FUSED FILAMENT FABRICATION (FFF) OF ELECTRICALLY CONDUCTIVE PLA/PCL/GRAPHENE NANOPLATELETS (GNP) BIONANOCOMPOSITES

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Introduction

Conductive nanocomposites have been developed to combine the advantages of the polymeric matrix such as the good processability and low density and the high electrical conductivity of the nanofillers. Their properties are applicable in domains such as electrostatic dissipation, electromagnetic interference shielding, multilayer printed circuits, and transparent conductive or antistatic coatings [1].

Materials and methods

In this research work, melt blending using the extrusion technique (Process 11, Thermo Scientific, United States) was used to produce PLA/PCL/ graphene nanoplatelets (GNP) composites (the weight percentages of PLA2003D (Natureworks) and PCL6800 Capa (Perstorp) were fixed at 80 wt.% and 20 wt.% respectively in the polymer total weight percentage and the GNP percentage was varied between 10 wt.% and 25 wt.%). Following the components mixing by twin screw extrusion, single screw extrusion via a mini single-screw extruder NEXT 1.0 (3devo, Netherlands) was carried out to produce calibrated filaments (2.85 mm diameter) for FFF. Finally, bar and disk shaped specimens were fabricated by FFF machine (A4v3, 3ntr, Italy) and their morphology and electrical resistivity were characterized. Injection molded samples having the same dimensions were also prepared by a mini injection moulding machine IM15 (Zamak Mercator, Poland) to assess the influence of the process on the material's electrical properties.

Results

Microscopy

The microstructure investigation using the atomic force microscopy (AFM) technique (MFP-3D infinity, Asylum Research AFM, Oxford instruments) using a tapping mode at ambient conditions by AC160TSR3 tip was carried out. Obtained images showed the selective localization of the GNP in the PCL phase as it is for example indicated by yellow circles in Figure 1. In this image the dark matrix represents the PLA phase and the brighter dispersed phase represents the PCL nodules. This finding was also reached in another work [2].

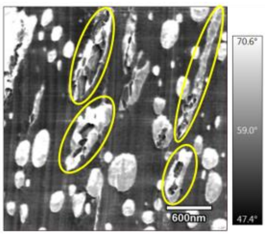

Fig. 1 – AFM phase image representing the microstructure of the injection molded PLA/PCL/10 wt.% GNP composite

The scanning electron microscopy (SEM) technique (FEI Quanta 200 SEM, Fisher Thermo Scientific) was used to observe the interface between two filaments in a final printed

PLA/PCL/15 wt.% GNP sample. Figure 2.a shows this interface of a sample that has been placed in toluene for 3 h at ambient temperature to dissolve the PCL phase while the PLA phase remains intact in these conditions. As indicated by the yellow arrows, the stacking of the graphene flakes at the interface is obvious from the zoomed image (Figure 2.b).

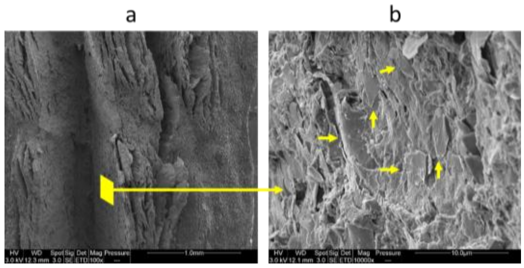

Fig. 2 – SEM image representing the interface of two PLA/PCL/15 wt.% GNP filaments after FFF (The sample was soaked in toluene before the SEM observation.)

Electrical resistivity

The electrical resistance measurement using the four probes method (Figure 3.a) was performed in order to calculate the electrical resistivity of the FFF and injection molded samples. These measurements revealed that for the same weight percentage of GNP, the injection molded samples are insulators whereas the FFF samples are semiconductors and their results are demonstrated in Figure 3.b. The reason behind this difference in the electrical resistivity between both processing techniques fabricated samples lies in their difference in morphology. For instance, in the 3D printed samples and as observed in Figure 2.b there is stacking of the graphene platelets at the interface of the filaments while this filament structure is absent in the injection molded samples and this might justify the obtained electrical resistivity results.

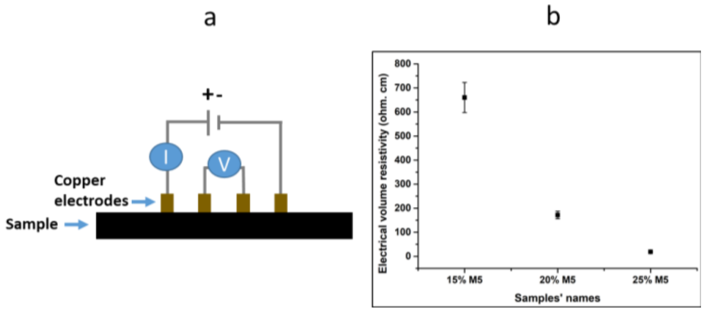

Fig. 3 – Four probes method setup scheme (figure 3.a) and the electrical volume resistivity results of the PLA/PCL/GNP composites made by FFF (figure 3.b)

Conclusions

This work aimed to produce conductive PLA/PCL/GNP composites by FFF. The atomic force microscopy proved selective localization of the GNP in the PCL phase. The scanning electron microscopy showed stacking of the graphene nanoplatelets at the interface between filaments. Thus, higher electrically conductive samples were obtained for the 3D printed samples in comparison to the injected ones at the same graphene content.

References

[1] Grossiord N., Kivit P.J.J., Loos J., Meuldijk J., Kyrylyuk A.V., van der Schoot P., Koning C.E. On the influence of the processing conditions on the performance of electrically conductive carbon nanotube/polymer nanocomposites. J. Polymer. 49(12); p. 2866-2872, 2008.

[2] de Aguiar J., Decol M., Pachekoski W.M., Becker D. Mixing-sequence controlled selective localization of carbon nanoparticles in PLA/PCL blends. J. Polym. Eng. Sci. 59(2); p. 323-329, 2019.