar un biomaterial nanocomposito (PLA/$MWCNT_f$) a partir de ácido poliláctico (PLA) y nanotubos de carbono multi pared funcionalizados ($MWCNT_f$) para evidenciar su potencial aplicación en la impresión 3D de dispositivos de fijación ortopédica. El nanocomposito de PLA/$MWCNT_f$ se preparó mediante la técnica de mezclado en solución, incorporando una proporción de 0,5% en peso de $MWCNT_f$ a la matriz de PLA. Se utilizó el análisis TGA de PLA/$MWCNT_f$ para determinar la estabilidad térmica, se encontró un ligero aumento en comparación con el PLA. La espectroscopía FTIR confirmó la presencia de grupos carboxilos en los $MWCNT_f$ lo que mejora una buena incorporación de los nanotubos en la matriz PLA. Además, se utilizó espectroscopía Raman y SEM para verificar que $MWCNT_f$ alcanzara la superficie de PLA de manera homogénea. La preparación de la manufactura aditiva se realizó mediante moldeo por extrusión de PLA/$MWCNT_f$ así como su impresión 3D.*

**Palabras clave:** Ácido poliláctico (PLA); Nanotubos de carbono multi pared (MWCNT); Impresión 3D; Biomateriales; Nanocompositos.

## 1. Introduction

Medical devices can be manufactured from a wide variety of materials using different techniques. Additive Manufacturing is a processes that allows us a personalized development of different medical devices, satisfying the particular needs of each patient [1], [2]. According to NOM-240-SSA1-2012, medical devices are manufactured for the purpose of diagnosing, monitoring or preventing disease in humans or auxiliary in the treatment of them and disability, as well as to be used in the replacement, correction, restoration or modification of the anatomy or physiological processes. Medical devices include products in the following categories: medical equipment, prostheses, orthesis, functional aids, dental supplies, surgical materials, among others [3]. Nanocomposite biomaterials are in constant research and development as they offer better properties than the materials commercially used in this area. Different metal alloys are used for the production of orthopedic prostheses (total hip replacement, total knee replacement) and also orthopedic fixation devices, specifically those used in osteosynthesis procedures (screws, plates, nails, rods). One of the most widely used metal alloy is Cobalt-Chromium, however, various authors and patients have reported adverse effects caused by this alloy [4].

According to literature, serum cobalt and chromium concentrations are increased in patients with prostheses made with this mentioned material, this condition is known as metallosis. Campbell et al. [5] shows that some of the effects caused by high Co concentrations are periprosthetic soft tissue reactions, cardiomyopathies and hypothyroidism. In addition, Green et al. [6] explains the emergence of neurological abnormalities caused by this metallosis, among which are: concentration problems, short term memory deficit, disorientation in place, neurocognitive deficits, even dementia, among others. Similarly, other registered symptoms are loss of weight and appetite, depression, low energy and metallic taste.

According to what has been explained, neurodegenerative problems, cardiopathies and polyneuropathies are some of the most dangerous adverse effects that have been evidenced due to Cobalt-Chromium prostheses metallosis [6–12]. Due to all these mentioned consequences, in 2020 cobalt was listed as a CMR (carcinogenic, mutagenic and toxic for reproduction). This event generates the need to develop new alternative materials to Co-Cr. Biodegradable polymers have been of great importance in biomedical applications, mainly due to their high acceptance by the human body (biocompatibility) and their low toxicity, being Polylactic Acid (PLA) one of those with best properties.

PLA being a biopolymer, it does not come from oil derivatives, instead at an industrial level it is produced from corn starch. In addition, PLA is biodegradable and biocompatible polymer. PLA is also bioabsorbable, due to this fact, it is used for the manufacture of bioabsorbable surgical sutures and orthopedic screws, which do not need to be removed as they are absorbed by the human body. Also, PLA is the most widely used material in various additive manufacturing (AM) processes such as 3D printing by FDM (Fused Deposition Modeling) and SLA (Stereolithography). PLA matrix nanocomposites biomaterials have had a strong development in recent years, mainly those reinforced with nanofillers such as carbon nanostructures (i.e., multi walled and single walled carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, carbon dots, among others) [13-29].

Nanocomposites are manufactured with the purpose of obtaining better properties (i.e., mechanical, electrical, thermal, biological) than



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those of their components alone. All these improvements give them a wide spectrum of applications, mainly in the manufacture of cell scaffolds, prostheses, biosensors, artificial tissues and drug delivery [31].

Chen, et al. [14] reported that adding graphene oxide (GO) to a copolymer of PLA-PU (Polylactic Acid-Polyurethane) notably improves the mechanical, thermal and biological properties of the composite compared to the PLA-PU alone. Also, they used the composite for 3D printing of a cell scaffold and evaluated its cell viability. Additionally, Liu et al. [15] manufactured a surgical suture from a composite of PLA reinforced with Multi Walled Carbon Nanotubes (MWCNT), achieving an increase in mechanical resistance. The nanocomposite they developed registered also an increase of up to 50% in the bioabsorption time as well as a 100% in the strength valid time.

Azizi et al. [23] developed a nanocomposite from a copolymer of Polypropylene/Polylactic acid (PP/PLA) with Multiwalled Carbon Nanotubes, they improved the mechanical strength of the copolymer as well as its biodegradation time in soil. They also suggest that this nanocomposite is a good candidate for use in food packaging. On the other hand, Spinelli et al. [24] studied the electromagnetic properties of a nanocomposite of Polylactic acid (PLA) with Multi Walled Carbon Nanotubes (MWCNT) and Graphene Nanoplatelets (GNP). They found an interest behavior, the electromagnetic efficiency of the nanocomposite depended on the aspect ratio of the nanofillers. As mentioned, adding carbon nanostructures to polymers such as PLA can improve various properties that can be used in different applications. In order to avoid the use of Co-Cr alloy for the manufacture of prostheses. The purpose of this study is to developed a PLA nanocomposite biomaterial reinforced with MWCNT to be used in 3D FDM printing of orthopedic fixation devices used in osteosynthesis procedures.

## 2. Methodology

### *2.1 Materials*

In this research, transparent PLA filament from Nature Works model Ingeo Biopolymer 3D850 was used as the polymeric matrix of the nanocomposite. The Multi Walled Carbon Nanotubes (MWCNT) were synthesized by spray pyrolysis technique to be used as reinforcement of the polymeric matrix [32]. Toluene ($C_7H_8$), ferrocene ($C_{10}H_{10}Fe$), chloroform ($CHCl_3$), sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$) and hydrochloric acid ($HCl$) used were from Sigma Aldrich.

### *2.2 MWCNT synthesis*

A Toluene/Ferrocene solution was prepared at 0.1 M, subsequently the solution was introduced under an inert atmosphere (Ar) to the synthesis system by a peristaltic pump SPETEC model PERIMAX with a flow of 10 ml/hr. The synthesis system consists of a Thermo Scientific Lindberg Blue M oven with a quartz concentric tube which must be at 850 °C. In addition, an Agilent nebulizer was used to introduce the Toluene/Ferrocene solution and a source of Argon (Ar) gas to maintain an inert atmosphere within the system. Once the precursor solution entered the oven together with Ar for 30 minutes, the synthesis was concluded. Finally, the MWCNT were extracted manually from the quartz tube with a metallic rod. Figure 1 shows the carbon nanotubes synthesis system used.



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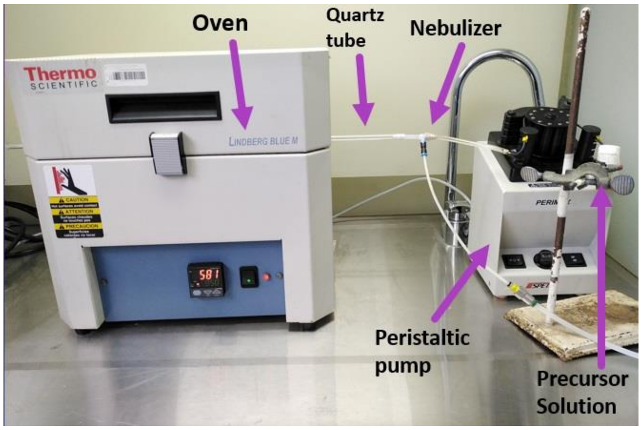


**Figure 1.** MWCNT synthesis system.

### *2.3 MWCNT modification*

In order to obtain a good interaction between the PLA polymer matrix and the MWCNT, the nanotubes were functionalized by incorporating COOH functional groups through an acid treatment [33]. 100 mg of MWCNT were placed in a solution of $H_2SO_4 : HNO_3$ in a ratio of 3:1 vol. for 5 hours in an ultrasonic bath, then 10 ml of HCl 1M was added and they were left to sonicate for 30 minutes. Subsequently they were diluted in deionized water and dried with a vacuum pump. The MWCNT functionalized with carboxylic acids (COOH) were called $MWCNT_f$.

### *2.4 PLA/$MWCNT_f$ nanocomposite development*

The nanocomposite biomaterial developed was called PLA/$MWCNT_f$, was synthesized using solution blending method [34]. The PLA was dispersed in chloroform under magnetic stirring. Similarly, the $MWCNT_f$ were dispersed in chloroform in an ultrasonic bath for 1 hour. Subsequently, both dispersions were mixed. The dispersions of PLA and $MWCNT_f$ before and after mixing are shown in Figure 2. Once the dispersion of PLA and $MWCNT_f$ was homogenized, it was dried at 50 °C for 24 hrs.

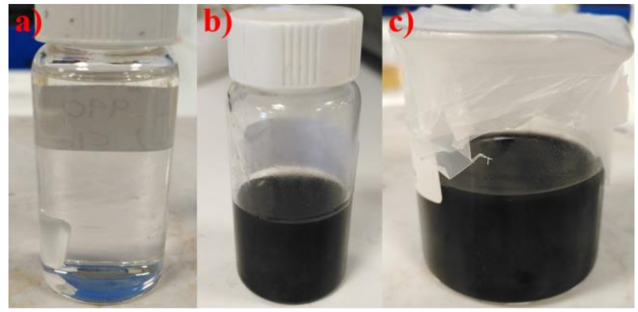


**Figure 2.** a) PLA dispersed in chloroform, b) $MWCNT_f$ dispersion c) PLA/$MWCNT_f$ dispersion.

Different characterizations were carried out to the elaborated materials. Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy were obtained with a Shimadzu IRSpirit and Thermo Scientific DXR Smart Raman 780 nm, respectively. For Thermogravimetric Analysis (TGA) a TA Instruments model SDT 2960 Simultaneous DSC-TGA was used. Scanning Electron Microscopy (SEM) micrographs were obtained with a TESCAN model VEGA3 microscope and FESEM JEOL. Atomic Force Microscopy (AFM) analysis was performed on a Nanosurf Easy Scan equipment.

### *2.4 PLA/$MWCNT_f$ nanocomposite molding*

To prepare the nanocomposite material for 3D Printing, the synthesized nanocomposite film (PLA/$MWCNT_f$) was subjected to a molding process which consisted of several steps. The film was crushed using a blender, subsequently the crushed nanocomposite was entered into a Filabot EX2 extrusion equipment. The extrusion machine was set at 170 °C to produce the 1.75 mm diameter nanocomposite filament, which is the most standard dimension used in 3D printers. Figure 3 shows the extrusion molding process of the PLA/$MWCNT_f$.



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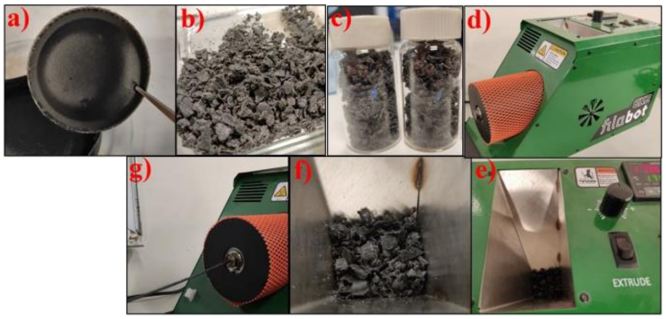


**Figure 3.** PLA/$MWCNT_f$ nanocomposite extrusion molding process.

## 3. Results

### *3.1 FTIR spectroscopy*

Figure 4 shows the spectra of the PLA polymer matrix and the PLA/$MWCNT_f$ nanocomposite. The stretching band of 1747 $cm^{-1}$ and a broad band between 3050-3142 $cm^{-1}$ correspond to the carboxyl groups (COOH) proper to the structure of PLA, while at 1181 $cm^{-1}$ corresponds to CO bonds of the steric chain matrix. Furthermore, in the same figure the FTIR spectra of the MWCNT and $MWCNT_f$ are presented, the wave number value of 1531 $cm^{-1}$ corresponds to the C=C bonds of the structure of carbon nanotubes while the value of 1731 $cm^{-1}$ correspond to the carbonyl CO groups from COOH added to the $MWCNT_f$.

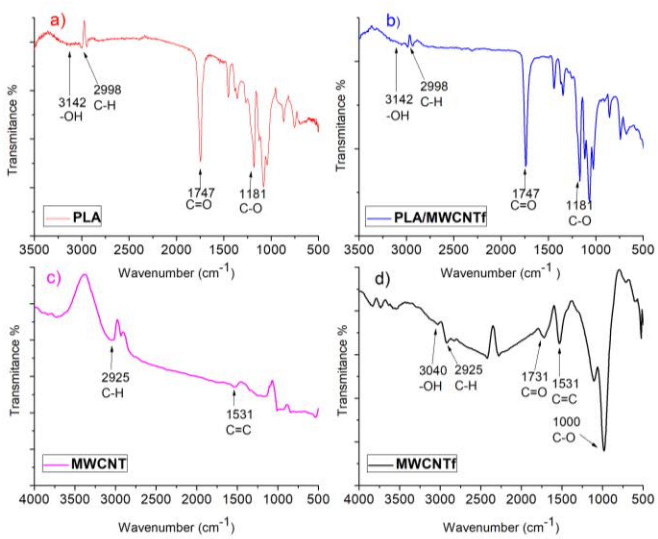


**Figure 4.** FTIR spectrums of: a) PLA, b) PLA/$MWCNT_f$, c) MWCNT and d) $MWCNT_f$.

### *3.2 Raman spectroscopy*

Raman spectroscopy is a very useful characterization technique since it is non-destructive with the sample and valuable information can be extracted from this spectroscopic technique. Multi Walled Carbon Nanotubes have a characteristic spectrum made up of two bands, D and G. The relationship between the intensity of both bands (D/G) give information about the number of defects that the MWCNT have, the higher this ratio, the greater the number of defects the nanotubes will have [35]. The D band is located at an approximate wave number value of 1300 $cm^{-1}$, while the G band is at an approximate value of 1600 $cm^{-1}$.

In Figure 5, D band presents greater intensity than the G, this is due to the defects that were generated in the nanotubes by the oxidative functionalization. Similarly, the spectrum of Polylactic Acid has several characteristic peaks, some of them are at 850 $cm^{-1}$, 1400 $cm^{-1}$, 1750 $cm^{-1}$, 2900 $cm^{-1}$. The Raman spectrum of a composite material clearly results in the sum of the spectra of the raw materials, showing a good incorporation of nanometric reinforcement into the polymeric matrix.

Most of all the characteristic peaks of each material is shown in the nanocomposite spectrum, including a new peak approximately at 2650 $cm^{-1}$suggesting binding forces between PLA and $MWCNT_f$ (see Figure 5).



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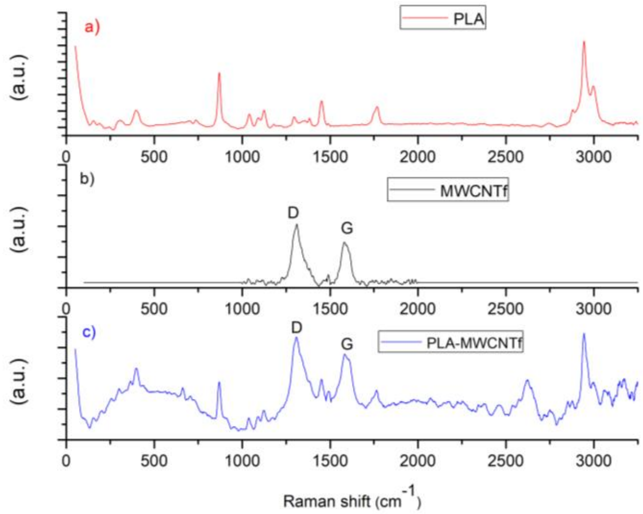


**Figure 5.** Raman spectra of: a) PLA, b) $MWCNT_f$, c) PLA/$MWCNT_f$.

### *3.4 Scanning Electron Microscopy (SEM)*

Figure 6 shows MWCNT, $MWCNT_f$ and PLA/$MWCNT_f$. Functionalized Multi Walled Carbon Nanotubes (b) show less agglomeration than the pristine Nanotubes (a), this behavior is consequence of the acid modification (functionalization). Using ImageJ, an open-source software, the calculated diameter of the $MWCNT_f$ was 28-60 nm, with an average diameter of 48 nm. The way in which $MWCNT_f$ physically interact with the polymeric matrix of Polylactic Acid (PLA) is shown in Figure 6 (c), it can be seen how the nanotubes are embedded within the polymer.

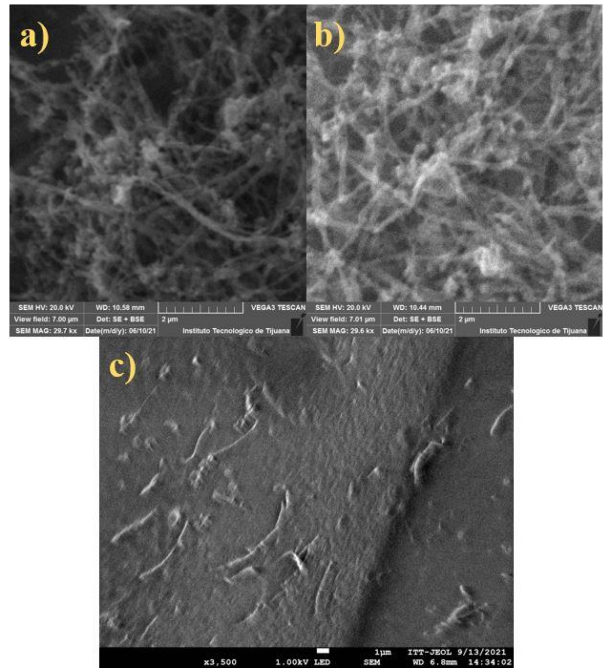


**Figure 6.** SEM micrograph of a) MWCNT, b) $MWCNT_f$, c) PLA/$MWCNT_f$.

### *3.3 Thermogravimetric Analysis (TGA)*

Functionalized Multi Walled Carbon Nanotubes ($MWCNT_f$) were analyzed in an inert atmosphere (Nitrogen) with a temperature of 0-800 °C and a heating ramp of 10 °C/min, while Polylactic Acid and PLA/$MWCNT_f$ nanocomposite were analyzed in air atmosphere at 0-600 °C and a heating ramp of 10 °C/min. Figure 7 shows $MWCNT_f$ thermogram, which has a decrease in their thermal stability due to the oxidative treatment and carboxyl functionalization.

Simultaneously, Figure 7 also shows the thermogram of PLA and PLA/$MWCNT_f$. The nanocomposite registered an increase in the thermal stability at different temperature intervals compared to the polymer (PLA), this enhancement is due to the incorporation of the $MWCNT_f$ to the polymeric matrix which allow a delay in the weight loss of the material. Additionally, Table 1 shows the temperature value at which the materials lose a specific



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weight loss percentage. This thermal stability improvement extends the application area of the nanocomposite, however in this study the material is proposed to be used at physiological temperatures (37 °C).

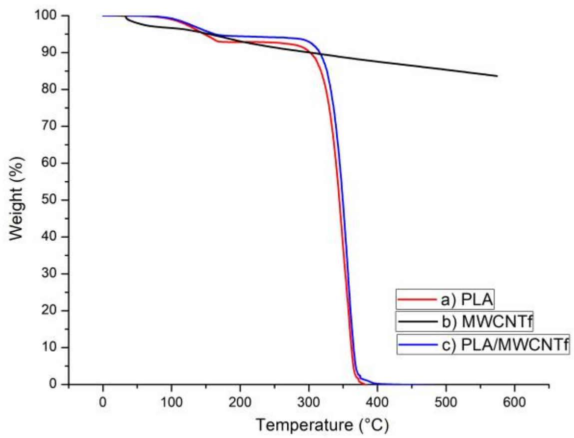


**Figure 7.** TGA thermograms: a) PLA, b) $MWCNT_f$, c) PLA/$MWCNT_f$.

**Table 1.** TGA weight loss values.

| Sample | $T_{10\%}$ weight loss (°C) | $T_{25\%}$ weight loss (°C) | $T_{50\%}$ weight loss (°C) | $T_{75\%}$ weight loss (°C) |
|---|---|---|---|---|
| PLA | 302 | 329.75 | 344.36 | 355.44 |
| PLA/$MWCNT_f$ | 315.5 | 336.04 | 349.34 | 358.84 |

### *3.5 Atomic Force Microscopy (AFM)*

Figure 8 presents the recorded AFM micrograph of the PLA/$MWCNT_f$ nanocomposite surface, it shows the surface generated by the incorporation between the polymeric matrix (PLA) and the nano reinforcement ($MWCNT_f$). Using ImageJ, the calculated average diameter of the circular bumps present on the surface was 57.16 nm, which coincide within the range of the diameter of the carbon nanotubes. It is proposed that these bumps are produced by the incorporation of the nano-reinforcement within the polymeric matrix.

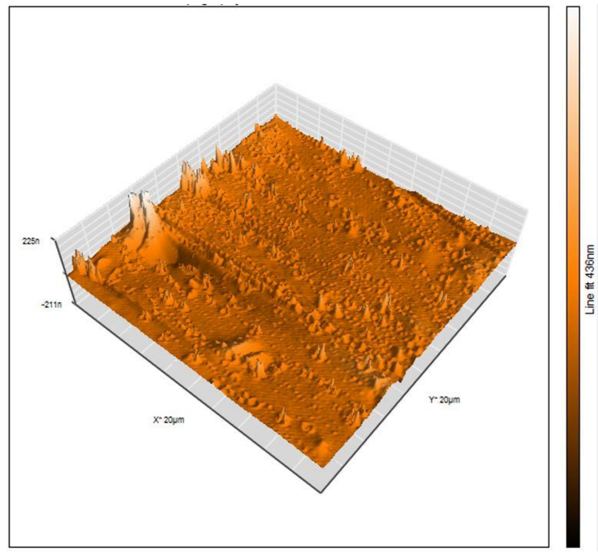

**Figure 8.** AFM micrograph of PLA/$MWCNT_f$.

### *3.6 3D Printing Extrusion*

The dimensions of the extruded PLA/$MWCNT_f$ nanocomposite filament were measured with a vernier caliper, obtaining a result of 1.75 mm in diameter. Subsequently, the filament was introduced into an Anet ET4 3D printer with a 0.4 mm extruder nozzle at a temperature of 220 ° C, thin filaments whose dimension was 0.48 mm were obtained. Figure 9 shows the extruded filament (a) with its diameter measure(b), additionally the 3D printed filament (c) and its diameter measure (d).

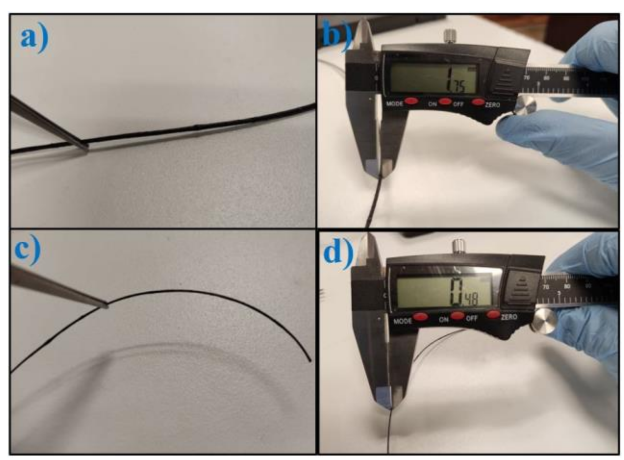


**Figure 9.** PLA/$MWCNT_f$ nanocomposite extruded filament (a-b) and 3D printed filament (c-d).



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## 4. Conclusions

Solution blending technique was successful to developed a PLA/MWCNT$_f$ 0.5 wt% nanocomposite for additive manufacturing (3D printing). In addition, through different characterizations some properties of the synthesized biomaterial were studied and determined complementing what has already been reported in the literature. The nanocomposite was successfully extruded and 3D printed, additionally it presented an increase in its thermal stability compared with the polymeric matrix (PLA). An interaction between the nanofillers (Multi Walled Carbon Nanotubes) and the polymer (PLA) was determined by the Raman spectroscopy SEM and AFM micrographs. Some of the techniques and procedures that will soon be used for PLA/MWCNT$_f$ are 3D printing of the orthopedic device and biocompatibility tests (hemolytic and cell viability).

## 5. Acknowledgements

To TecNM Project Number: 10716.21-P, Tecnológico Nacional de México/IT de Tijuana and CONACYT.

## 6. Authorship and contribution

*Manuel Alejandro Cardona Salcedo:* Project conceptualization, manuscript redaction-edition, methodology, research, analysis and validation. *Mercedes Teresita Oropeza Guzmán:* Revision, redaction, project supervision-administration, methodology and analysis. *Grecia Isis Moreno Grijalva:* Methodology and analysis. *Zizumbo López Arturo:* Data analysis, validation. *Juan Antonio Paz González:* Methodology and analysis. *Gochi Ponce Yadira:* Redaction, project supervision, analysis.

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