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Evaluation of Thermal and Electrical Conductivity of Carbon-based PLA Nanocomposites for 3D Printing

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Abstract. PLA nanocomposites for fused-deposition modeling (FDM) technique are considered. Thermal and electrical conductivity of carbon-based PLA nanocomposites are investigated looking at the different morphological characteristic of the carbon nanoparticles. In particular commercial multi-walled carbon nanotubes (CNTs) and graphene nanoplates (GNPs) are considered as_filler in order to realize filament for 3D printed devices for electrical and thermal application. In this paper a filler concentration up to 12% in weight is investigated. Transient Plane Source (TPS) measurements of thermal conductivity show that better heat conduction is obtained through the incorporation in the PLA matrix of carbonaceous nanostructures with predominantly two-dimensional shape (GNPs). DC electrical measurements show that the nanocomposite filled with the predominant mono-dimensional carbon nanoparticle (i.e. CNT) exhibits lower electrical percolation threshold, whereas a greater post percolation electrical conductivity is established with the two-dimensional filler (i.e. GNP). Such characteristics are to be considered in order to make robust and cost effective 3D printed device, by preferring 1D filler or 2D filler for electrical or thermal application respectively. Moreover, multiphase nanocomposites obtained with an optimized combination of CNT and GNP nanoparticles could be exploited to realize devices for joint electrical and thermal application.

Keywords: additive manufacturing; nanocomposites; 3D printing; carbon-based materials, FDM.
PACS: 83.80.Ab; 83.80.-k; 83.50.Ax; 72.80.Tm

INTRODUCTION

Three-dimensional (3D) printing (*aka*, additive manufacturing) is revolutionizing the manufacturing of components in different important industrial areas such as aerospace, automotive, semiconductor and plastics ones due to the ability to print in short periods of time 3D parts characterized by complex shape and variable size ranging up to micrometer dimensions, layer by layer given by CAD specifications [1,2]. Among the various techniques, printing based on fused-deposition modeling (FDM) using thermoplastics resin such as poly-lactic acid (PLA) that requires low melting temperature and rapid solidification times is widely adopted for the simplicity of the method [3,4]. The allure of the recent introduction of nanotechnology into this innovative field is the expectation of remarkable improvements and diversifications in properties of the resulting materials exhibiting optimized properties and multifunctionality, especially as concern the thermal and electrical conductivity thus overcoming the currently limitation to print electrically conductive parts [5]. In particular, for this aim there is more recently, an increasing interest in the development of high performance composites suitable for 3D printing, achieved via the introduction of carbon-based fillers with unique properties such as nanotubes, graphene and its derivate in the host polymers [6]. In

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this paper thermal and electrical conductivity of carbon-based PLA nanocomposites are investigated. More in details, commercial multi-walled carbon nanotubes (CNTs) and graphene nanoplates (GNPs) are considered as_filler in order to realize filament for robust and cost effective 3D printed devices for electrical and thermal application. The role of the predominant geometric characteristic of the filler is stressed by comparing the nanocomposites properties with the same weight concentration (wt) up to 12%.

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 (CNTs) adopted as nanofillers were supplied from Times Nano, China. GNPs purity is 90% and true density is 2.2 g/cm^3, whereas CNT purity is 95%, true density is 2.1 g/cm^3 and its OH-content is 2.48%. The weight cost of GNP and CNT filler is equivalent. Their specific geometric features are collected in Table 1. Nanocomposites of GNP/PLA and CNT/PLA were prepared by melt extrusion as varying the filler contents from 0 up to 12 wt%.

The thermal conductivity measurements were carried out using the Hot Disk® thermal constants analyzer (Hot-Disk AB Sweden) based on the Transient Plane Source technique (TPS) [7, 8]. In TPS method, an electrically insulated flat nickel sensor, placed between two pieces of a sample under investigation, plays a role of the heater and thermometer simultaneously (Figure 1).

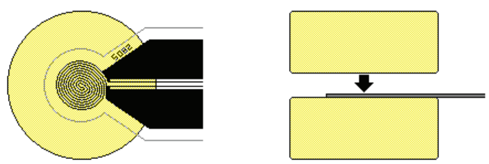

Figure 1. Schematic diagram of TPS sensor and Experimental set-up for the measurements of thermal conductivity

The thermal measurements were performed by using disk-shaped specimens of about 10 mm thickness and 50 mm diameter (Figure 2). During the measurement, a current pulse is passed through the sensor which generates heat. The time and the input power (P) are chosen so that the heat flow is within the sample boundaries and the temperature rise of the sensor is not influenced by the outer boundaries of the sample. In our case, the optimum probing depth was achieved for P= 0.100 W with a measurement time of 40 seconds at ambient temperature.

The measurements of the DC 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 measurement system is composed by a multimeter Keithley 6517A with function of voltage generator (max ± 1000 V) and voltmeter (max ± 200 V) and the ammeter HP34401A (min current 0.1 fA). Two tests were performed for each composition. All electrical measurements were carried out at room temperature.

TABLE 1. Geometric details of CNTs &GNPs

CNTs	GNPs
Outer diameter 10-30 nm	Number of layer < 30
Length 10-30 µm	median size 5-7 µm
Aspect ratio ~1000	Aspect ratio ~240

Results and discussions

FDM for sample preparation

Test samples for this study (Figure 2) were prepared by layer-to-layer deposition using Fused Deposition Modeling (FDM-FFF) type 3D printer X400 PRO German RepRap at a temperature of 200ºC and an extrusion speed of 100 mm/s. Samples were printed with a layer height of 0.2 mm and 100% infill, in a perpendicular direction of one layer to another. Extrusion nozzles with diameters of 0.4 and 0.5 mm were used for PLA and nanocomposites, respectively.

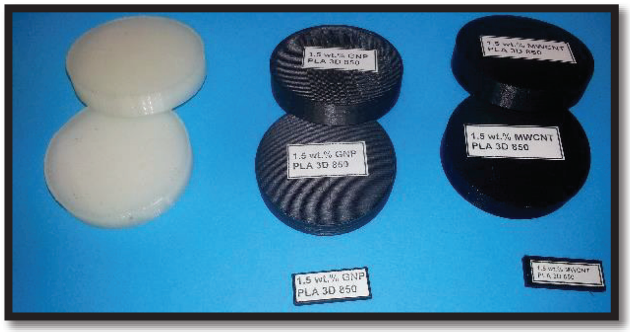

Figure 2. Some samples for thermal measurement produced with FDM technique.

Thermal measurements

Thermal conductivity results by means of Transient Plane Source Analyzer, shown in Figure 3, revealed that effectively better heat conduction is realized in PLA systems (i.e. PLA/GNP) loaded with 2-D predominant shape of Graphene (GNP) nanoparticles. For this system, experimental measurements showed an increase in the value of the thermal conductivity of about 265% compared to the net resin and an increase of about 82% with respect to the resin loaded with CNTs (i.e. PLA/CNT).

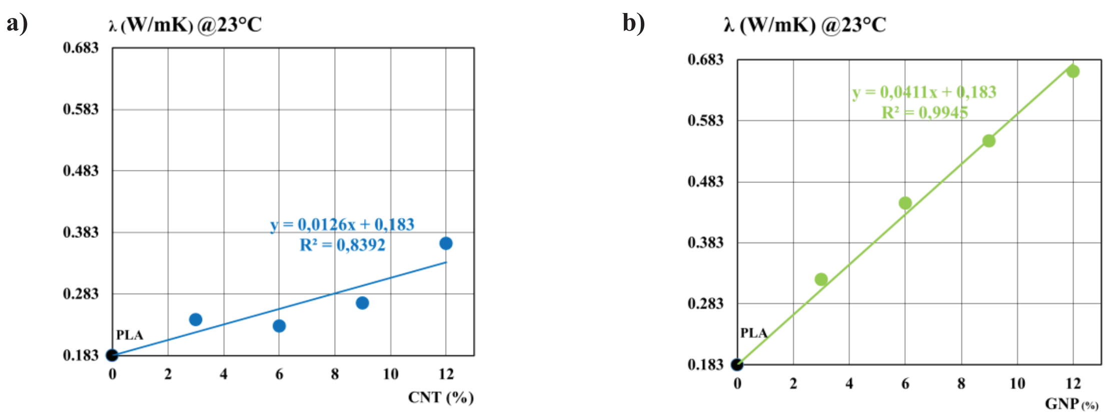

Figure 3. Thermal conductivity as varying the filler contents for CNT/PLA (a) and (b) GNP/PLA composites, respectively. Dots show the experimental data and lines the fitting curves.

In order to understand, at least roughly, the differences observed in the thermal conduction behavior, we can consider that the inner surfaces of entangled 1-D tubular CNTs may not be easily wetted by the PLA matrix adversely affecting the interfacial contact of the filler with the organic matrix resulting in a high thermal boundary resistance between CNTs filler and matrix material, that is a high value of Kapitza resistance (R_k). In the case of 2-D predominant nanofiller (GNP), it is very likely that their planar structures significantly increase the interfacial contact area between the PLA matrix and filler. This means that the interface contacts, between GNP and matrix, are characterized by a much lower thermal Kapitza resistance (R_k) if compared with carbon nanotubes. The easiest wetting of all surfaces of the nanofiller promotes the strong binding of bi-dimensional graphene sheets to the PLA based matrix providing an environment where the arrangement of graphene planes creates a network within the composite. A such arrangement is ideal for a more efficient phononic heat flow.

Electrical properties

Figure 4 shows the results regarding the electrical properties of the composites investigated in terms of electrical conductivity and percolation threshold (EPT, i.e. the minimum amount of nanofiller that changes the electrical behavior of the nanocomposites from an insulator to an electrically conductive one [9]). In particular, it is reported the variation of the bulk conductivity of the composites as a function of the filler amount (wt %) for the two types of considered carbon-based particles.

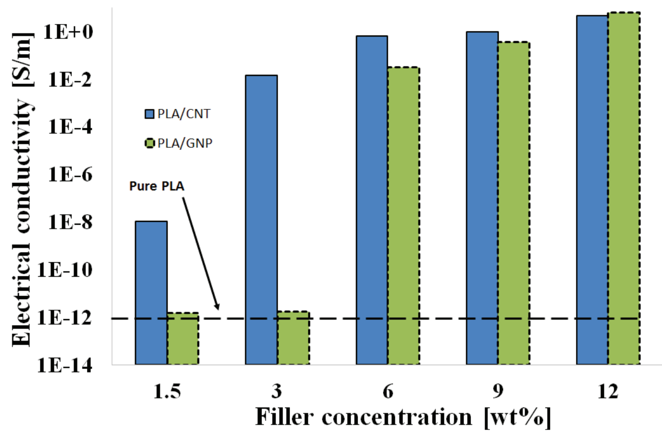

Figure 4. Conductivity of nanocomposite systems as a function of the fillers concentrations (wt%).

It is evident that the electrical conductivity increases with the increasing weight percentage of conductive carbon-based filler. Higher aspect ratio filler (CNT, see Table 1) reports a nanocomposite with an EPT that falls in the range [1.5-3] wt% with respect [3-6] wt% obtained in the GNP/PLA (four time smaller aspect ratio, Table 1). In fact, up to these minimum amounts, considerable values of electrical conductivity are observed respect to the pure PLA (few pS/m, marked by black dashed line in Figure 4). 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 CNTs and GNPs, respectively.

Conclusions and future works

Transient Plane Source (TPS) measurements of thermal conductivity show that better heat conduction is obtained through the incorporation in the PLA matrix of carbonaceous nanostructures with predominantly two-dimensional shape (GNPs). Moreover, the results shown that the nanocomposite filled with the predominant mono-dimensional carbon nanoparticle (i.e. CNT) exhibits lower electrical percolation threshold, whereas a greater post percolation electrical conductivity is established with the two-dimensional filler (i.e. GNP). Such characteristics are to be considered in order to make robust and cost effective 3D printed device, by preferring 1D filler or 2D filler for electrical or thermal application respectively. Moreover, multiphase nanocomposites obtained with an optimized combination of CNT and GNP nanoparticles could be exploited to realize devices for joint electrical and thermal application.

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