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Carbon nanotubes vs graphene nanoplatelets for 3D-printable composites

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Abstract. Polymer-based composites with nanocarbon fillers are of great interest for the wide
application range including the needs of wireless communication and the development of precise
measuring means and medical devices. However, the composite properties such as excellent
electromagnetic energy dissipation or tailorable conductivity are not enough to solve practical
problems in engineering. To be fully applicable, the composite material must be low-cost and
suitable for conventional methods of fabrication, for example 3D-printing. In current research
the electromagnetic properties of PLA-based composites with graphene nanoplatelets and
multiwall carbon nanotubes were investigated in microwave frequency range. The synergistic
effect of two fillers was observed, the investigated materials proved to be prospective for 3D-
printable composite production for electromagnetic applications such as fabrication of complex
geometry microwave shields and antennas.

1. Introduction

Carbon nanofillers such as multiwall carbon nanotubes (MWCNT) or graphene nanoplatelets
(GNP) of low concentrations can change the thermal, mechanical [1] and electromagnetic
properties [2, 3, 4, 5] of a composite making it suitable for many practical applications [6].
Nevertheless the use of nanocomposites in industry is very limited due to the processing
complexity and expensiveness.

The current research is focused on the application of conventional polymer technologies to
nanocomposites development with an intent to overcome the technological limitations and bring
carbon nanocomposite materials closer to industrial applications. It is obvious that besides the
target properties (conductivity, mechanical strength, etc.) a new material must be compatible
with conventional processing methods. For instance, additive technologies are perfect for
creation of complex structures for electromagnetic applications [7, 8]. The fused deposition
modeling (FDM) 3D-printing technology is the most popular among the diversity of additive
technologies. The working principle of the FDM 3D-printer is simple: the polymer filament is
extruded through the heated nozzle placed on moving head and deposited layer by layer forming

a part. Due to its simplicity and low cost the FDM printers are widely used around the world for prototyping and creation of custom parts and devices.

The most popular materials for FDM 3D-printing are polymers: Nylon, acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA) which can be used as a dielectric matrix for a composite material. The sufficient impact of nanocarbon fillers such as MWCNT to the permittivity ε of a composite allows to reach the desirable ε values properties with minimal necessary filler content and, thus, minimize the deterioration of mechanical properties. High filler contents can cause composite fragility and lead to the growth of melted material viscosity. The latter plays an important role in FDM printing process: the problem with flow caused by high viscosity can lead to an instability in layer forming. Thus the minimization of filler content is an important problem for further application of 3D-printable composites. Besides the intrinsic properties of filler particles, the effect of filler addition depends on its distribution inside the polymer. The spatial dispersion of filler particles can be affected by the agglomeration, polymer matrix properties and technical process peculiarities [9]. One of possible ways to optimize the filler content is the use of a synergistic effect between two fillers with different properties.

2. Theory
The standard approach for relatively low concentrations of nanoscale fillers inside of a dielectric matrix the Maxwell Garnett (MG) theory:

$$\varepsilon_{eff} = \varepsilon_m + \sum_{filler} \frac{1/3 \sum_{i=a,b,c} n\alpha_i/V}{1 - 1/3 \sum_{i=a,b,c} \frac{N_i n\alpha_i/V}{\varepsilon_m}}, \tag{1}$$

where ε_m — is the polymer matrix permittivity, n — volume concentration of filler, represented as ellipsoid with semiaxes a, b, c; α_i and N_i — are ellipsoid polarizability and depolarization factor in direction i respectively. Such a representation of filler particles as randomly oriented ellipsoids with intrinsic polarizability is conventional for composites with nanoscale filler modeling [10, 5]. It is important to understand that for real composite the ellipsoid in MG model stands not for actual nanoparticles with their specific parameters, but for effective particle which can be an agglomerate or aggregate. Thus without exact knowledge about the inner structure of the composite equation 1 may be represented as:

$$\varepsilon_{eff} = \varepsilon_m + \sum_{filler} \varepsilon_{add\ filler}, \tag{2}$$

where $\varepsilon_{add\ filler}$ — is an addition to effective complex dielectric permittivity made by specific amount of filler. In case of two non-interacting fillers A and B the electromagnetic response will be:

$$\varepsilon_{eff} = \varepsilon_m + \varepsilon_{add\ A} + \varepsilon_{add\ B}. \tag{3}$$

In this case the values of ε_m, $\varepsilon_{add\ A}$ and $\varepsilon_{add\ B}$ can be evaluated from the experimental data obtained from the measurements of empty matrix and composites containing only fillers A and B. In order to account the possible interaction between fillers and following synergistic effect the ε_{syn} addition can be introduced as:

$$\varepsilon_{eff} = \varepsilon_m + \varepsilon_{add\ A} + \varepsilon_{add\ B} + \varepsilon_{syn}. \tag{4}$$

3. Materials & Methods
To check the synergy in composites with nanocarbon the set of PLA-based (Ingeo PLA 3D850 was used) composites with industrial MWCNT and GNP (TimesNano, China) fillers was made. As the main aim of the research is to come up with an industrially applicable technology, the

conventional method of melt mixing was used. Twin screw extruder was used to distribute fillers inside the polymer and obtain two masterbatches with 6 wt. % of GNP and MWCNT concentrations respectively. Composites with lower filler contents and combinations of two fillers were obtained by masterbatches dilution with pure PLA. Samples for measurements were then hot-pressed in plane layers of ~1 mm thickness.
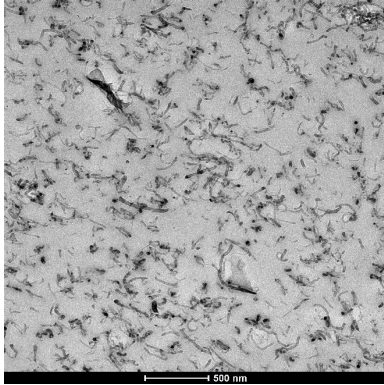

Figure 1. TEM image of composite containing 1.5 wt. % of GNP and 4.5 wt. % of MWCNT. The most of particles are well-dispersed
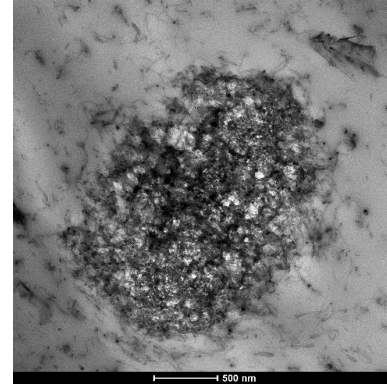
Figure 2. TEM image of composite containing 4.5 wt. % of GNP and 1.5 wt. % of MWCNT. The agglomeration is observed in between well-dispersed nanoparticles

The inner structure of the composites was investigated by means of transmission electronic microscopy. The microscopic images show that the most of filler particles are dispersed well and separated from each other (figure 1), but besides the separated particles all composites contain agglomerates (figure 2). As reported before [11, 12], the percolation threshold for the investigated composites was between 1.5–3 wt. % for MWCNT-filled, 3–6 wt. % for GNP-based and 1.5–3 wt. % for 50/50 bifiller composite. The percolation threshold for GNP particles in different polymers starts from ~5–10 % [3, 13].

The electromagnetic response of all investigated composites was measured in two microwave ranges of 0.01–18 GHz and 26–37 GHz (Ka-band) using MICRAN R4M vector analyzer and Elmika R2-408R scalar network analyzer respectively. The plane-parallel layers of investigated composites were precisely cut to match the dimensions of coaxial airline (in case of vector analyzer) and rectangular waveguide (scalar analyzer) and positioned normally to the wave vector of initial radiation (figure 3).
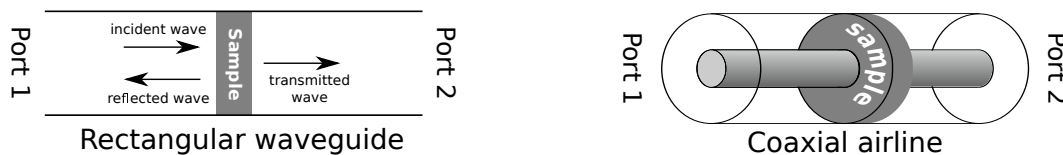
Figure 3. The sample fixture in rectangular waveguide (left) and coaxial airline (right).

The electromagnetic response was registered as ratios between the amplitude of reflected (transmitted) and incident radiation (S-parameters). The conductivity and complex dielectric permittivity were recalculated from S-parameters by standard methods [14] solving the following equations:

$$S_{11} = \frac{-j[(k_z/k_{2z})^2 - 1]\sin(k_{2z}\tau)}{2j(k_z/k_{2z})\cos(k_{2z}\tau) + [(k_z/k_{2z})^2 + 1]\sin(k_{2z}\tau)} \tag{5}$$

$$S_{21} = \frac{2(k_{2z}/k_z)}{-2(k_{2z}/k_z)\cos(k_{2z}\tau) + j[(k_{2z}/k_z)^2 + 1]\sin(k_{2z}\tau)} \qquad (6)$$

where τ is sample thickness, a is waveguide width, $k_z = \frac{\pi}{2\lambda}\sqrt{4a^2 - \lambda^2}$ and $k_{2z} = \frac{\pi}{2\lambda}\sqrt{4a^2\varepsilon - \lambda^2}$ ($k_z = \frac{2\pi}{\lambda}$ and $k_{2z} = \frac{2\pi\varepsilon}{\lambda}$), where λ is wavelength and ε is dielectric permittivity, are wavenumbers in waveguide and freespace (or coaxial airline) respectively.

4. Results & Discussion

4.1. Monofiller composites

The electromagnetic response of composites containing 0, 1.5, 3, and 6 wt. % of GNP and MWCNT was measured in both available frequency ranges. In both ranges MWCNT-based composites demonstrate higher dielectric permittivity and conductivity values than GNP-based ones.
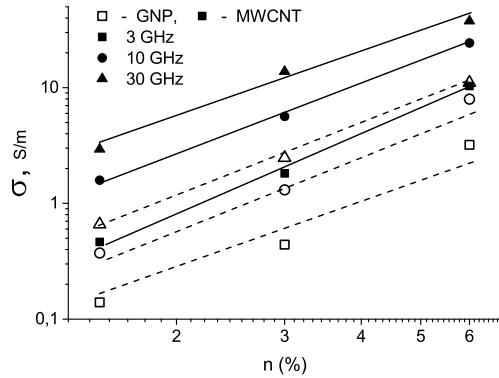
Figure 4. Composites conductivity dependence on filler content has exponential character similarly to a well-known empiric law $\sigma \simeq (n - n_0)^t$, where n_0 is percolation threshold concentration, $t \in [0, 1]$.

Such a behavior is in a good agreement with literature and can be explained by the difference in fillers aspect ratios [15] and volume resistivities (about 240 and <0.15 $\Omega{\cdot}$cm for GNP particles versus 1000 and >0.01 $\Omega{\cdot}$cm for carbon nanotubes). As shown at figure 4, the conductivity dependence on filler concentration follows the exponential law.

4.2. Bifiller effect to complex permittivity

Filler combinations with total concentrations of 3 and 6 wt. % were prepared. Their complex permittivity is in figures 5–6. The first to be noticed that the value of permittivity's imaginary part ε'' is proportional to MWCNT concentration for both tested filler contents. The highest permittivity values at the series with 3 wt. % of total nanocarbon concentration were reached by the composite with 3 wt. % of MWCNT. In contrary, for the series with 6 wt. % of total filler content the highest values of ε' in Ka-band were reached by the composites containing mixtures of two fillers (figure 6). In the lower frequency range the ε' values for MWCNT-only and 4.5 % MWCNT+1.5 %GNP composites are also very close.

Such a difference between 3 and 6 wt. % series can be explained by the fact that in first case the GNP concentration is lower than its percolation threshold, whilst in second case it is close to percolation. In case of 4.5 % MWCNT+1.5 %GNP the nanotubes exceed can compensate the above-percolation value of GNP content.
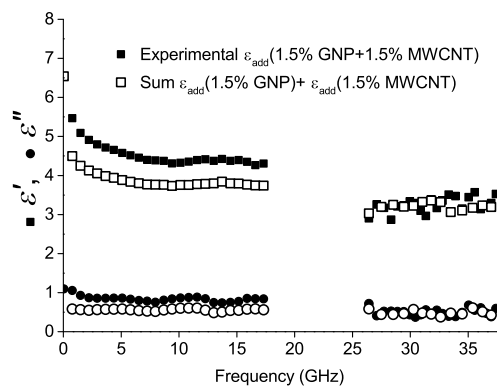
4.3. The synergistic effect observation

The permittivity additions for composites containing 1.5 and 3 wt.% of GNP, 1.5 and 3 wt.% of MWCNT and mixtures of total 3 and 6 wt.% (1.5 wt.% of GNP + 1.5 wt.% of MWCNT
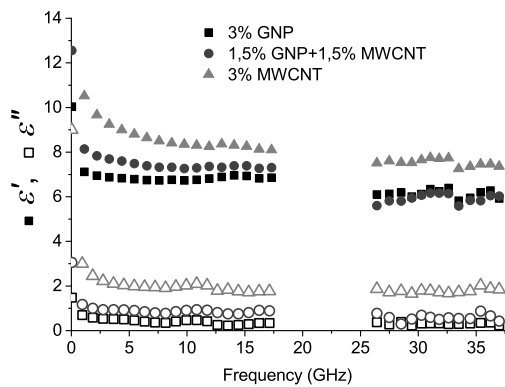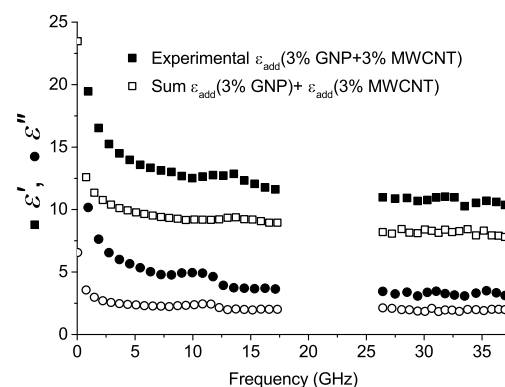
Figure 5. The complex permittivity of composites with 3 wt. % total filler content.
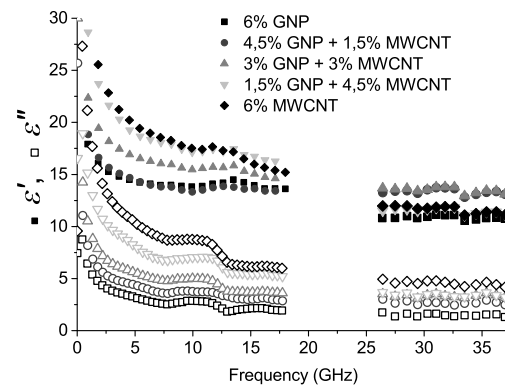
Figure 6. The complex permittivity of composites with 6 wt. % total filler content.

Figure 7. The complex permittivity addition by 1.5% GNP +1.5% MWCNT filler mixture vs sum of permittivity additions by 1.5% GNP and 1.5% MWCNT fillers. Experimental data is in good agreement with sum in 26–37.5 GHz range

Figure 8. The complex permittivity addition by 3% GNP +3% MWCNT filler mixture vs sum of permittivity additions by 3% GNP and 3% MWCNT fillers. The value of separate filler additions is lower than experimental data

and 3 wt.% of GNP + 3 wt.% of MWCNT respectively) of nanocarbon content were calculated according equation 3. Monofiller additions were summarized and compared with bifiller ones.

According to obtained experimental data, for composites containing 3 wt.% of total nanocarbon content the synergistic exceed is more or less noticeable only in lower of two measured frequency ranges (figure 7). In Ka-band the electromagnetic response of bifiller composite is in agreement with a sum of two additions taken from monofiller composites. Thus in 26–37 GHz range the GNP and MWCNT fillers can be considered as non-interacting.

The different situation is observed at total 6 wt.% series (figure 8). The complex permittivity value increase of synergistic origin is noticeable in both measured ranges. Such an effect can be explained by interactions between fillers nanoparticles. MWCNT/GNP agglomerations must have different typical dimensions in comparison with aggregates of only GNP or MWCNT.

5. Conclusions
The PLA-based composites containing different concentrations of GNP, MWCNT and their combination were produced by melt-mixing technique and investigated in microwave frequency

region. The frequency-dependent synergistic effect between GNP and MWCNT fillers was observed in form of a complex permittivity value increase. This effect makes possible the minimization of filler content which is vital for 3D-printing applications. The difference in effect of investigated fillers to real and imaginary parts of permittivity was demonstrated: MWCNT filler affects both parts of complex permittivity whilst GNP impacts mainly ε'. These fillers properties can be useful for the electromagnetic response tailoring which simplifies the fabrication of FDM filaments with specified dielectric permittivity. Such materials can be applied for the production of microwave optical elements, complex geometry electromagnetic shields, etc. The use of conventional melt-mixing method for composite preparation appears to be prospective: in spite of having a certain amount of agglomerates the most of filler particles are dispersed well. Further work in this direction must be focused on decrease of filler content and enhancement of dispersion stability.

Acknowledgements

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