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Electromagnetic Properties of Filaments Containing Nanofillers For 3d Printing

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PLA filaments filled with different percentages of commercial graphene nanoplates (GNP) and multi-walled carbon nanotubes (CNT), produced for Fused Deposition Modeling (FDM) 3D-printing, are here considered. In particular, the electromagnetic properties of the filament obtained with two different processes are compared in order to assess the influence of the different procedures, named solution blending (SB) and melt extrusion (ME), on the Ka-band (26-37 GHz) behavior of the nanocomposites. First, the method of measurements of electromagnetic response of rod-shaped samples in the instrumentation waveguide is studied and implemented. Then, the electromagnetic properties of filaments loaded with nanocomposites in a maximum of 6wt% are investigated, assuming for each filler the possible value of {0,3,6} wt%. The experimental results in terms of reflection and absorption are used to estimate the complex permittivity and the AC electrical conductivity in samples under study by using a suitable created code. Filaments prepared by ME show higher values of both components of dielectric permittivity compared to SB. The highest values of relative permittivity are obtained for the bi-filler filament (3wt% GNP and 3wt% CNT) in ME processes (max value 12.73), whereas a maximum of 11.84 is reached for the relative permittivity of SB produced filament. Maximal AC conductivity is observed for composites containing 6wt% of GNP and 6wt% of CNT for SB and ME respectively. Electrical percolation thresholds (EPT) consistent with literature available DC results are detected, ranging in the explored filler amount, except for the SB produced CNT-based filament.

1. Introduction

Additive Manufacturing, generally named 3D printing, is an efficient manufacturing technology that has a variety of applications. Less quantity of materials can be used to build complex structures with flexible design freedom, thus providing more possibilities for the quality manufactory of advanced products (Guo et al., 2019). Depending on the application, several thermoplastic and thermosetting polymeric materials can be used (Wang et al., 2017). Polylactic acid (PLA) is a thermoplastic polymer derived from natural sources and it is biodegradable. It is used in several applications and has been proposed for 3D printing (Gonçalves et al., 2017; Lasprilla et al., 2011). In recent studies, nanofillers of carbon nanotubes (CNT) and Graphene (GNP) have been loaded in PLA in order to improve properties such as mechanical strength, electrical conductivity, thermal stability and bioactivity. The combination of CNT and GNP nanofillers loaded in PLA have synergetic effects on the structure and on the electrical and thermal conductivity (Ivanov et al., 2019), also on the final applications of filaments. The CNT content improves the tensile properties as a result of better filler dispersion in the polymer matrix, while the incorporation of GNP in the composite matrix has influence on the crystallinity of PLA (Batakliev et al., 2019). In multiphase PLA nanocomposites, CNT content seems to be responsible of the electrical conductivity improvement, whereas GNP amount has been highlighted as the most influencing filler in term of thermal properties, with effects on the final applications (Lamberti et al., 2018; Spinelli et al., 2019). The coexistence of both fillers leads to combination of properties in a defined range of values that the

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user could select in order to accomplish with specific Electro Magnetic (EM) constrains. The use of 3D printing for the preparation of objects with several electrical applications is particularly promising because of the improved EM characteristics as result of the peculiar structure void/filled provided. Among the most used methods to obtain a dispersion of nanofillers into a polymer matrix to produce a filament there are the solution blending (SB) and melt extrusion (ME), also known as melt blending (Kim et al., 2010; Lee et al., 2017). In SB, the polymer is dissolved in a solution and the nanofiller are mixed in order to have a homogenous dispersion, then the solvents evaporated. In ME the nanofillers are added into the molten polymer, and this allows optimization of the dispersion state by adjusting processing parameters such as mixing speed, time and temperature. The properties of the composite material may change due to the aging of the PLA polymeric structure or to the transformation steps that are carried out from the manufacturing to the use in the 3D printer. In this work, several samples of filaments loaded with different percentages of GNP and CNT, produced by two different techniques, are analyzed. The aim is to investigate the Ka-band EM properties of nanocarbon containing filaments used for 3D-printing and estimate the AC conductivity in the samples, comparing the properties of filaments obtained with different techniques. Since the structures obtained with the 3D printer take advantage of the characteristics of the filaments used, the measured properties are expected to be effective also on the final prototype. The experimental results are used to estimate the AC conductivity in samples under study and compared with DC results. The EM properties of the samples have been derived by simulation and elaboration using a program in "Phyton" environment.

2. Materials and methods

The PLA Ingeo 750 1D (Nature Works, Minnetonka, MN, USA) was used for the SB samples. A different viscosity PLA (Ingeo PLA 3D850) was adopted in the case of ME filament. GNP and CNT produced from Times Nano, China were used for preparation of nanocomposites: TNGNP and TNFN-8 for SB process and TNIGNP and TNIMH4 for ME process. The characteristics of PLA, GNP and CNT used are shown in Table 1.

Table 1: Typical material properties of raw materials used in this study (Spinelli et al., 2018)

Name /Producer	**Grade**	**Characteristics**
Polylactic acid polymer Ingeo Biopolymer/NatureWorks, USA	PLA 700 1D	Specific gravity, 1.24; MFR (210°C) = 6 g/10 min; Tg = 55-60°C; Crystalline melt temp., Tc = 145-160°C
	PLA 3D850	Specific gravity, 1.24; MFR (210°C) = 7-9 g/10 min; Tg = 55-60°C; Crystalline melt temp., Tc = 165-180°C
Graphene Nanoplatelets/ Times Nano, China	TNGNP	Purity>99.5wt%; Layers<20; Thick. 4-20nm,Size $D_{(0.5)}$=5-10μm
	TNIGNP	Purity>90wt%; Layers<20; Thick. <30nm, Size $D_{(0.5)}$=5-7μm
Multiwalled Carbon Nanotube/ Times Nano, China	TNFN-8	OD >50nm, Purity >95%, Length1-5μm
	TNIMH4	OD 10-30nm, Purity >95%, Length:10-30μm

Filaments have been made using two different techniques: solution blending (SB) and melt extrusion (ME).
With SB technique the PLA was dissolved in chloroform (ratio 1:3) whereas a suspensions of graphene nanoplatelets GNP (TNGNP) and industrial CNT (TNFN-8) were prepared in 200 mL chloroform by ultrasonic mixing and added to the dissolved PLA in a ratio according to the desired concentration. The final mixture was mechanically stirred, dried in a vacuum oven for 24 h at 70°C, milled and extruded to filament. As it concerns ME technique, fillers and polymer were dried before the composite preparation. First, two master batches of 6wt% GNPs and CNTs were prepared by melt mixing of the filler and the polymer in twin screw extruder. The masterbatches were then diluted with neat PLA by extrusion to produce nanocomposites with the desired concentration. Finally, the composite pellets were extruded to filament (Spinelli et al., 2018). The filaments produced by these techniques have the same macroscopic rod shape (1.75 mm diameter for 3D printing by FDM process) and a piece of that is reported in Figure 1 (left).

Figure 1: Filament sample (left), sample in the waveguide cell (right)

The EM properties of investigated rod samples were measured in terms of scattering parameters. Transmitted/input (S_{21}) and reflected/input (S_{11}) signals have been measured in Ka-band (27-37 GHz) using a scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania). Reflection (R), transmission (T), and absorption (A) coefficients are derived from the measured S-parameters as $R=S^2_{11}$, $T=S^2_{21}$ and A=1-R-T. The results, in terms of R and T vs frequency, have been elaborated by a suitable algorithm in order to extract the Real (*Re*) and Imaginary (*Im*) part of the complex electrical permittivity that are related to the material energy storage and energy losses capability respectively (Nielsen, 1969). Moreover, from the imaginary part of the complex permittivity also the AC electrical conductivity is derived as $\sigma_{AC}(f)=2\pi f\varepsilon_0 Im$ where $\varepsilon_0=8.854\times10^{-12}$ [F/m] is the vacuum permittivity. For that purpose, the cylindrical shaped samples were carefully placed in the middle of a waveguide perpendicular to its large side (Figure 1, right). The filaments have been mechanically reduced in size in length and, when necessary, in diameter in order to fit in the waveguide.

3. Validation of the rod method

The analytical method and the elaboration program developed have been validated measuring a filament of neat PLA and a filament of the commercial “Black Magic” (BM) (Paddubskaya et al., 2016). The results for the *Im* and *Re* part of dielectric permittivity agree with the typical insulator nature of PLA and the conductive behavior of BM. PLA filament demonstrated a quite constant complex permittivity in the explored frequency range, with a real part of about 2.8 and imaginary part 0.2 (Figure 2). The values are comparable to the experimental results performed by Paddubskaya et al. (Paddubskaya et al., 2016) on material printed with the same filament.

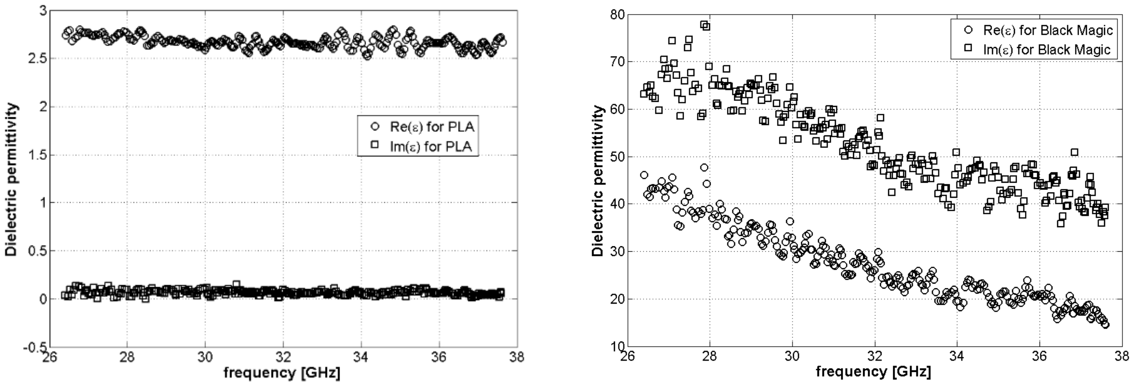

Figure 2: Results for neat PLA (left) and BM (right)

As it concerns the commercial BM filament, that is claimed to be a good electrical conductor, higher value of *Re* and *Im* part of the complex permittivity are measured. In particular, the *Im* part, containing information related to the material energy losses, confirms the presence of the unavoidable conductive loss. For this filament the AC electrical conductivity, $\sigma_{AC}(f)$, falls in the range [73, 120] S/m, with slightly increasing values with decreasing frequency, approaching the DC property σ_{DC}=167 S/m claimed by the manufacturer.

4. Results and discussion

In Table 2 the nanocomposite filaments analyzed in this work are reported.

Table 2: Samples analysed

sample	description	GNP, wt%	CNT, wt%	Preparation method
#36	6wt%CNT melt extrusion	-	6	ME
#38	3wt%CNT melt extrusion	-	3	
#39	3wt%GNP melt extrusion	3	-	
#40	6wt%GNP melt extrusion	6	-	
#43	3wt%GNP3wt%CNT melt extrusion	3	3	
#73	3wt%GNP solution blending	3	-	SB
#74	6wt%GNP solution blending	-	6	
#78	3wt%CNT solution blending	-	3	
#79	6wt%CNT solution blending	6	-	
#82	3wt%GNP3wt%CNT solution blending	3	3	

In Figure 3 the *Re* and *Im* part of the complex permittivity derived from the measured Reflection and Transmission coefficients of the SB (left) or ME (right) process filaments are reported and compared with the pure PLA data of Figure 2.

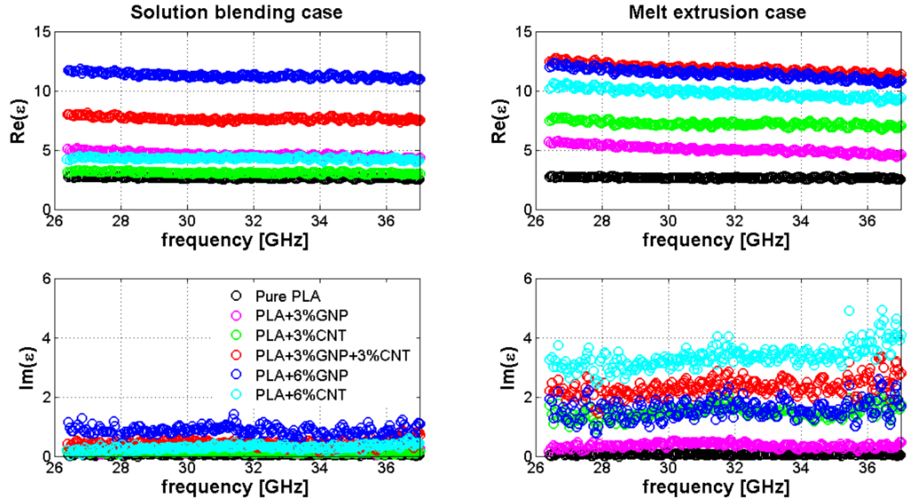

Figure 3: Re and Im part of the complex permittivity for SB (left) and ME (right) nanocomposites filaments compared with pure PLA

Re part of the dielectric permittivity slightly decreases with frequency for all the nanocomposites, faster for ME case. The introduction of fillers increases the relative permittivity of the pure PLA in all the considered cases, and consequently the energy storage material capability. The highest values are obtained for the monofiller 6wt% GNP ($10.85 \leq \varepsilon_r \leq 11,84$, left blue data) and for the bi-filler 3wt% GNP-3wt% CNT ($11.13 \leq \varepsilon_r \leq 12,73$, right red data) in the SB and ME case respectively. The latter outperform of about 4% the relative permittivity obtained measuring ME produced monofiller 6wt% GNP filament ($10.54 \leq \varepsilon_r \leq 12.36$, right blue data). A very small contribute of the filler particles is observed in the *Im* part frequency behavior of the complex permittivity for SB obtained filaments, near the pure PLA values. It means that nanocomposites keep the energy losses of the matrix. Conversely, higher ad much more scattered values of Im(ε) for ME filaments are derived for all the considered samples, except for nanocomposite filled with 3wt% of GNP nanoparticles (pink data), showing higher and different losses phenomena with respect to the neat PLA.

It is interesting to observe that the samples with the same amount of one single kind of filler show a differently pronounced effect depending on the production technique: ME samples have a higher dielectric permittivity in comparison to SB samples for both 3wt% and 6wt%. This might be related to the distribution of the filler in the matrix, that is more likely affected by the technique: in the ME preparation the polymer is melted by high temperature, with a consequent higher viscosity of the matrix, compared to the SB preparation in which the polymer is dissolved in a solvent with a viscosity of the obtained solution closer to a liquid. Consequently, during the mixing, the filler can be distributed in a more homogenous and a more organized way in the ME samples compared to the SB. In all the cases, the dielectric permittivity increases with the increasing of the total amount of fillers. Nevertheless, if the same concentrations are considered, CNT loading has a more pronounced effect in ME samples, whereas GNP in SB samples. These different results are related to the combination filler/technique. Likely, the ME allows the optimal distribution of nanometric, mainly mono-dimensional filler like CNT, whereas SB allows the distribution of plate and bi-dimensional fillers like GNP (Batakliev et al., 2019). Another important contribution to the effect discussed might be due to the different molecular weight, density and viscosity of PLA used for SB and ME techniques. The PLA used for SB has lower viscosity compared to the one used for ME, thus superimposing to the effect due to the differences in the process procedure. The general effect is that the higher viscosity of the polymeric matrix allows a better distribution of mono-dimensional CNT and lower viscosity allows a better distribution of bi-dimensional GNP.

Figure 4 reports the AC electrical conductivity of the measured filaments in Ka-band for the SB (left) and ME (right) process, compared with the pure PLA data ranging [10, 260] mS/m. The introduction of fillers increases the AC electrical conductivity of the pure PLA in all the considered cases. ME samples are much more conductive that the respective SB filaments, except for 3wt% GNP filled filament that offers a range values of [0.2,1.0] S/m doubling the [0.1,0.6] S/m derived for SB case (pink marked data). The highest σ_{AC} values are obtained for the ME filament filled with 6wt% CNT, for which 3.8 S/m$\leq \sigma_{AC} \leq$10 S/m has been found (cyan marked data in Figure 4, right).

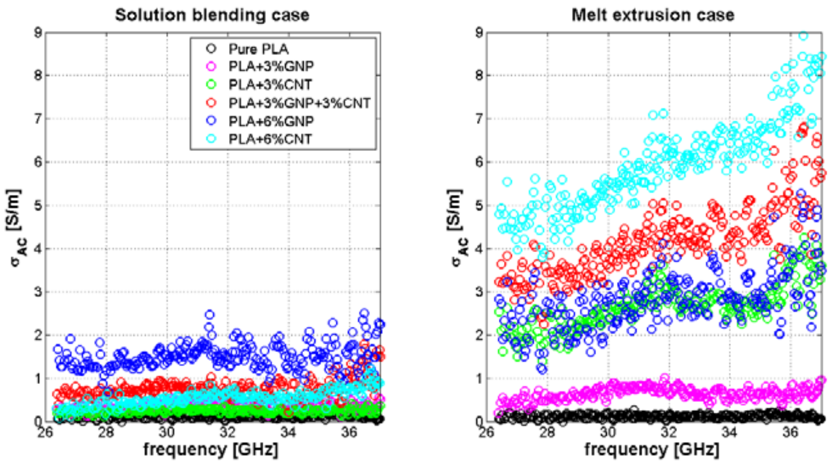

Figure 4: AC electrical conductivity for SB (left) and ME (right) filament samples compared with pure PLA

When comparing the AC conductivity measurements performed on all the samples, it can be observed that conductivities are generally higher in ME than in SB filaments and this characteristic, similarly than the case of the complex permittivity, is not dependent by the kind of filler. Though, the combination of the production technique with filler seems to influence the properties of filaments: the CNT content affects the conductivity of ME filaments, nevertheless the GNP content affects the conductivity of SB filaments. This behavior might be explained by the combination of densities with filler shape, as filler/technique peculiarity.
AC electrical conductivity of Figure 4 can be used to relate the dependence of this electrical characteristic to the filler amount. By fixing the frequency to 26 GHz or 30 GHz, the electrical conductivity percolation curves for each filler and for the different production process are plotted for the initial (up) and center (down) Ka-band frequency respectively (Figure 5). In the same figure the σ_{AC} values for the bi-filler filaments are also reported.

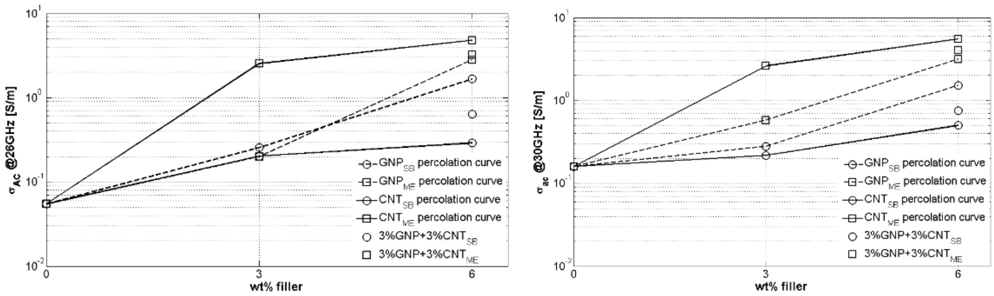

Figure 5: AC electrical conductivity, at fixed frequency of 26 GHz (left) and 30 GHz (right), vs filler amount.

Figure 5 shows that also in Ka-band the introduction of conductive fillers in the insulator matrix leads to a nonlinear dependence of the electrical conductivity with respect to the filler amount, with a slightly lower pronounced effect as the frequency increases. A synergic effect of the two fillers is highlighted from the position of the bi-filler-filament conductive value that is higher than that obtained by summing the single-filler-filament of 3wt% nanocomposites value. Furthermore, the data reported in Figure 5 agree with the DC electrical measurements performed by (Spinelli et al., 2018), showing that the electrical percolation threshold (EPT), that is the percentage of filler content that generates an increase of the electrical conductivity of some order of magnitude with respect to the pure matrix, is lower than 3wt% for the ME, whereas it is not yet reached up to 6wt% for SB produced filaments filled with CNT. Furthermore, EPT is between 3wt% and 6wt% for GNP based nanocomposites both in the case of SB than ME production process. Therefore, also in the Ka-band, it seems that EPT is dependent on the production process for CNT mono-dimensional filler whereas it is irrespective in case of GNP two-dimensional filler. Since the structures obtained with the 3D printer take advantage of the multifunctionality given to the filament by the nanofillers, we expect that the introduction of CNT modifies the electrical properties and improves the conductivity and the permittivity and of the GNP improves the thermal performances and modifies the properties of the starting polymer (PLA) that is an insulator, producing structures able to interact with the electromagnetic radiation with improved thermal properties.

5. Conclusions

Generally, samples prepared by ME show higher values of both components of dielectric permittivity, *Re* part and *Im* part, compared to SB prepared samples. Maximal AC conductivity is observed for composites containing 6wt% of GNP and 6wt% of CNT for SB and ME respectively and the highest absolute value related to the CNT loaded filaments obtained by ME. All the effects on the properties of the filaments loaded with CNT and GNP can be related to the combination of the kind of filler, mainly in relation to the specific shape, and the production technique, mainly related to the modification of the viscosity of the polymeric matrix during the process.In future, it would be interesting to compare the results of AC conductivity analyses of the filaments with DC analyses. Moreover, we expect that in the final application the structures obtained with the 3D printer might take advantage of the multifunctionality given to the filament by the combination of the nanofillers. In future works it is planned to compare the properties of filaments with the final prototype obtained.

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