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Study of thermal and rheological properties of PLA loaded with carbon and halloysite nanotubes for additive manufacturing

PURPOSE:

This paper proposes using polylactic acid (PLA) as an alternative to nanocomposites in additive manufacturing processes in Fusion Deposition Modelling (FDM) systems and describes its thermal and rheological conditions with multiwall carbon nanotubes (PLA/MWCNTs) and halloysite nanotubes (PLA/HNTs) composites for possible applications in additive manufacturing processes.

DESIGN/METHODOLOGY/APPROACH

PLA/MWCNTs and PLA/HNTs were obtained through fusion in a co-rotating twin-screw extruder. PLA was mixed with different percentages of MWCNTs and HNTs at concentrations of 0.5 wt. %, 0.75wt. %, and 1wt. %. Differential Scanning Calorimetry (DSC) and Capillary Rheometry were used to characterise these products, together with an analysis of the Melt Flow Index (MFI).

FINDING:

The DSC data revealed that the nanocomposites had a glass transition temperature Tg = 65 ± 2°C and a melting temperature Tm = 169 ± 1°C.

The crystallisation temperature of PLA/MWCNTs and PLA/HNTs was between 107± 2°C, and 129 °C, respectively. The PLA / MWCNTs and PLA / HNTs viscosity data obtained by capillary rheometry indicated that the viscosity of the materials is the same as that of neat PLA.

These results were confirmed by the higher fluidity index in the MFI analysis.

Originality /value:

This paper presents an alternative for the applications of nanocomposites in additive manufacturing processes in Fusion Deposition Modeling (FDM) systems.

KEYWORDS: 3D printing, additive manufacturing, carbon nanotubes, halloysite nanotubes, thermal, rheological.

INTRODUCTION

PLA, a natural biopolymer, is now becoming an alternative to diminishing oil resources for use in FDM processes. Although PLA has good mechanical properties, it also has certain disadvantages, such as low thermal resistance and low shear and crystallization rates, however there are different PLA nanocomposites that use different mixing methods (Raquez *et al.*, 2013).

As PLA is biodegradable, research groups all over the world are studying how to apply it to polymer transformation processes for different uses(Auras *et al.*, 2011).

Natural biodegradable polymers and synthetic polymers based on renewable materials are the basis for the sustainable development of new eco-efficient plastics(Auras *et al.*, 2011).

While lactic acid is the most frequently occurring natural carboxylic acid, PLA is a thermoplastic with similar stiffness to polyethylene (PE) or ethyl poly terephthalate (PET) (Auras *et al.*, 2011)(Ren, 2011).

PLA has been tested for possible use in injection and additive manufacturing processes. Its rheological, mechanical and thermal characteristics have been analysed in order to determine the agents that improve its properties for manufacturing by injection. Studies have also been made on applying PLA to fused deposition modelling (FDM) to determine suitable strategies to improve the mechanical characteristics of components obtained by additive manufacturing (Harris and Lee, 2008)(Song *et al.*, 2017)**.**

Carbon nanotubes (CNTs) and halloysite nanotubes in a PLA polymer matrix create a class of novel materials with a wide range of characteristics and applications.

HNTs are derived from clay. Halloysite is formed by the weathering of different types of igneous and non-igneous rock (Yuan, Tan and Annabi-Bergaya, 2015) and is chemically similar to kaolinite, except that halloysite unit layers are separated by a nanowire of water droplets

Carbon nanotubes are cylindrical structures between ten and fifty thousand times thinner than a hair, with ends may be either open or closed by a hemispherical cap, while they can reach a macroscopic scale in length (Angel Herráez, 2011).

The aim of this work was to determine the influence of carbon nanotubes and halloysite nanotubes on a PLA polymer matrix and to analyse the thermal properties and rheology of the nanocomposites obtained for use in additive manufacturing. The halloysite nano compound is designed for use in the regenerative medicine and pharmaceutical science fields.

The nanocomposite consisting of materials based on multi wall carbon nanotubes is aimed at FDM 3D component printing applications.

MATERIAL AND METHODS

MATERIALS

PLA (lactic acid) was supplied by Ingeo ™ Biopolymer 6201D, of Nature Works (Minnetonka, Minnesota, USA) and was used as matrix for nanocomposites made from PLA/MWCNTs and PLA/HNTs.

NC 7000 multi-wall carbon nanotube was supplied by NANOCYL (Sambreville, Belgium) and halloysite nanotube was obtained from SIGMA – ALDRICH (Darmstadt, Germany).

NANOCOMPOSITE PRODUCTION

In order to avoid degradation by hydrolysis(Murariu and Dubois, 2016)(Carrasco *et al.*, 2010), before extrusion the material was dried in a G-ESN Series PIOVAN hot air dryer from Nature Works (Minnetonka, Minnesota, USA) at temperatures between 45 and 60 ° C for 8 hours.

For each nanocomposite mix, 0.5%, 0.75% and 1% by weight of multi wall carbon nanotubes (figure 1a) and halloysite nanotubes, respectively, were added to 1 kilo of PLA. The mixes were then homogenised in a vibrating drum before extrusion. Figure 1b show a SEM image of PLA/MWCNTs filament obtained from 3D printer.

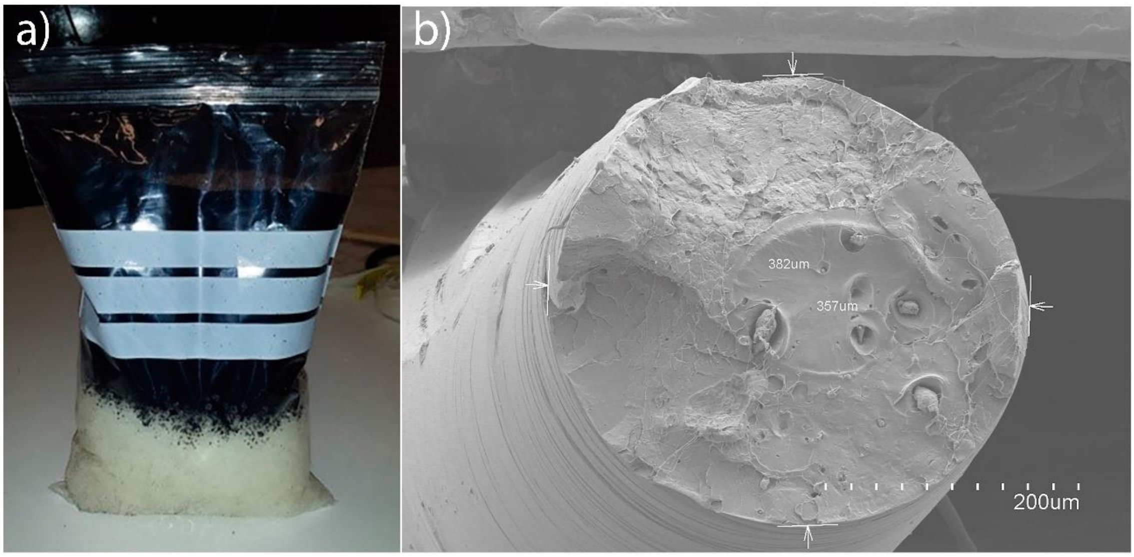

Figure 1: a) PLA + MWCNTs before mixing.

b) SEM of 0.5% wt. PLA/MWCNT filament obtained from 3D printer.

PLA / MWCNTs and PLA / HNTs nanocomposites were prepared by the direct melt method, and the materials were mixed in a co-rotating twin-screw extruder (DUPRA), with a screw diameter of 30 mm and L / D ratio = 20 and turning speed at 40 RPM. The temperature profile of the four controllers ranged between 190, 195, 200 and 205 ° C.

Prior to thermal and rheological characterisation, the composites were dried at 60 degrees for 8 hours.

NANOCOMPOSITES CHARACTERIZATION

Differential scanning calorimetry (DSC)

To determine any changes in the Tg transition melting temperatures of the materials containing different percentages of MWCNTs and HNTs and the amount of heat absorbed or released at a constant temperature for a given period of time (Suriñach *et al.*, 1992)(Richard, 2008), the thermal properties of the samples were studied by a DSC calorimeter (Mettler-Toledo 821),with a temperature program of 30 to 350 °C at 10 °C / min in a nitrogen atmosphere of 66 ml, in accordance with ISO_11357-1 and ISO_11357-3.

Capillary Rheometry Testing

Capillary rheometry can identify shear viscosity, which is the primary measure of flow resistance, and thus affects the actual processes, especially under changes in temperature and flow rate. The Cross-WFL model was used to fit the curves.

For the tests, a capillary rheometer was used (Malvern Instruments Model RH2000) according to the ASTM 3835-10.

Melt Flow Index (MFI)

A Melt Flow Tester (INDEXER MFI 3000 Series QUALITEST) was used to measure the flow of a thermoplastic polymer, defined as the weight in grams that flows through a capillary tube of a specific diameter and length in 10 minutes at a temperature of 210 °C, in accordance with ISO 1133.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC)

Figure 2 compares the DSC curves of neat PLA and the different percentages of PLA with MWCNT nanocomposites. The values of their thermal properties are given in Table 1.

Table1: PLA thermal parameters with different MWCNT concentrations obtained by differential scanning calorimetry (DSC).

MWCNTs (%)	PLA/MWCNTs Thermal Properties			
	T_g (ºC)	T_{cc} (ºC)	T_m (ºC)	T_d (ºC)
0	64.33	105.55	170.69	328.19
0.5	63.86	105.45	171.53	322
0.75	64.74	108.26	171.87	329.78
1	64.41	105.14	170.90	325.12

The neat PLA DSC curves (Curve 2a) and those of PLA nanocomposites with 0.5 wt.%, 0.75 wt.% and 1 wt.% MWCNT (2a, 2b, 2c, 2d, respectively) show that the glass transition temperature is Tg = 64.22ºC (2a) , Tg = 63.86ºC(2b), Tg = 64.74ºC(2c) and Tg = 64.41ºC (2d), in agreement with the findings of Y. Gao, O. T. Picot, E. Bilotti and Peijs (Gao *et al.*, 2017).

In the neat PLA curve (2a) exothermic peak of the crystallization temperature is present, however, the endothermic peak Tm = 169.81°C gives the melt temperature and the material's degradation temperature, Td = 325.26°C.

Temperature is a crucial parameter in the crystallization process, both for production and the manufacture of products (López *et al.*, 2009).

In Figure 2, in the thermograms of PLA / 0.5%, 0.75%, and 1% MWCNT, crystallisation peaks can be seen during the DSC cycle of the nanocomposites, indicating that the PLA polymer chains did not crystallise completely. The crystallisation temperatures were 105.45ºC, 108.26ºC and 105.14ºC, respectively.

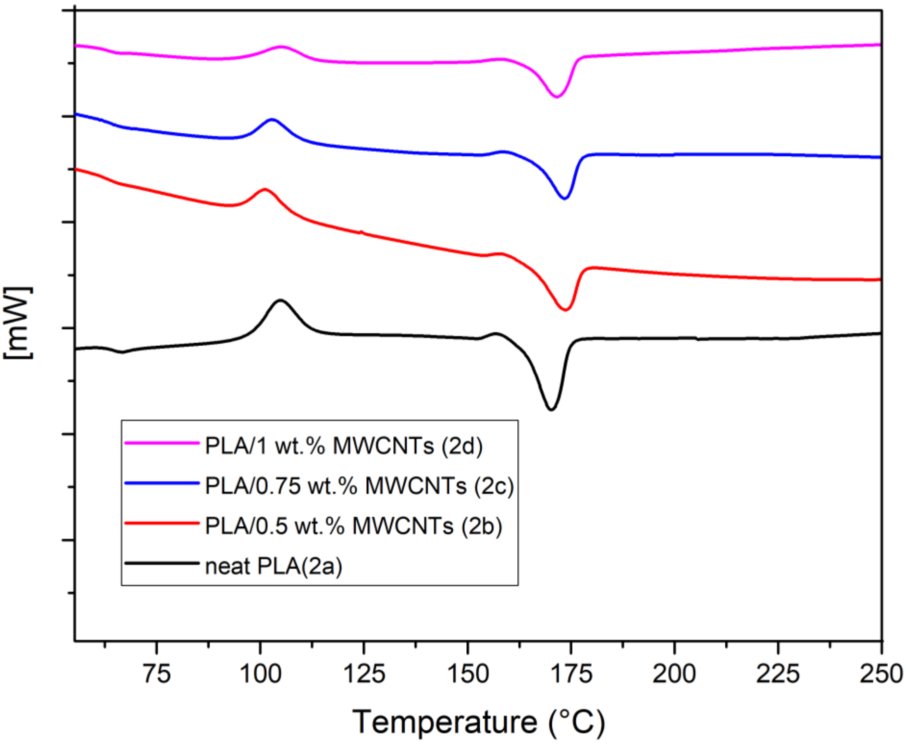

Figure2. DSC (melting temperature peaks) of PLA / MWCNT nanocomposites and neat PLA.

Neither fusion temperature nor melting temperature differed significantly from the neat PLA. As be seen in Table 1, the melting temperature (Tm) for neat PLA is 169.81 °C, that of PLA / 0.5 wt.% MWCNT is 171.53 °C, PLA / 0.75wt.% MWCNTs is 171.87 °C and PLA / 1% MWCNTs is 170.90 °C. The difference between the melting temperature of PLA nanocomposites and MWCNTs is 2 ° C, indicating that carbon nanotubes do not influence the processing temperature.

The degradation temperature of the PLA / MWCNT nanocomposites and neat PLA oscillates between 322 and 325.12 ºC, due to PLA degradation after the rupture of the polymer chains and the loss of hydrogen (Kim *et al.*, 2010).

Figure 3 gives the comparative curves of neat PLA DSC and PLA nanocomposites with halloysite nanotubes. Their thermal properties can be seen in Table 2.

Table 2: Thermal parameters of PLA at different HNTs concentrations obtained by differential scanning calorimetry (DSC).

HNTs (%)	**PLA/HNTs Thermal Properties**			
	T_g (ºC)	T_{cc} (ºC)	T_m (ºC)	T_d (ºC)
0	64.33	105.55	170.69	328.19
0.5	64.81	129.23	171	318.51
0.75	65.62	129.01	170.87	323.06
1	65.77	129.91	171.02	326.44

In the DSC curves of PLA nanocomposites with 0.5 wt.%, 0.75 wt.% and 1 wt.% HNT (3b, 3c, 3d, respectively) and neat PLA (3a), the glass transition temperature is Tg=64.20ºC, Tg=64.81ºC, Tg=65.62ºC, Tg=65.77ºC. These results are similar to the glass transition temperature of the DSC curves of PLA/MWCNTs nanocomposites (see Table 1) and agree with previous findings (Gao *et al.*, 2017)(Wu *et al.*, 2013).

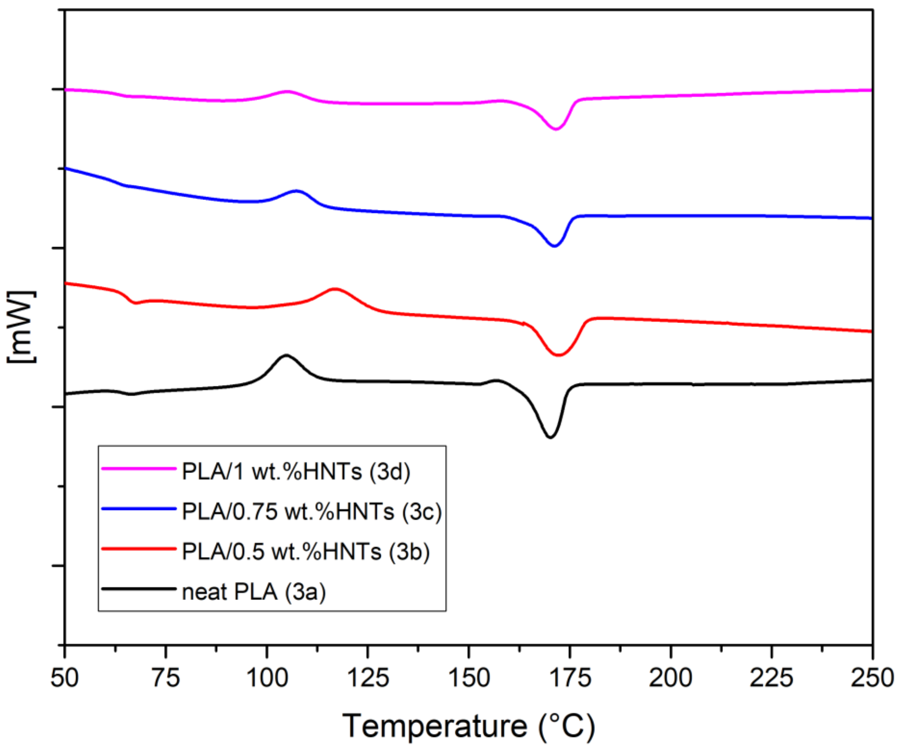

Figure 3. DSC (melting temperature peaks) of PLA / HNT nanocomposites and neat PLA.

The neat PLA curve (3a) shows an exothermic peak crystallisation temperature, although there is an endothermic peak for the melting temperature, Tm=169.81°C. The degradation temperature of the material is Td=319.15°C.

As can be seen in Table 2, the crystallisation temperature obtained in the different PLA / HNT nanocomposite tests is 129 °C, or 24 ° C higher than the PLA / CNT nanocomposites. This variation is due to difference in the coefficient of thermal conductivity.

The melting temperature of PLA / HNT nanocomposites is 170 ± 2 °C, similar to that of the PLA / MWCNT compounds, indicating that the halloysite nanotubes do not influence the material's melting temperature, as found in (Dong *et al.*, 2011).

The PLA / HNT compounds' degradation temperatures were between 318 and 326 ° C, values similar to those obtained from PLA / MWCNT nanocomposites, showing that halloysite nanotubes do not affect the degradation temperature.

Capillary Rheometry Testing

The tests were rehearsed at temperatures of 175, 185, 195, 205 and 210 ° C to observe the influence of nanocharges on the cutting speed of the material (flow resistance), which has a practical effect on polymer transformation processes.

Curve fitting was performed on MatLab software with the capillary rheometry data to determine the Cross WLF parameters.

The rheological behaviour curves of neat PLA at different temperatures show that PLA viscosity (flow resistance) decreases as the temperature of the material increases (see Fig. 4).

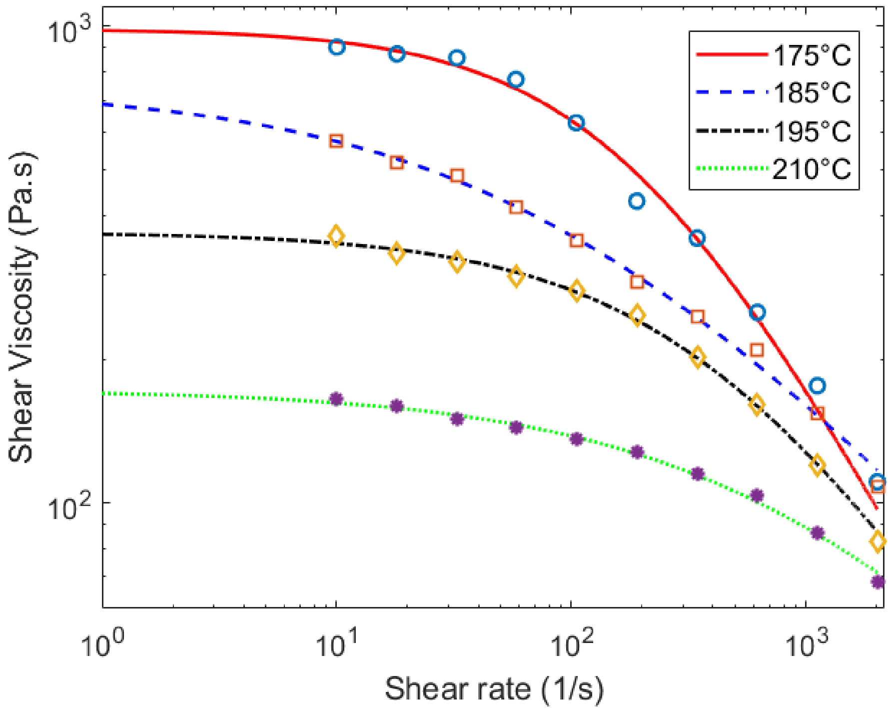

Figure 4. Variation of melt viscosity with shear rates for neat PLA.

Figure 5 shows shear viscosity versus shear rate graphs for PLA / MWCNT nanocomposites at different temperatures. As shear stress increases the viscosity of the material decreases, showing the typical behaviour of a non-Newtonian pseudo-plastic material (Hamad, Kaseem and Deri, 2011)

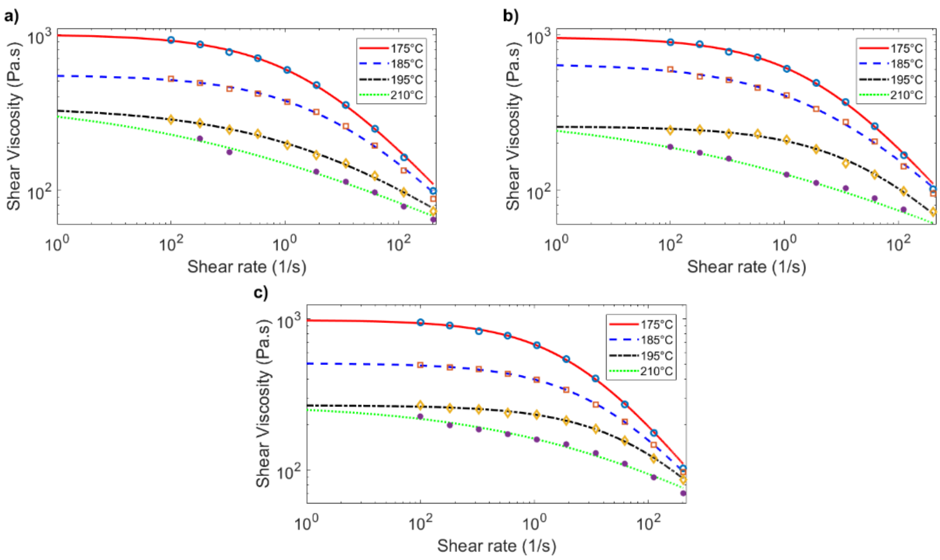

Figure 5. Variation of shear viscosity with shear rate for PLA/MWCNT blends.

a) PLA/0.5 wt.% MWCNTs, b) PLA/0.75 wt. % MWCNTs, c) PLA/1 wt. % MWCNTs.

When the temperature of the nanocomposites goes above 175 ° C the material does not offer greater flow resistance, and viscosity is the same as neat PLA, due to the influence of the carbon nanotubes. No appreciable difference in viscosity was found among the PLA / 0.5, 0.75 and 1% MWCNT nanocomposites, as was found between the neat PLA graph and that of the nanocomposites.

Figure 6 shows the shear viscosity graphs versus the PLA / HNT nanocomposites shear rate at different temperatures.

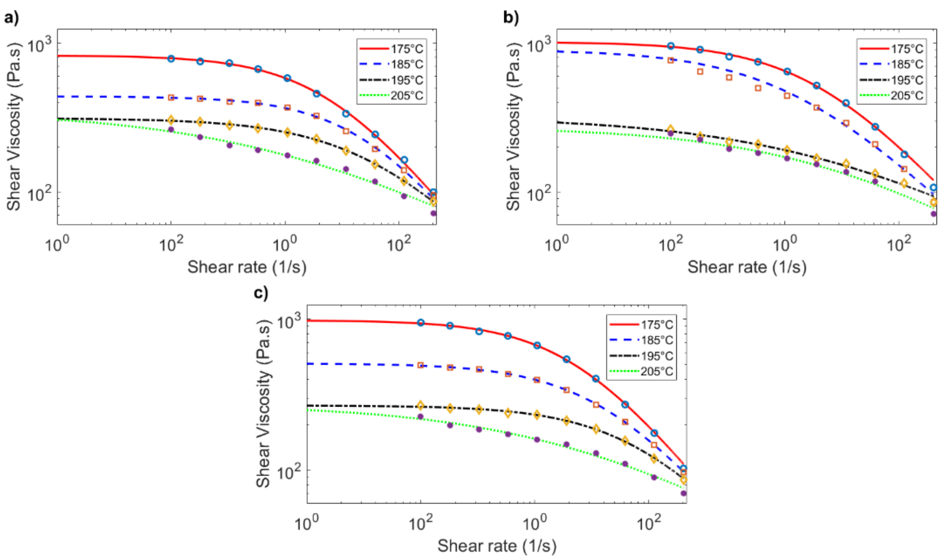

Figure 6. Variation of shear viscosity with shear rate for PLA/HNT blends.

a) PLA/0.5 wt.% HNTs, b) PLA/0.75 wt. % HNTs, c) PLA/1 wt. % HNTs.

As shown in Figure 6, as the percentage of halloysite nanotubes increases flow resistance decreases due to the poor stiffness of the nanotubes, which allows them to change direction with the flow, also due to the chain scission by hydrolysis, which reduces the viscosity of the nanocomposites (Singh *et al.*, 2016). It was not possible to test PLA / 1% HNTs at 210 ° C because the material flowed too fast to obtain any data, as was found in (Singh *et al.*, 2016)

Melt Flow Index

The melt flow index (MFI) properties of the neat PLA and the PLA / MWCNTs and PLA / HNTs nanocomposites were studied using a Melt Indexer 3000Q2 plastograph (Qualytest Instruments) under UNE-EN_ISO_1133.

The MFI test on neat PLA, PLA / MWCNTs and PLA / HNTs carried out in load percentages of 0.5, 0.75 and 1% can be seen in Figure 7. Increasing the percentage of MWCNT reduced the MFI, which was the opposite with the HNT load.

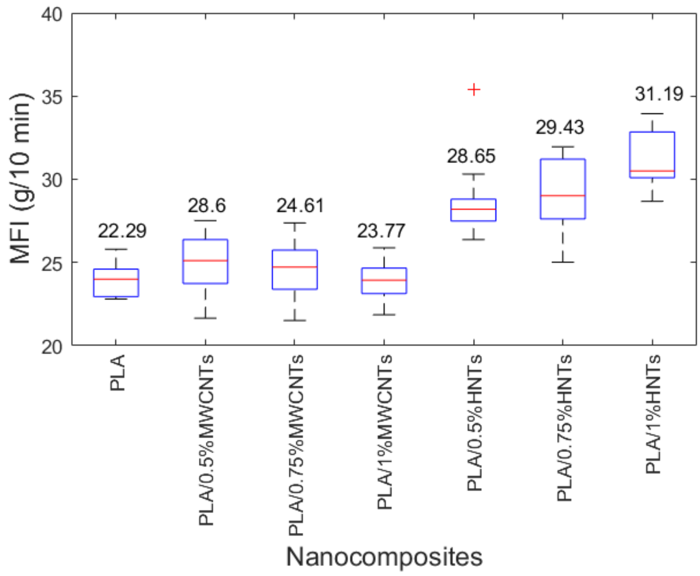

Figure 7. The melt flow indexes (MFI) of neat PLA and nanocomposites of PLA / MWCNT and PLA / HNT with varying percentages of nanocharges.

In Figure 7 it can be seen that MFI is reduced as the percentage of carbon nanotubes increases, probably due to the stiffness of the nanocharge, unlike the HNTs, whose MFI increases with higher nanocharges. This is probably due to the exfoliation / intercalation of a molecule or group, in this case assumed to be the water contained in the nanotubes, in agreement with the results obtained in (Li *et al.*, 2006).

The analysis of the behaviour of each of the nanocharges in the polymeric matrix indicates that the MWCNTs reduce their fluidity as the weight percentage increases, while HNTs increase their fluidity as this percentage rises. The higher fluidity of these composite materials than that of neat PLA is due to the PLA degradation during extrusion caused by the cleavage of the PLA's oxygen chains (Ferri Azor, Balart Gimeno and Fenollar Gimeno, 2017), which involves the loss of molecular weight, as was found in (Li *et al.*, 2006).

CONCLUSIONS

PLA mixtures with MWCNTs and HNTs were obtained from a twin-screw cutting process to analyse the rheological properties of the materials for a future study of FDM applications.

A comparison of the results indicates that the variation of the glass transition temperature, melting temperature and degradation is within a range of 4 ° C.

A significant variation of 24 ° C was found in the crystallisation temperature, which was assumed to be due to the MWCNTs' higher thermal conductivity, unlike halloysite.

PLA / MWCNT viscosity values increase due to the division of the PLA chain by hydrolysis. PLA / HNT viscosity increases considerably with the inclusion of halloysite nanotubes, due to the excision present in the extrusion process, taking into account that halloysite is a material that absorbs humidity.

As the MFI values confirm the results of the capillary rehometry, it can be concluded that the nanomaterials studied could be used in FDM and Injection Moulding Processes.

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