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INFLUENCE OF THE ADDITION OF 0.5 AND 1% IN WEIGHT OF MULTI-WALL CARBON NANOTUBES (MWCNTs) IN POLY-LACTIC ACID (PLA) FOR 3D PRINTING

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Abstract

This research paper presents the characterization of a nanocomposite of polylactic acid (PLA) and carbon nanotubes (MWCNTs) with different percentages of mixture in weight. This thermal characterization determines the influence carbon nanotubes have when those are added into PLA. This last one been used for additive manufacturing (FFF technology).- Once finished the tests, it was observed that the nanocomposite PLA/MWCNTs have a positive application during 3D printing. The extrusion temperatures used in tests were between 177 and 185°C. The parameters given for the SLISER software, obtained a promising result for the application of a PLA / MWCNT nanocomposite into 3D printing.

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1. Introduction

Nowadays, the new materials development is centered on the study of composite materials, with the aim of improving polymeric thermal characteristics. Moreover, to determine their applications is also aimed.

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The natural polymers, biodegradable and synthetic polymers which are based on renewable materials; are the basis of sustainable development of the XXI century. All of them being considered eco-efficient plastics. These materials will progressively replace the polymeric materials derived from petroleum due to the low raw material. It will produce an increase in cost and competitive performance [1]. In this paper, a study of two materials will be carried out by which we want to generate a compound for its application in a low cost rapid prototyping. One of the biodegradable materials that is currently used is the polylactic acid (PLA). Carbon nanotubes (CNT), on the other hand, are used as reinforcement material [6,9].

Nomenclature

PLA	Polylactic acid
CNT	Carbon nanotubes
MWCNT	Multi-walled carbon nanotubes
T _g	Glass transition temperature
MFI	Melt flow index
FFF	Fused filament fabrication
T _d	Degradation temperature
T _m	Melting temperature

1.1. Procedure

The first step in the 3D printing goes on virtual planes of the pieces to be printed, using a computer-aided design (CAD).

The STL extension file is the standard interface data (file extension) between the CAD software and the printing machine. An STL file is a triangular mesh format that helps to improve the surface quality of 3D design [2], fig 1.

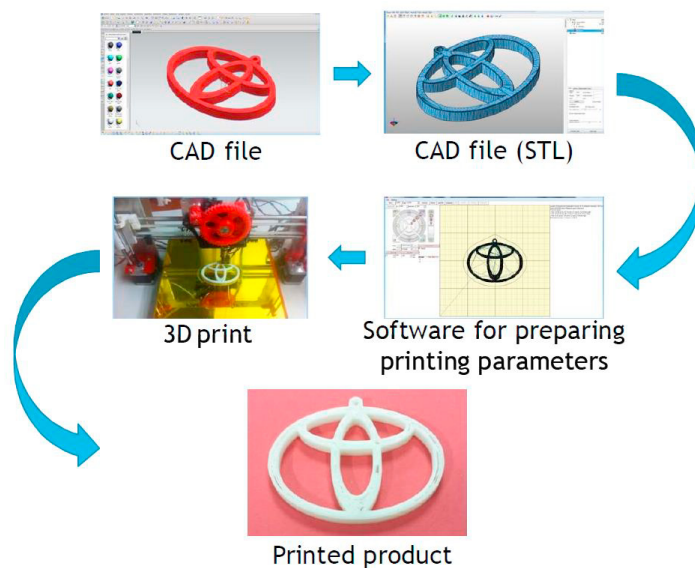


Fig. 1.- 3D printing process

Furthermore, when it comes to low cost printers, the file is recovered by means of an open source software. Depending on the desired parameters, the division of the layered model is made for the 3D printing.

The third step is to determine the G code paths (ISO) in order to proceed with the printing modelling. The fused deposition modelling process (FDM) uses the additive manufacturing, depositing materials layer by layer to perform the creation of the piece [3,4]. The plastic material (filament), coil supplied, is introduced to the hot end extrusion process. In the last step, the semi-fused filament, through a nozzle that heats the material to the melting temperature, can give the three movements in x, y, z.

The 3D printing (FFF) low cost process gives us several study possibilities of the parameters that are involved in the 3D printing process. Said possibilities are:

- deposition rate,
- layer thickness,
- type of nozzle suitable for extruding the material (nozzle diameter),
- distance between the impression base and nozzle tip, and
- The speed of movement of the extrusion die [5].

2. Objectives

The main objectives developed in the present work include the thermal and rheological analysis of the PLA reinforcement. In addition, it was also studied the influence multi-wall carbon nanotubes (MWCNTs) of 0.5 and 1% in weight, have when added into poly-lactic acid (PLA).

3. Methodology

The nanocomposite preparation was carried out using the direct fusion method, figure 2. The materials (PLA / MWCNT) were mixed by stirring in a bag and then placed in the extruder.

In addition, the preparation of the first phase of the nanocomposite was carried out in order to obtain a base material (master batch): PLA / MWCNTs 5% by volume by weight. Said master batch was obtained by mixing 475 g of PLA and 25 g of MWCNT.

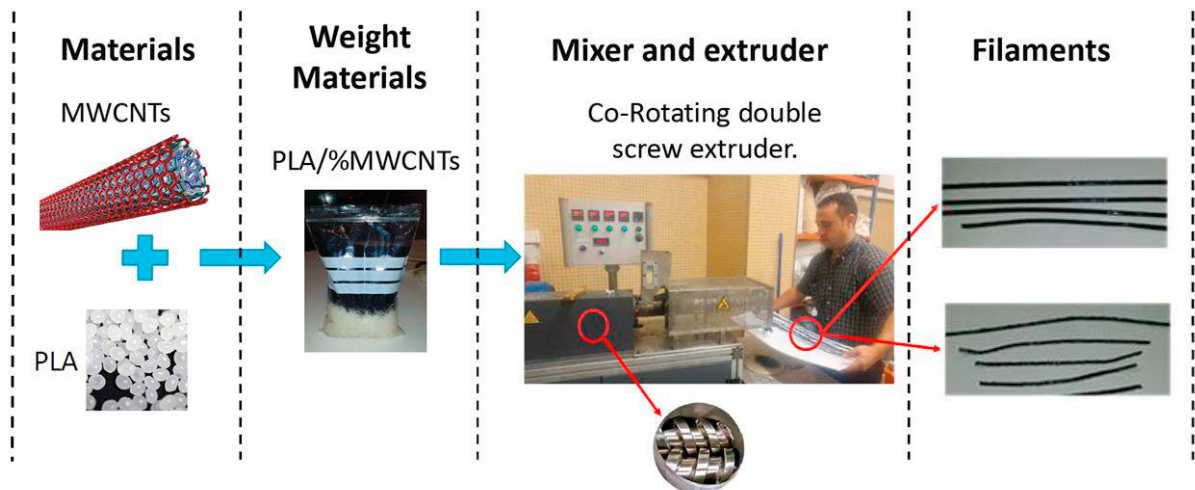


Fig. 2. Workflow of samples preparation

The mixing was carried out in a co-rotating twin-screw extruder, using a screw at the speed of 40 rpm. The

movement of materials in a twin-screw extruder depends on the direction of the spindles' rotation.

Moreover, for the preparation of nanocomposites with 0.5 and 1% of MWCNTs, the previously obtained masterbatch was used as the base material. Only an additional amount of PLA was added, with the interest of reducing the corresponding amount of MWCNTs for each nanocomposite. For the work carried out, tests were performed for each sample. These tests were: Differential Scanning Calorimetry (DSC) and Melt Flow Index (MFI). Finally, these tests give as a result the materials processing conditions.

4. Results and discussion

The purpose of the DSC study was to determine the changes in the glass transition temperatures T_g and the melting temperature (T_m) of the materials, both with different load percentages of MWCNTs. The glass transition temperature is identified as a baseline jump due to heat capacity change, increasing the material plasticity. The MFI is used as a flow knowledge tool in the materials thermoplastic's properties. In addition, the MFI also determines if the material is within the range of fluidity.

Table 1.- Differential Scanning Calorimetry (DSC)

Nano compound	T_g (°C)	T_m (°C)	T_d (°C)
PLA virgin	68.43	178.12	298.16
PLA/MWCNTs 0.5%	70.14	184.00	320.73
PLA/MWCNTs 1%	67.10	177.00	316.26

If one analyses the virgin PLA analysis graph, table 1, which is obtained by means of the differential scanning calorimetry (DSC) test, a small endothermic peak is observed. It corresponds to the glass transition temperature (T_g), which is 68.43°C. The next endothermic peak corresponds to the material melting temperature (T_m), which is 178.12°C. Finally, it can be observed that the material is degraded by pyrolysis before the 298.16°C (degradation temperature T_d).

In the PLA/MWCNT 0,5% analysis results, a small endothermic peak is observed, which corresponds to the glass transition temperature (T_g), which is 70.14°C. The following endothermic peak corresponds to the material fusion temperature, this one being 184°C. Finally, it can be observed that the material degrades by pyrolysis before reaching a temperature of 320.73°C.

In the PLA/MWCNT 1% analysis results, a small endothermic peak is observed that corresponds with glass transition temperature (T_g), which is 67.10°C. The next endothermic peak corresponds to the material fusion temperature, this last one being 177°C. Finally, it's observed that the material degrades by pyrolysis before reaching the 316.27°C.

The MFI, fig 3, has shown that the virgin PLA flow rate is 24.40 g/10 min, which is higher than the nanocomposites. This indicates that the addition of the MWCNTs causes a decrease in the fluidity of the material.

It can also be indicated that when the PLA/MWCNT1% analysis is performed, the fluidity decrement is considerable. This result indicates that the material has become more rigid and more viscous

Moreover, for the 3D printing tests with the nanocomposite, the PLA / MWCNTs extrusion at 1 and 0.5% (previously updated to obtain filament) is performed.

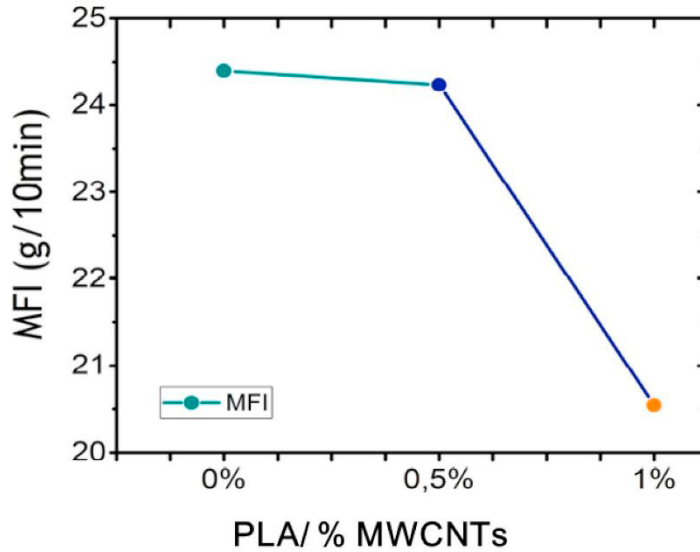


Fig. 3. MFI results

The printing tests were carried out in the FabLab VLC, with a low cost FDM printer brand PRUSA model I3, fig 4, with an extruder (hotends) brand J-Head Mk V-BV. In order to accomplish the printing tests, two software were used: Slicer and Pronterface.

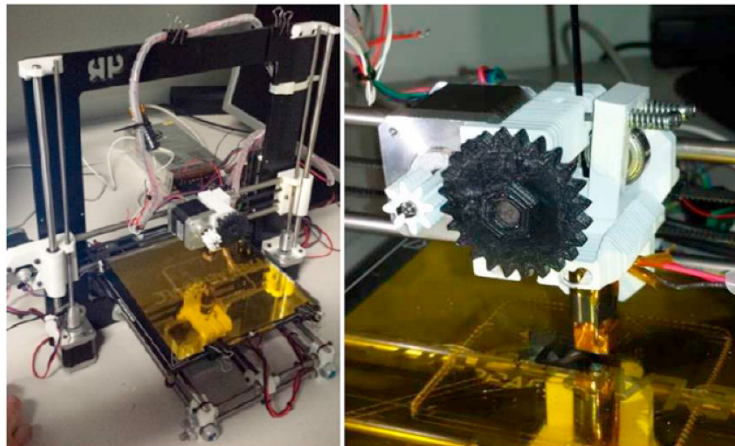


Fig. 4. Prusa 3D printer

Finally, the tests carried out show the following 3D printing results, table 2:

On test one we found a good material temperature and good base; the perimeter speed was worthy. We found a fill speed too high.

On 2nd test we found that hot ends temperature very high. Also, encountered material dripping. We determine that fill speed too high.

On 3rd test the low filling rate used improves the deposition of the material. Its work perimeter dripping and the speed will be increased.

On 4rd test reduction speeds in a 20% improves printing, but the printing process is very slow.
On 5rd test the best printing.
On 6rd test not so good printing results.

Table 2.- Test results

5. Conclusion

In conclusion, the study has been carried out with the intention of gathering information about the materials (PLA-MWCNTs). We research the thermal properties, observe applications of each material, and then perform an analysis of studies made with PLA / MWCNTs nanocomposite. The developed applications show that the study trend of this nanocomposite has increased from 2010 to date. The preparation of a nanocomposite of PLA / MWCNTs at 0.5 and 1% by volume of weight was carried out; with the use of the melt state mixture with a twin screw extruder (spindle speed of 40 rpm). When it comes to the nanocomposite thermal and fluid analysis, we obtained that the amount of carbon nanotubes in the mixture increases with PLA. However, we found that the fluidity decreases, concerning the melting temperature and the glass transition temperature. In addition, the change in temperature is not considerable \pm

3°C and $\pm 5^\circ\text{C}$ respectively. Finally, regarding the tests carried out with the nanocomposite, it can be stated that the application of a nanocomposite of PLA / MWCNTs is possible for the 3D printing process FFF Low Cost.

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