Effect of Maleinized Linseed Oil (MLO) on thermal and rheolological properties of PLA/MWCNT and PLA/HNT nanocomposites for additive manufacturing

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Abstract

Purpose – This paper aims to describe the influence of maleinized linseed oil (MLO), when used as a lubricant, on the thermal and rheological properties of PLA/MWCNTs (polylactic acid/multi-walled carbon nanotubes) and PLA/HNT (halloysite nanotubes) nanocomposites, as a reference for application in 3D printing processes.

Design/methodology/approach – Nanocomposites were obtained by melting in a twin-screw extruder, mixing PLA with MWCNTs and HNTs in different percentages of 0.5, 0.75 and 1 Wt.% for subsequent mixing by the same process with 5 phr MLO, for application in additive manufacturing, as analyzed by means of differential scanning calorimetry (DSC), capillary rheometry, melt flow rate (MFL) and field emission scanning electron microscopy (FESEM).

Findings – The results obtained for thermal characterization by using DSC indicate the non-variation of glass transition temperature $Tg = 62 \pm 2°C$ and a melting temperature (Tm) around 170°C. Crystallization temperature dropped by approximately 12°C, which should be kept in mind during the transformation processes. The values obtained by capillary rheometry indicate that the material's viscosity is reduced by the influence of the MLO plasticizer's lubricant effect on the PLA's molecular structure. The melt flow index values confirm a rise of approximately 46% in the flow index and back up the capillary rheometry results. The values obtained were as follows: PLA/0.5 Wt.% MWCNT/MLO 5 phr 54.07, PLA/0.75 Wt.% MWCNT/MLO 5 phr 53.46, PLA/1 Wt.% MWCNT/MLO 5 phr 51.84y PLA/0.5 Wt.% HNT/MLO 5 phr 61.8, PLA/0.75 Wt.% HNT/MLO 5 phr 68.3 and PLA/1 Wt.% HNT/MLO 5 phr 71.2 g/10 min. Apart from the nanocharge distribution, the information obtained from the FESEM shows the existence of a cluster, which could have been avoided by more energetic stirring during the nanocompound manufacturing process.

Social implications – This paper presents an analysis of the insertion of plasticizer in nanocomposites for the application in additive manufacturing processes in fusion deposition modelling (FDM) system.

Originality/value – This is a novel original research work.

Keywords 3D printing, Additive manufacturing, Carbon nanotubes, Halloysite nanotubes, Polylactic acid, Maleinized linseed oil, Thermal, Rheological

Paper type Research paper

Introduction

Polylactic acid (PLA) has similar properties to petroleum-based polymers and thus is a viable alternative because of its biodegradability and reproducibility. The environmental

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impact of the present huge demand for plastic products has led researchers to look for new PLA applications, because it can be obtained from renewable resources and has similar thermal and mechanical properties to the traditional polymers obtained from non-renewable petroleum (Platt and Rapra Technology Limited, 2006). PLA can be obtained from crops such as maize, wheat, tapioca, sugarcane and sugar-beet (Auras *et al.*, 2010; Ren, 2011). Because of its interesting mechanical properties, at the present time, studies are being carried out on the possibility of using it for food packaging (Cheng *et al.*, 2015), surgical sutures (Grijpma *et al.*, 2002) and various other applications (Platt and Rapra Technology Limited, 2006).

New nanocompounds have been produced by mixing carbon and halloysite nanotubes (HNTs) to improve PLA's mechanical and processing characteristics (Ali, 2013; Dong *et al.*, 2015). Nanotubes behaviour within the PLA polymer matrix varies according to their structure, whereas the percentage of nanocharges reduces their elongation at break and increases their tensile strength (Ali, 2013). The length and tensile strength can be increased by adding halloysite to the polymer matrix, which has an additional elongating effect (De Silva *et al.*, 2014). However, it should be noted that these results were obtained from specimens produced by injection.

Maleinized linseed oil (MLO) is a natural crosslinker derived from linseed, a crop widely grown in Europe, which contains 40 per cent oil, 30 per cent fibre, 20 per cent protein, 4 per cent ash and 6 per cent moisture. Linseed oil contains approximately 9-11 per cent saturated fatty acids (mainly 5-6 per cent palmitic acid and 4-5 per cent stearic acid), 75-90 per cent non-saturated fatty acids (mainly 50-55 per cent linolenic acid, 15-20 per cent oleic acid and 10-15 per cent linoleic acid) (Bayrak *et al.*, 2010). MLO is a widely available bio-oil, which in small quantities acts as a plasticizer in PLA, facilitates the movement of the polymer chains and improves its processing, thermal stability and ductile characteristics (Ferri *et al.*, 2017).

The aim of the present research is to determine the influence of MLO on thermal and rheological properties of nanocomposites of PLA/MWCNTs and PLA/HNTs for its application in additive manufacturing.

Material and methods

Materials

The nanocomposites used in the present studies were PLA/MWCNT and PLA/HNT, in different percentage concentrations by weight (0.5, 0.75 and 1) (Cobos *et al.*, 2019).

The plasticizer was MLO in weight percentages of 5 phr (*Oleochemicals and Linseed*, 2018).

Nanocomposite production

Before obtaining the nanocomposites, the PLA was dried for 8 hours at a 60°C temperature.

The PLA/MWCNT and PLA/HNT were first mixed in different wt. % by direct melting in a co-rotating twin-screw extruder (DUPRA) with a 30 mm diameter screw, L/D ratio = 20, at a speed of 40 rpm and a temperature profile of 200-205°C.

The nanocomposites were pelletized for mixing with MLO at a percentage of 5 phr in each sample, mixed with MLO in the extruder described above. For the FESEM analysis, the filaments were obtained by means of a 3D printer FDM. The filaments were divided after freezing them in liquid nitrogen to avoid the orientation of the nano charges due to the tensile stress caused by its fracture.

Nanocomposite characterization

Differential scanning calorimetry

The thermal properties of the samples were analyzed by differential scanning calorimetry (DSC) to determine the amount of heat absorbed or given off when kept at a constant temperature for a certain time (Suriñach *et al.*, 1992; Richard, 2008) and thus verifying the effect of MLO on the glass transition temperature, Tg, crystallization temperature, Tc, and melting temperature, Tm, of the nanocomposites mixed with MLO at 5 phr. The tests were carried out according to ISO_11357-1 and ISO_11357-3 standards.

A Mettler-Toledo 821 (Mettler-Toledo, Schwerzenbach, Switzerland) was used for the tests with a temperature program of 30-350°C at a rate of 10°C/min in a 66 ml nitrogen atmosphere.

Capillary rheometry testing

Capillary rheometry consists of subjecting the nanocomposites to melting temperature and then passing them through a nozzle to simulate the extrusion or injection moulding process to obtain the shear rate and shear viscosity properties, which are the main properties in the study of nanocomposite fluidity and the effect of MLO on the mixture. Cross-Williams–Landel–Ferry (Cross-WLF) model was used to fit the curves.

A Malvern Instruments capillary rheometer Model rh2000 was used for the tests under ASTM 3835-10 standards.

Melt flow index

The melt flow index (MFI) is the basic tool for controlling thermoplastic materials' flow qualities and determining whether they are within the required range.

The MFI 3000 Series Indexer (QUALITEST) was used to measure the nanocomposite flow index, defined as the weight in grams of the material that passes through a capillary tube of given diameter and length in a period of 10 min at a temperature of 210°C, with reference to ISO 1133.

Field emission scanning electron microscopy

The morphology of the PLA with MWCNT and HNT nanocomposites with and without 5 phr MLO plasticizer was analyzed by means of a ZEISS ULTRA 55 field emission scanning electron microscope.

Results and discussion

Differential scanning calorimetry

Figure 1 shows a graph of the PLA nanocomposites with different per cent weights of MWCNT and MLO 5 phr. Neat PLA and the DCS thermal property values are given in Table I.

Figure 1 DSC of PLA/MWCNT/MLO 5 phr nanocomposites at different percentages, and neat PLA

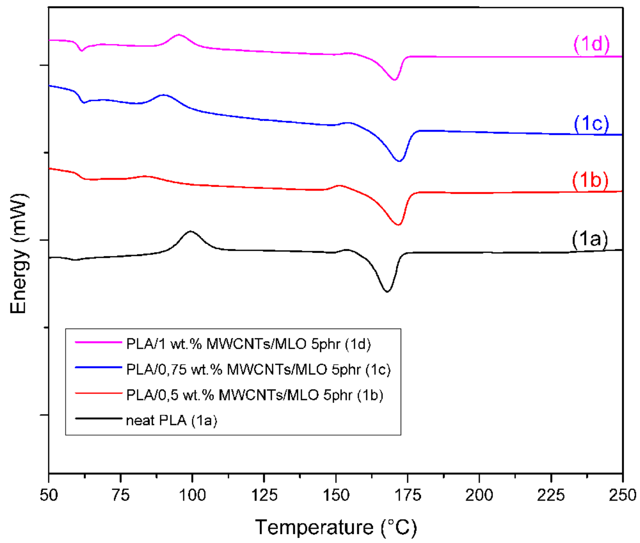


Figure 2 DSC of PLA/HNT/MLO 5 phr nanocomposites at different percentages and neat PLA

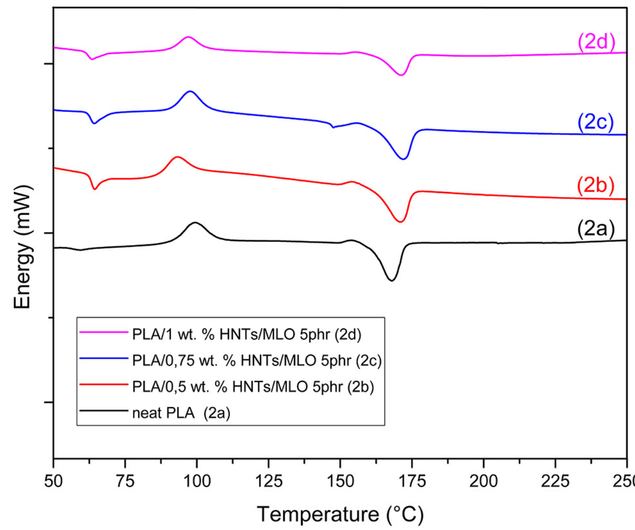


Table I Thermal parameters of PLA nanocomposites with different concentrations of MWCNTs and MLO 5 phr obtained by differential scanning calorimetry (DSC)

	PLA/MWCNTs/MLO 5 phr thermal properties			
MWCNTs (%)	**Tg (°C)**	**Tcc (°C)**	**Tm (°C)**	**Td (°C)**
0	64.33	105.55	170.69	328.19
0.5	62.68	84.51	171.56	312.37
0.75	61.39	90.73	171.83	320.17
1	61.27	95.64	170.59	331.64

Table II Thermal parameters of nanocomposites PLA with different concentrations of HNTs and MLO 5 phr obtained by differential scanning calorimetry (DSC)

	PLA/HNTs/MLO 5 phr thermal properties			
HNTs (%)	**Tg (°C)**	**Tcc (°C)**	**Tm (°C)**	**Td (°C)**
0	64.22	105.55	170.69	328.19
0.5	63.81	93.21	170.62	319.39
0.75	63.73	97.93	171.83	324.87
1	63.14	97.21	171.39	325.49

Table I shows the thermal parameters of nanocomposites obtained with MLO using the DSC test. Those with 0.5, 0.75 and 1 wt. % MWCNTs mixed with MLO 5 phr (Curves 1a, 1b and 1c, respectively) have a glass transition temperature of Tg = 62.68°C (1a), Tg = 61.39°C (1b) and Tg = 61.27 (1c), with a difference of ±2 °C between the composites, as was found in previous studies (Hua *et al.*, 2018; Zhao *et al.*, 2015).

The crystallization temperature (Tc) of PLA/MWCNTs/MLO was found to be considerably lower than that of neat PLA due to the lubricating effect of MLO. The MLO lubricant molecules become embedded in the PLA chain and cause a greater free volume in the polymer chain (chain separation), inducing a lubricating effect and facilitating chain movement so that crystallization requires less energy and occurs at a lower temperature (Li and Huneault, 2007; Ferri *et al.*, 2016a; Ferri *et al.*, 2017).

However, Tc can be seen to rise as MWCNT content increases, because of the latter reducing the movement of the polymer chain and thus raising Tc (Alam *et al.*, 2014).

As can be seen, the melting temperature between different of nanocomposites and neat PLA was around 170 ± 1°C.

Figure 2 shows the DSC curves obtained from neat PLA and those of PLA with different percentages of HNTs plus MLO plasticizer at 5 phr. The thermal property values are given in Table II.

For neat PLA (Curve 2a) and PLA nanocomposites/MLO 5 phr/HNTs at 0.5, 0.75 and 1 wt. % (Curves 2b, 2c and 2d, respectively), the glass transition temperatures are Tg = 64.22°C, Tg = 63.81°C, Tg = 63.73°C, Tg = 63.14°C for each material, respectively. It can be seen that there is little variation of 1°C in the glass transition temperature, which agrees with previous findings (Ferri *et al.*, 2016b).

Table II gives the crystallization temperatures obtained for the nanocomposites PLA/HNT/MLO: Tm = 93.21°C, Tm = 97.93°C and Tm = 97.21°C for those composed of 0.5, 0.75 and 1 per cent HNT, respectively. As in the case of PLA/MWCNTs/MLO, the MLO acted as a lubricant.

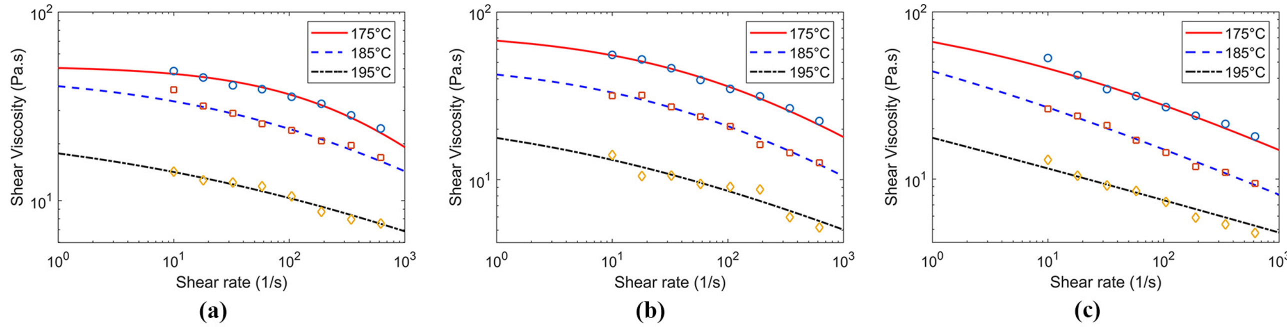
The melting temperature of the PLA/HNT/MLO 5 phr is 171 ± 1°C, similar to that of PLA/MWCNT/MLO 5 phr, indicating that MLO does not influence this material's melting temperature, in agreement with Dong *et al.* (2011), who studied neat PLA, and the findings of Ferri *et al.* (2016b), who analyzed PLA with different percentages of MLO.

The small variation of 1 °C between the Tg values of neat PLA and nanocomposites is due to MLO low degree of miscibility with PLA (Carbonell-Verdu *et al.*, 2017).

Capillary rheometry testing

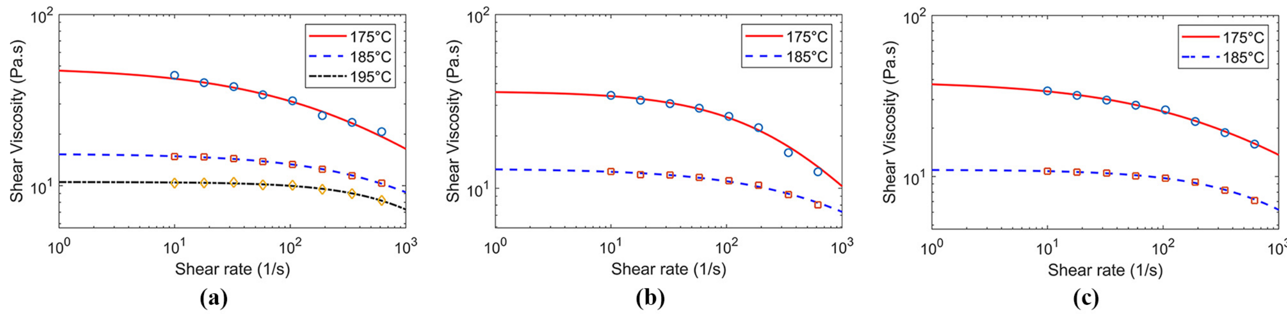
The tests were carried out at 175°C, 185°C and 195°C to determine the lubricating effect of MLO on nanocomposite

Figure 3 Variation of melt viscosity with shear stress for PLA/MWCNTs/MLO blends



Notes: (a) PLA/0.5 wt.%/ MWCNTs; (b) PLA/0.75 wt. % MWCNTs; (c) PLA/1 wt. % MWCNTs, mixed with 5 phr MLO

Figure 4 Variation of melt viscosity with shear stress for PLA/HNTs/MLO blends



Notes: (a) PLA/0.5 wt.%/ MWCNTs; (b) PLA/0.75 wt. % MWCNTs; (c) PLA/1 wt. % MWCNTs, mixed with 5 phr MLO

shear rate (resistance to flow), which is a practical parameter in polymer transformation processes.

The curves of the results of the capillary rheometry tests were fitted with the Cross-WLF model to obtain the model parameters.

Figure 3 gives the shear rate vs shear viscosity of the studied nanocomposites at different temperatures. Viscosity can be seen to diminish as shear strength increases. The flow index obtained for each material by curve fitting are below $n < 1$, confirming the pseudo-plastic behaviour (Fang and Hanna, 1999).

Flow resistance is seen to diminish as the temperature is increased in the capillary rheometer tests, because of the lubricating effect of MLO on the nanocomposites, allowing easier displacement of the polymer chains and nanocharge, which reduces the inter-molecular fraction (Ferri Azor *et al.*, 2017).

The shear viscosity versus shear rate of nanocomposites graph at different temperatures can be seen in Figure 4.

In Figure 4, it can be seen that the samples were analyzed at temperatures of 175°C, 185°C and 195°C for PLA/0.5% HNTs/MLO and that the nanocomposites containing 0.75 and 1 wt. % halloysite were only analyzed at 175°C and 185°C. This was due to the halloysite nanotubes favouring the flow due to their being easily oriented during the process and the scission of the PLA polymer chain (Kalia *et al.*, 2011; Singh *et al.*, 2016), in addition to MLO lubricant effect, reducing viscosity.

The aim of the characterization was to carry out tests up to the manufacturer's recommended temperature of 210°C for neat PLA, or the temperature at which it is used in 3D printing. As explained above, we were not able to do this at the required temperature because of the low viscosity, although the results obtained were encouraging with regard to the fluidity index,

Figure 5 The melt flow indexes (MFI) of nanocomposites of PLA/MWCNT and PLA/HNT in various nanocharge percentages with MLO 5 phr

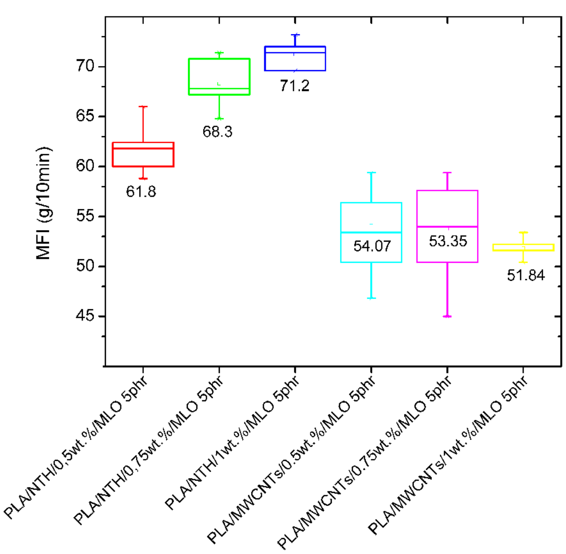


Figure 6 FESEM image of cryo-fractured cross section of 3D-printed extruded filament and nanocharge dispersion of (a) PLA/0.5% MWCNTs and (b) PLA/0.5% HNTs

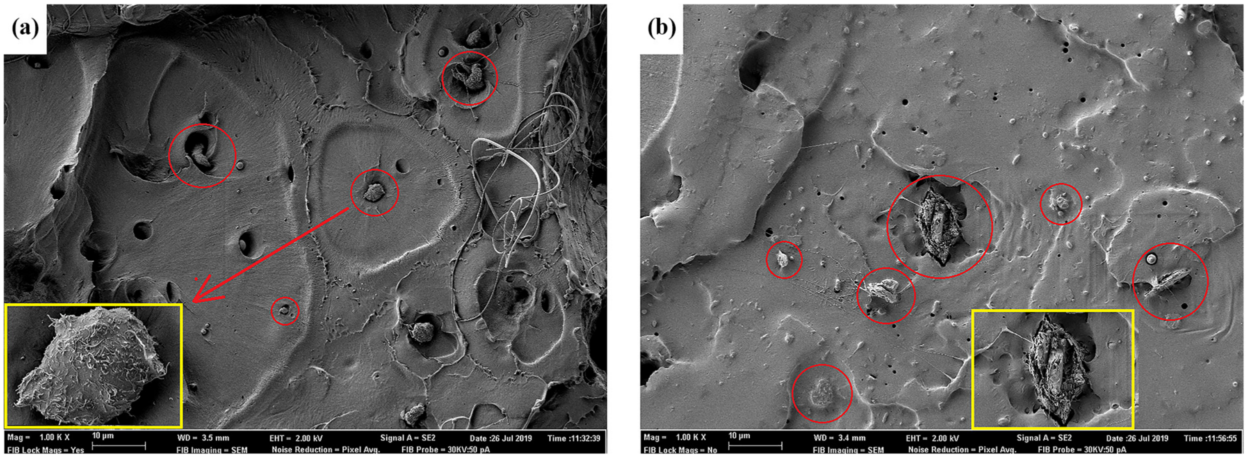
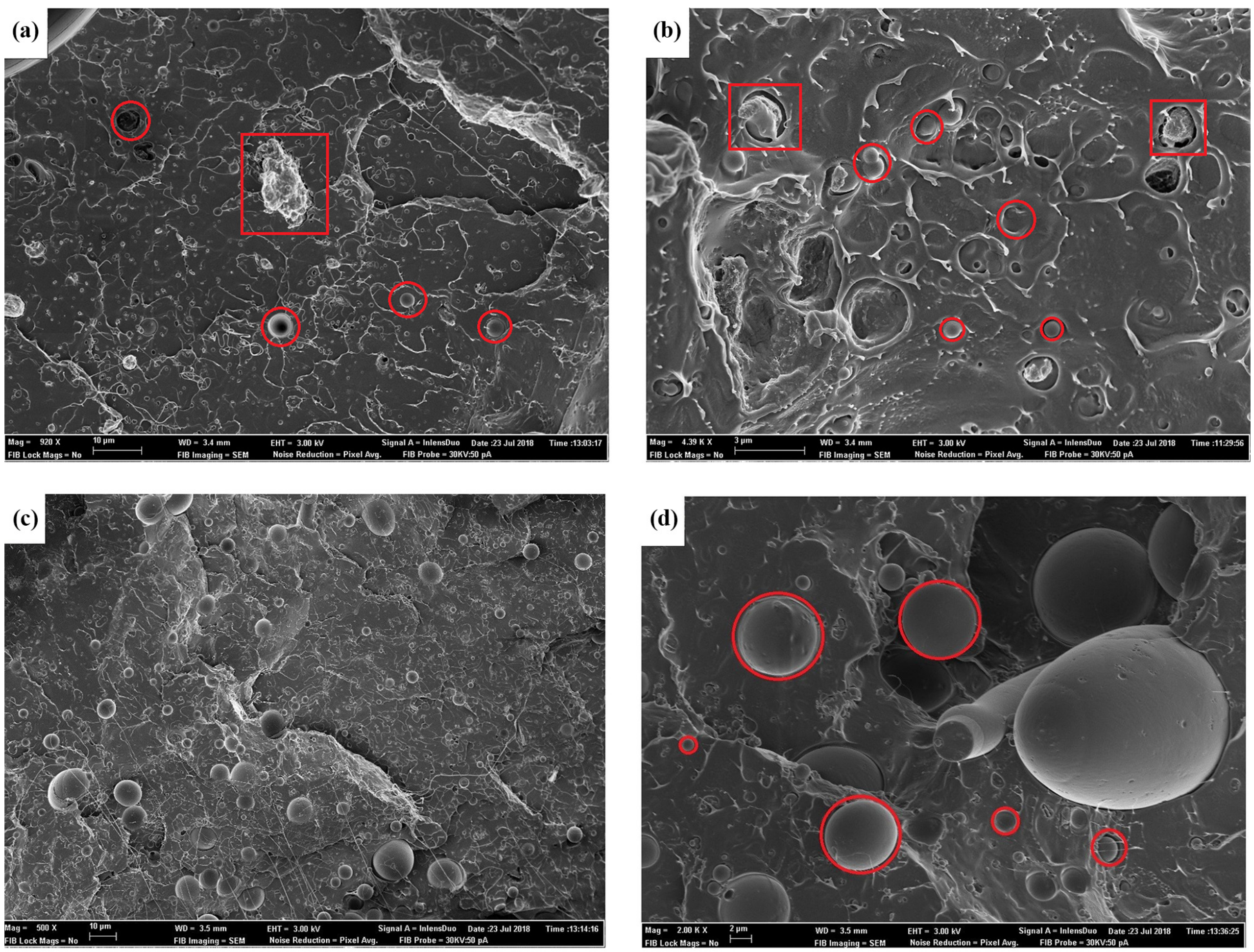


Figure 7 Imagen FESEM de sección transversal crio-fracturada de filamento extruido impreso en 3 D de dispertión de nanocarga y MLO



Notes: (a-b) PLA/0.5%MWCNTs with MLO 5 phr; (c-d) PLA/0.5%HNTs with MLO 5 phr and should allow us to print the material without blockages at the hot end of the printer.

Melt flow index

The MFI tests were carried out on a Melt Indexer 3000Q2 Plastograph (Qualitest Instruments) according to UNE-EN_ISO_1133.

Figure 5 shows that the PLA/MWCNT and PLA/HNT nanocomposites significantly increase their flow index and reduce stiffness when mixed with MLO plasticizer. These materials' MFI rose approximately 47 per cent higher than those without MLO (Cobos *et al.*, 2019) and also than those studied in Cobos Maldonado *et al.* (2014).

Field emission scanning electron microscopy

The nanocharge distribution and lubricant effect can be seen in the FESEM images.

The FESEM images of non-plasticized nanocomposites show the typical topology of fragile polymer material (Figure 6). The existence of MWCNT and HNT clusters indicates non-homogeneous dispersion of nanotubes in a fragile PLA polymer matrix [Figure 6(a) and (b)]. The plasticizing effect can also be noted in the images of nanocomposites with 5 wt. % MLO, with low PLA/MLO miscibility and spherical plasticizer shapes Figure 7(a, b, c, d), indicating MLO saturation, as described in Ferri *et al.* (2017); Carbonell-Verdu *et al.* (2017).

Conclusions

PLA/MWCNT and PLA/HNT nanocomposites were mixed with MLO in a co-rotating twin-screw extruder to study the effects of MLO on the rheological properties in subsequent FDM application tests. The DSC results indicate the non-variation in the glass transition Tg = 62 ± 2°C, and a melting temperature (Tm) around 170°C.

The composites containing MLO were found to have crystallization temperatures around 12°C lower than those of neat PLA because of the lubricant effect, which generates a higher free volume in the polymer chain, facilitating movement and reducing both the energy and temperature required for crystallization.

The capillary rheometry viscosity values of the nanocomposites with MLO were lower than without MLO.

It was not possible to carry out capillary rheometry at 195°C on the PLA/0.75 wt. % HNTs/MLO 5phr and PLA/1 wt. % HNTs/MLO 5phr nanocomposites since the halloysite nanotubes increased PLA fluidity. When MLO was included, its lubricant effect raised fluidity even higher and made it impossible to carry out the rheometry tests on the nanocomposites at the planned temperatures.

The MFI values confirmed the capillary rheometry results, with approximately 47 per cent higher fluidity in (g/10 min) than the nanocomposites without MLO.

The FESEM images showed the distribution of the nanocharges in the polymer matrix; however, there were clusters because of the lack of dispersion of the materials during the acquisition of the nanocomposites.

Also, MLO drops were observed in FESEM images.

The results obtained can therefore be considered to be encouraging since the nano-materials mixed with MLO raised the fluidity index and made the materials more versatile for 3D printing applications due to the low pressures used in this process to eject the material through the nozzle.

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