Morphological, Rheological and Electrical Study of PLA reinforced with carbon-based fillers for 3D Printing Applications

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Abstract. Three dimensional printing (3DP) is a technique that, assisted by a computer-aided design (CAD), allows fast, direct and accurate fabrication of composites with complex 3D features and a broad range of sizes. However, poor mechanical stability and the impossibility to print electrically conductive objects remain critical problems to be solved because of the thermoplastic polymer used with a 3D printer based on fused-deposition modeling (FDM). In the present work, in order to overcome such limitations, the use of polylactic acid (PLA) reinforced with two types of highly conductive nano-carbon fillers, i.e. multi-walled carbon nanotubes (MWCNTs) and graphene nanoplates (GNPs) as a novel materials for 3D printing is proposed. In particular, a morphological, rheological and electrical characterization is carried out to support their potential applicability.

Keywords: additive manufacturing; nanocomposites; 3D printing; carbon-based materials.
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INTRODUCTION

Additive manufacturing (AM), also referred to as three-dimensional (3D) printing, holds so much promise in different industrial areas since it enables much more quickly and without expensive molds or tools the fabrication of 3D physical objects that, based on 3D computer-aided design (CAD) data, may show complex microstructural arrangements respect to conventionally machined parts [1, 2, 3]. 3D printing is expected to revolutionize the prototyping of functional parts without the need for assembly and with tailored material properties and therefore new technologies are currently required in order to improve the 3D printing process and to extend its application fields [4, 5]. Among the different 3D printing systems available such as selective laser sintering (SLS), solvent-cast 3DP (SC3DP), UV-assisted 3DP (UV3DP), printing based on fused-deposition modeling (FDM) using thermoplastics polymer is commonly widespread due to the simplicity and potential applicability of the technique [6,7,8]. Although the continuous progress in the optimization of processing parameters, many critical issues still remain to be solved such as the inherently poor mechanical properties of products fabricated and the limitation of printing electrically conductive materials, both due to the nature of the polymers used. More recently, the research efforts are trying to investigate the benefits of adding nanomaterials, among which carbon-based particles, into the host matrix in order to improve the sintering characteristics and the mechanical, thermal and electrical properties of the 3D printed materials [9,10]. In this paper a novel formulation of thermoplastic composites of Polylactic acid (PLA) filled with two types of highly conductive nano-carbon fillers, i.e. multi-walled carbon nanotubes (MWCNTs) and graphene nanoplates

(GNPs) is presented. A systematic morphological, rheological and electrical characterization of the resulting nanocomposites is presented in order to exploit their potential use as new materials for 3D printing with improved general properties respect to commercial filaments currently used. The obtained nanocomposites could be used in different applications, as for example for charge storage or electromagnetic compatibility (EC) devices.

Material & Methods

The poly(lactic) acid (PLA) polymer used in this study was Ingeo™ Biopolymer PLA-3D850 (Nature Works) with MFR 7-9 g/10 min (210°C, 2.16kg), peak melt temperature 165-180 ºC, glass transition temperature 55-60 °C, tensile elongation 3.1%. Ingeo™ 3D850 is a grade developed for manufacturing 3D printer filament having some remarkable 3D printing characteristics such as precise detail, good adhesion to build plates, less warping or curling, and low odor. Industrial Graphene Nanoplates (GNPs) and Industrial Grade OH-Functionalized multiwall carbon nanotubes (MWCNTs) adopted as nanofillers were supplied from Times Nano, China. Their specific features are collected in Table 1. Nanocomposites of GNP/PLA and MWCNT/PLA were prepared by melt extrusion as varying the filler contents from 0 up to 12 wt%. Scanning Electron Microscope (SEM) was carried out by using FEI Quanta 200 FEG. at different magnifications. SEM analysis of the nanocomposites blends were done using brittle fractured composite surface prepared using liquid nitrogen. In order to make SEM analysis, the sample surface was covered with AU/Pd using EMITECH K575X. The rheological measurements were performed with AR-G2 Rheometer (TA Instruments), at steady-state shear flow using parallel-plate geometry. Steady-state viscosity was measured versus the shear rate in the range of 0.05 – 100 s^{-1}, at 200ºC and the gap size between plates of 500 µm. The measurements of the electrical properties of the composites were performed by using disk-shaped specimens of about 1 mm thickness and 50 mm diameter that are thermally pre-treated at 40 °C for 24 h. In order to reduce eventual surface roughness and to ensure Ohmic contacts both the sides of the samples have been metallized (circular form of about 22 mm of diameter) with silver paint (RS 186-3600 with Volume resistivity 0.001 Ω cm when fully hardened). The AC properties were determined in the frequency range 10 Hz–1MHz by using a Quadtec7600 dielectric analyzer. Two tests were performed for each composition. All electrical measurements were carried out at room temperature.

TABLE 1. Details of GNPs & MWCNTs

Property	**GNPs**	**MWCNTs**
Purity [wt%]	90	95
Number of layer	< 30	x
Diameter/median size [µm]	5-7	x
Aspect ratio	~240	~1000
True density [g/cm^3]	2.2	2.1
OH-content [%]	x	2.48
Length [µm] ; Outer diameter [nm]	x	10-30 ; 10-30

Results and discussions

Morphological analysis

In order to analyze the nanofiller dispersion in the PLA, the formulation with MWCNTs at 12 wt% and GNPs at 12wt% was investigated by means of scanning electron microscopy (see Figure 1 a) and b), respectively).

a) **b)**

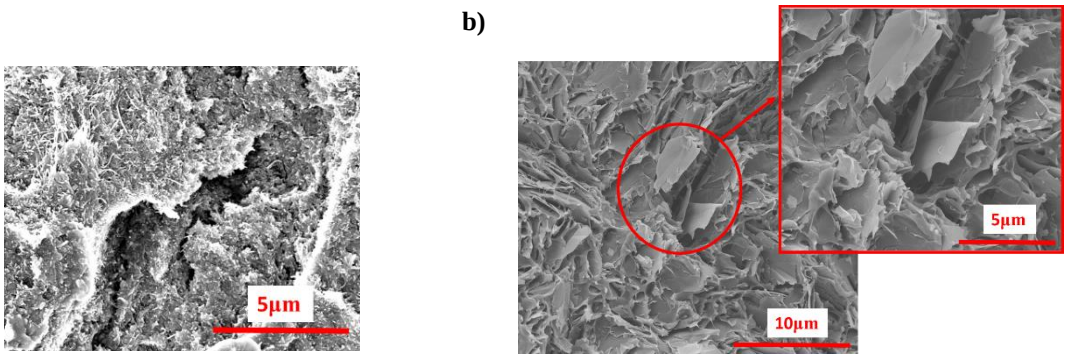

FIGURE 1. SEM images of PLA reinforced with 12 wt% of (a) MWCNTs and (b) GNPs, respectively.

A careful observation highlights that, for both fillers, a large number of the apparently discrete aggregates tend to form a network of interconnected conduction pathways inside the resin thus making it electrically conductive.

Rheological behavior

The rheological behavior in a steady-state flow mode was studied for the mono-filler systems as varying the filler contents from 0 to 12 wt%. The Figure 2 presents the viscosity (η) vs. shear rate ($\dot{\gamma}$) for: a) GNP/PLA and b) MWCNT/PLA composites. The experimental data are fit with the Carreau viscosity model (eq.1)

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\lambda\dot{\gamma})^2\right]^{(n-1)/2} \quad (1)$$

where: η_0, η_∞ are the low and the high Newtonian viscosities, λ and *n* are parameters.

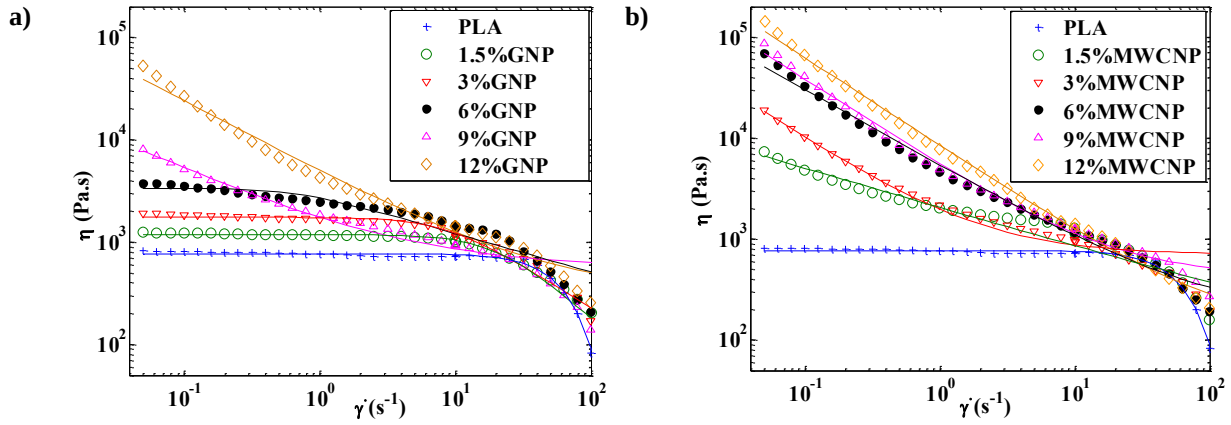

FIGURE 2. Steady-state viscosity vs. shear rate: (a) GNP/PLA and (b) MWCNT/PLA composites, as varying the filler contents. Dots show the experimental data and lines - fit with Carreau model.

As seen from Figure 2a), all the composites up to 6 wt% GNP/PLA show a high viscosity Newtonian plateau similar for that of the matrix PLA, while at 9 – 12 wt% GNP/PLA the pseudo-plastic flow behavior is observed. In contrast, the Figure 2 b) shows that a high viscosity Newtonian plateau appears only for the neat PLA, while all composites from 1.5 to 12 wt% MWCNT/PLA show a pseudo-plastic flow behavior. The transition from Newtonian to pseudo-plastic flow behavior is usually related with the rheological percolation threshold, that was determined at $\varphi_p \geq 6$ wt% and $\varphi_p \leq 1.5$ wt% for the GNP/PLA and the MWCNT/PLA composites, respectively. A good fitting of the experimental viscosity data with the Carreau viscosity model was observed.

Electrical properties

Figure 3a) shows, for both types of composites (i.e. GNP/PLA and MWCNT/PLA), the electrical conductivity as function of the filler concentration evaluated at the low frequency of 10Hz.

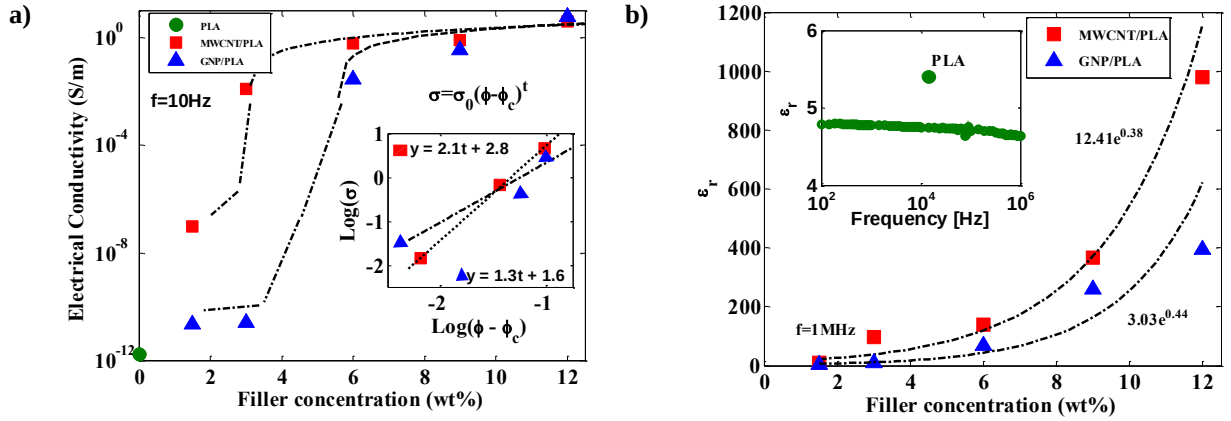

FIGURE 3. a): Conductivity of nanocomposite systems as a function of the fillers concentrations (wt%). The inset shows the log-log plot of the electrical conductivity as a function of (ϕ-ϕ_c) with a linear fit. b): relative electrical permittivity (i.e. ε_r) of the composites as function of the filler loading evaluated at the frequency of 1MHz. In the inset the spectrum of the permittivity of the neat resin (i.e. PLA) in the frequency range (10 Hz ÷ 1MHz).

It is evident that the electrical conductivity increases with the increasing weight percentage of conductive carbon-based filler. In fact, due to the formation of an electrical network of neighboring conductive particles and the possibility for electrons to flow by means of a tunneling effect, the conductivity undergoes a sharp transition respect to that of pure PLA, suggesting a percolation threshold (i.e. *EPT*) that falls in the range [1.5-3] wt% and [3-6] wt% for MWCNT/PLA and GNP/PLA, respectively. At the highest investigated concentration (i.e. 12 wt% for both fillers) the conductivity achieves the value 4.54 S/m and 6.27 S/m for PLA reinforced with MWCNTs and GNPs, respectively. When the amount of the filler exceeds the EPT, the electrical conductivity follows the well-known power law of the form:

$$\sigma = \sigma_0(\phi - \phi_c)^t \quad (2)$$

where σ_0 is the intrinsic conductivity of the filler, ϕ_c is the *EPT* and t is the so called critical exponent. In particular, its value can be obtained as the slope of the curve-fitting of the experimental data of the log–log plot of the electrical conductivity as function of the filler amount, as shown in the inset of the Figure 3a). As a result, it can be observed that the exponent t (i.e. 2.1 and 1.3 for MWCNT/PLA and GNP/PLA systems) depends on the predominant shape (3D or 2D) and morphological arrangement of the filler within the resin [11].

Due to their high breakdown strength and other interesting mechanical, thermal and chemical properties, neat polymers are the best choice of dielectric materials for charge storage applications. However, their practical applications are limited by the low value of dielectric permittivity (i.e. ε_r). Polymer nanocomposites have shown great potential in overcoming such limitation since the introduction of small amount of nanofillers can increase ε_r of resulting materials, without sacrificing the remaining properties typical of the host matrix [12]. Figure 3b) shows the exponential behavior of the dielectric permittivity as function of the filler loading evaluated at the frequency of 1MHz, whereas the inset shows the spectrum of the dielectric permittivity of the PLA in the range [100Hz÷1MHz]. Higher values for ε_r compared to that of unfilled resin (about 4.7) are observed already with small fillers amounts. Therefore, good electrical conductivity and remarkable dielectric properties achieved with the introduction of nanofillers are favorable elements for the adoption of such reinforced PLA for the fabrication through modern 3D printers of electrically conductive parts. Moreover, the possibility with a CAD design of realizing them in complex and suitable shape can strongly improve their electromagnetic (EM) interference shielding efficiency (EMI SE) thus suggesting their use for solving electromagnetic compatibility (EC) problems.

Conclusions and future works

The novel formulation of nanocarbon/poly(lactic) acid (PLA) filled with multi-walled carbon nanotubes (MWCNTs) and graphene nanoplates (GNPs) allows to achieve low percolation thresholds and high value of the electrical conductivity. The optimal composition can be defined on the basis of the application requirements. Devices with tailored characteristics can be easily manufactured due to the easy processability of the composites.

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