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Graphene 3D

Multifunctional Graphene-based Nanocomposites with
Robust Electromagnetic and Thermal Properties for
3D-printing Application



Conference on Nanoscience and Nanotechnology (n&n) Frascati, Italy, 18-20
December, 2018

Electromagnetic characterization of binary and ternary polyethylene nanocomposites based on GNPs and MWCNTs

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Introduction

RISE PROJECT GRAPHENE 3D

MULTIFUNCTIONAL GRAPHENE-BASED NANOCOMPOSITES WITH ROBUST ELECTROMAGNETIC AND THERMAL PROPERTIES FOR 3D-PRINTING APPLICATION

OBJECTIVES:

- Develop and produce polymer nanocomposite material, doped by graphene and carbon nanotubes, with robust multifunctional properties for 3D printing application.
- Fabricate 3D printed cellular structures for power electronics application with predefined properties (electromagnetic wave absorption, thermal conductivity, mechanical strength and lightness) on the basis of modeling, simulation and experimental validation.
- Create “Joint Laboratory on Graphene-Polymer Research” for long-term knowledge impact.

<http://graphene3d.imbm.bas.bg>
graphene3d.project@gmail.com

Materials and preparation

Powder of HDPE -> ROWALIT N100-20



- Size of particles 0-80µm;
- Melting Flow Index (MFI) 20;
- Density 0.956 g/cm³;
- Melting range 125-128°C;
- Heat resistance of 110°C;

Graphene nanoplatelets -> TNGNP



- Purity 99.5%;
- Thickness 4-20nm;
- Number of layers < 20;
- Average size of 5-10 µm;
- Aspect ratio ~500;

MWCNTs-> NANOCYL® NC7000™



- Purity 90%;
- Surface area 250-300 m²/g;
- Average diameter 9.5*10⁻⁹m;
- Aspect ratio ~150;

Binary composites



Wrapped by ball mill



Melt mixing of binary and ternary nanocomposites

Characterization of nanocomposites

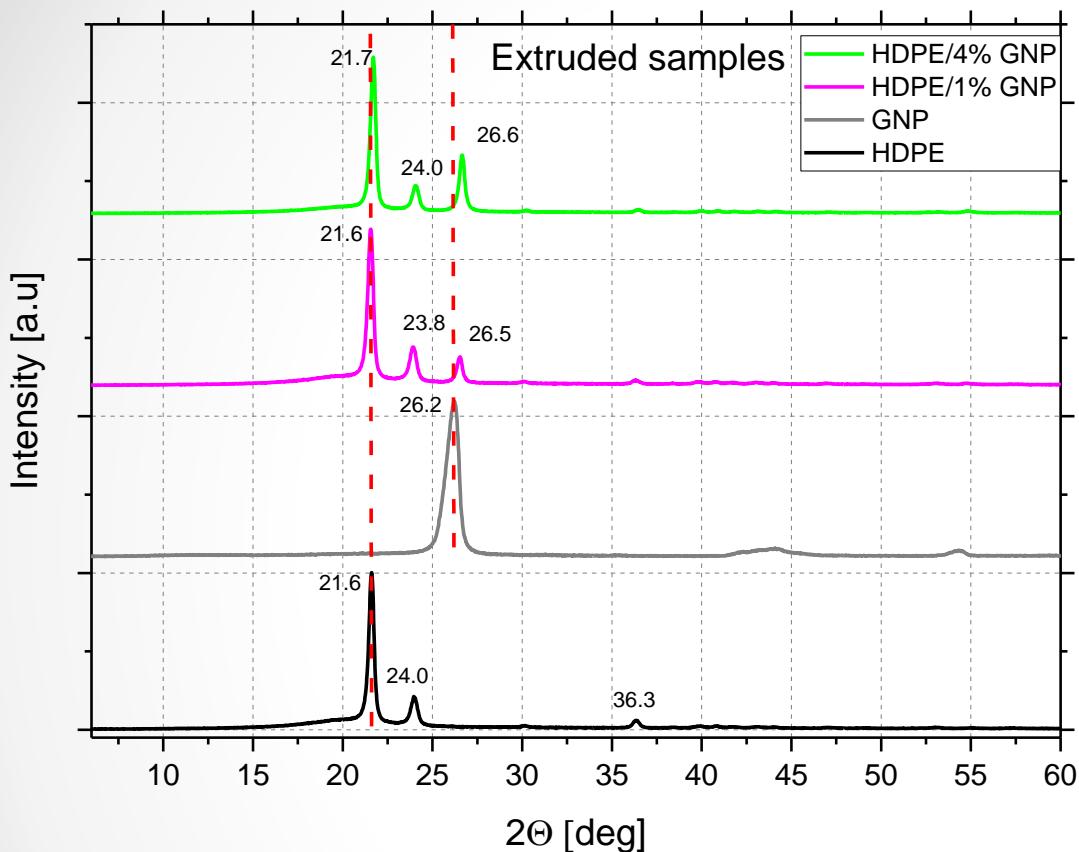
- ✓ X-ray diffraction of binary composites by Rigaku “MiniFlex” benchtop X-ray diffractometer

EMI shielding characterization of binary and ternary composites

- ✓ Measurements at low frequency by a capacitance bridge “HP4284 A”
(20 Hz – 1 MHz)
- ✓ Two GHz ranges:
 - Vector network analyzer Micran R4M
(12 – 18 GHz)
 - Scalar network analyzer Elmika R2408R
(26 – 37 GHz)
- ✓ Measurements at high frequency
(0.2 – 1 THz)

Type of composite	Filler content [wt%]
Binary	0.5
	1
	2
	3
	4
Ternary	0.25 + 0.25
	0.5 + 0.5
	1 + 1
	1.5 + 1.5
	2 + 2

XRD of binary nanocomposites



Extruded samples

- HDPE/4% GNP
- HDPE/1% GNP
- GNP
- HDPE

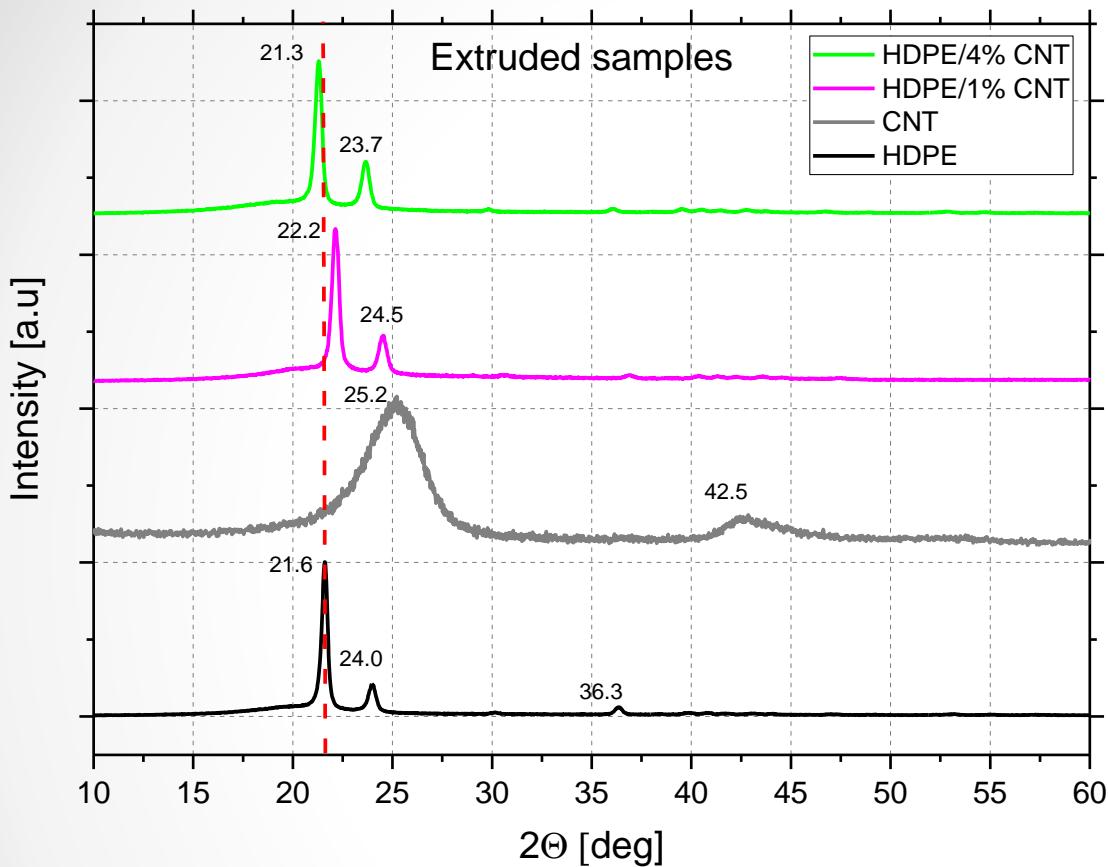
21.6° and 24.0°
 \downarrow
 $(1\ 1\ 0)$ and $(2\ 0\ 0)$ lattice planes of the HDPE crystals

Crystallinity
 \downarrow
Nucleation effect

Extruded samples	Crystallinity [%]
Pure HDPE	25.7
HDPE/1wt% GNP	30.8
HDPE/4wt% GNP	28.9

[1] B.J. Kim, K.M. Bae, M.K. Seo, K.H. An, S.J. Park, Mater. Sci. Eng. A 528 (2011) 4953.

XRD of binary nanocomposites



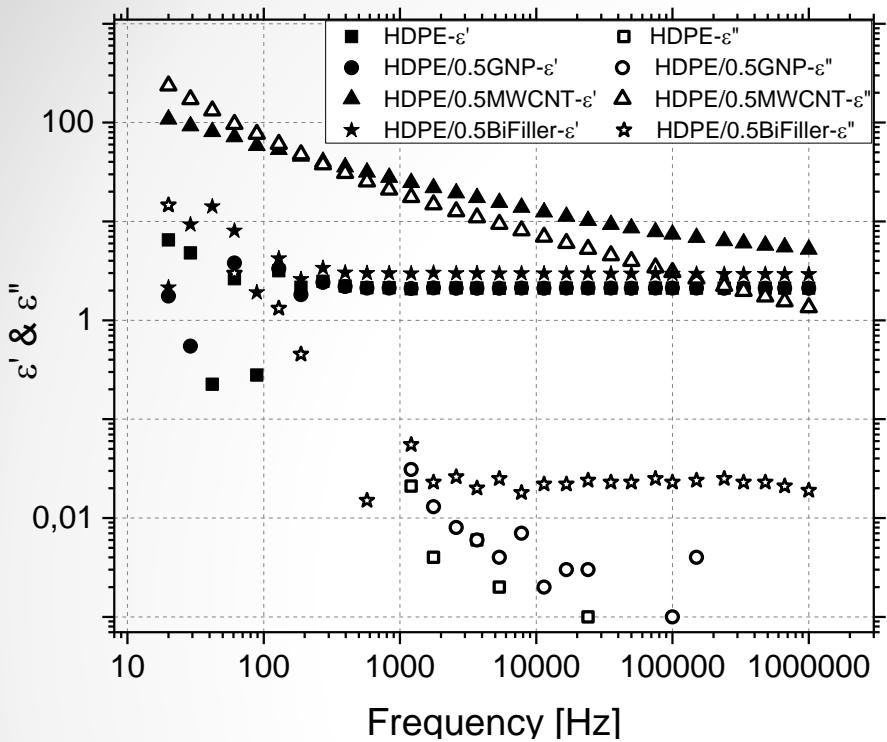
Lack of MWCNT peaks

An efficient mix of the
MWCNTs in HDPE

Extruded samples	Crystallinity [%]
Pure HDPE	25.7
HDPE/1wt% MWCNT	25.1
HDPE/4wt% MWCNT	29.0

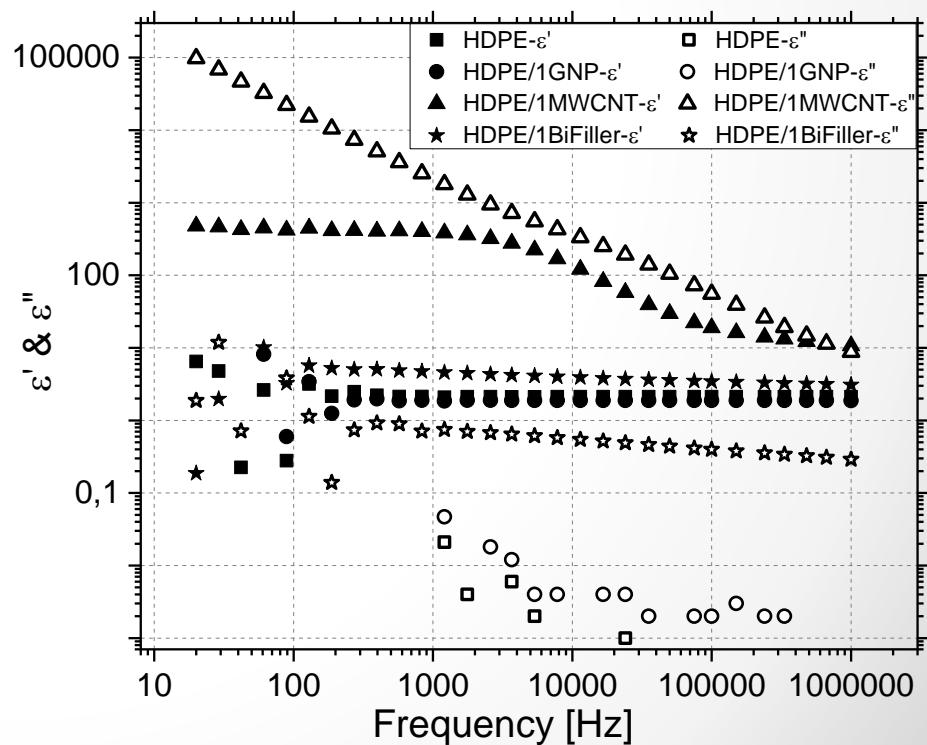
[2] T. McNally, P. Potschke, P. Halley, M. Murphy, D. Martin, S. Bell, G.P. Brennan, D. Bein, P. Lemoine, J. Quinn, Polymer 46 (2005) 8222.

Low frequency

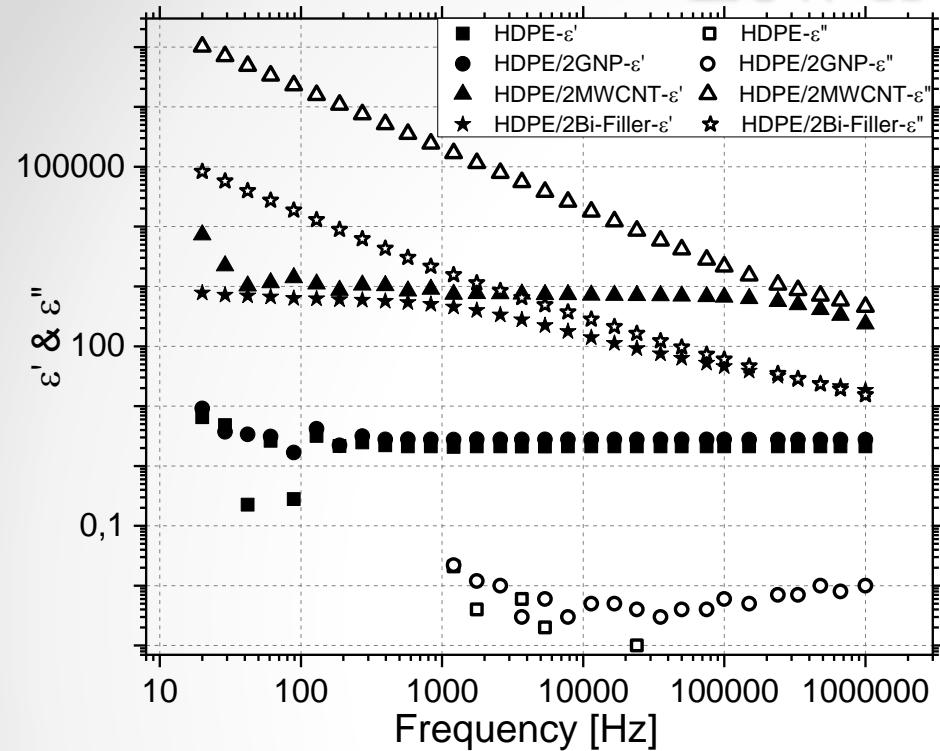


Not significant effect in GNP
and Bi-Filler nanocomposites

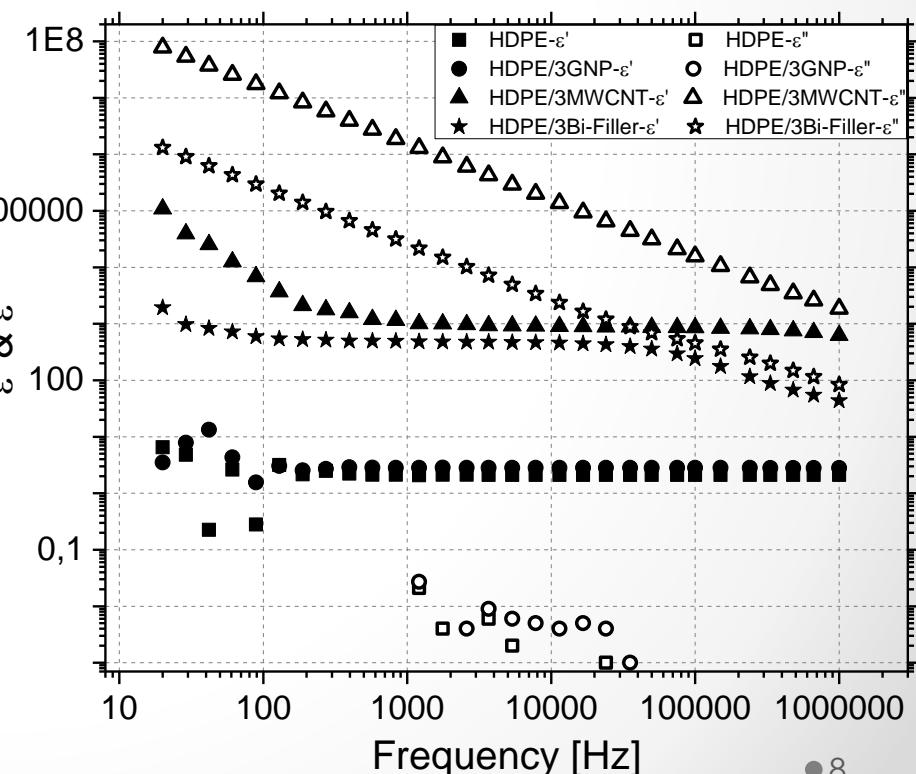
20 Hz – 1 MHz



Low frequency

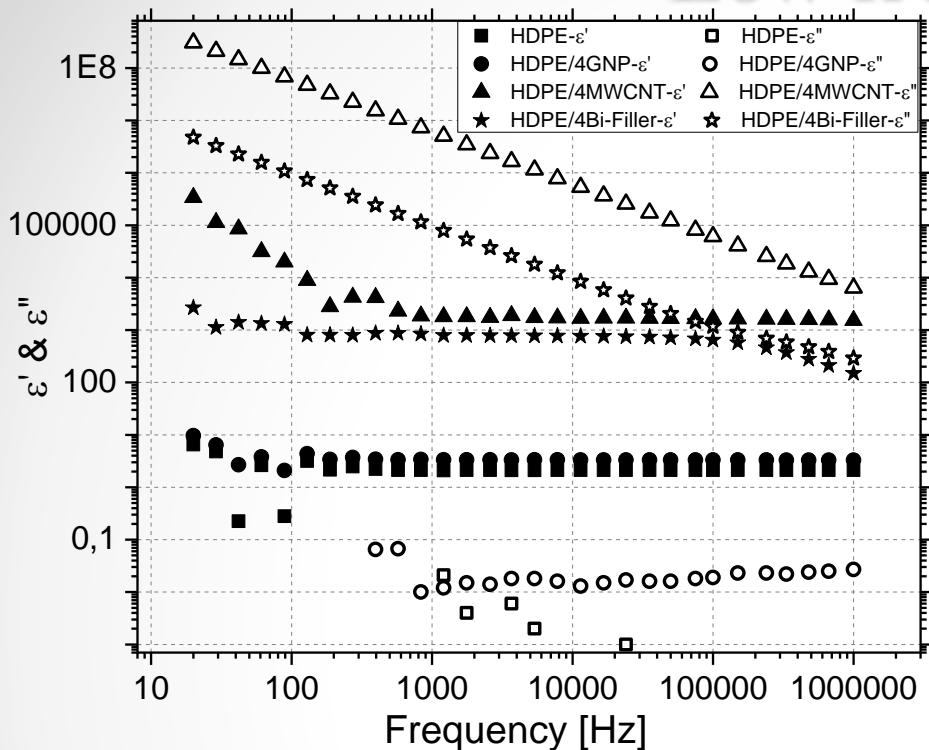


20 Hz – 1 MHz



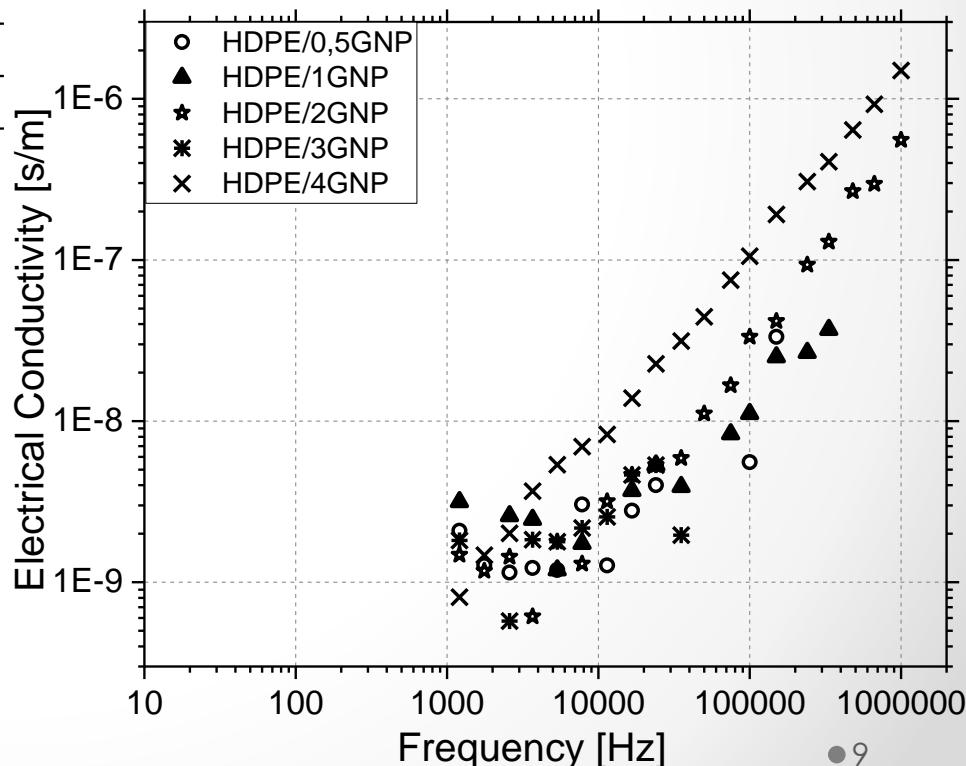
Enhanced dielectric
permittivity in MWCNT and
Bi-Filler composites

Low frequency

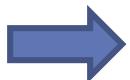


20 Hz – 1 MHz

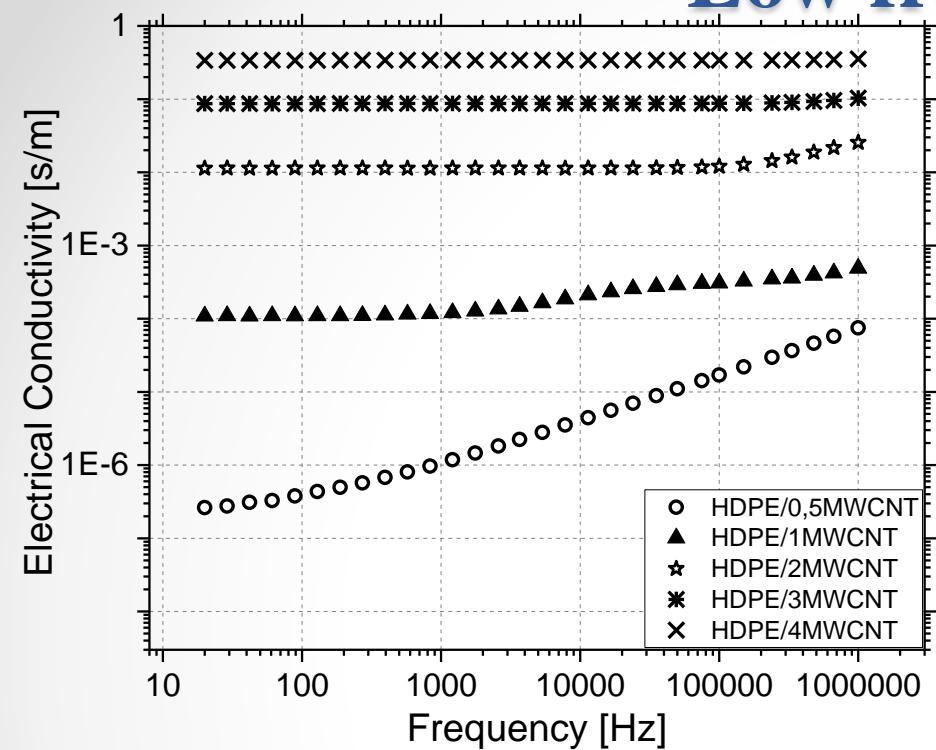
Not conductive GNP composites



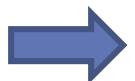
$$\sigma = 2\pi\epsilon_0\nu\epsilon''$$



Low frequency



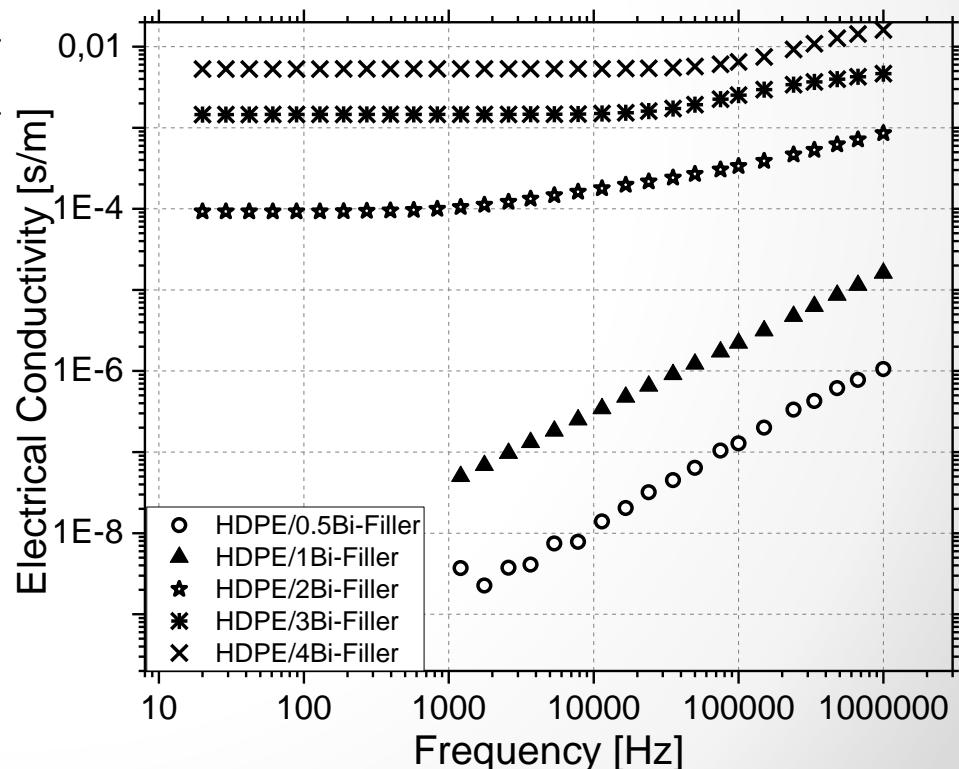
$$\sigma = 2\pi\epsilon_0\nu\epsilon''$$



20 Hz – 1 MHz

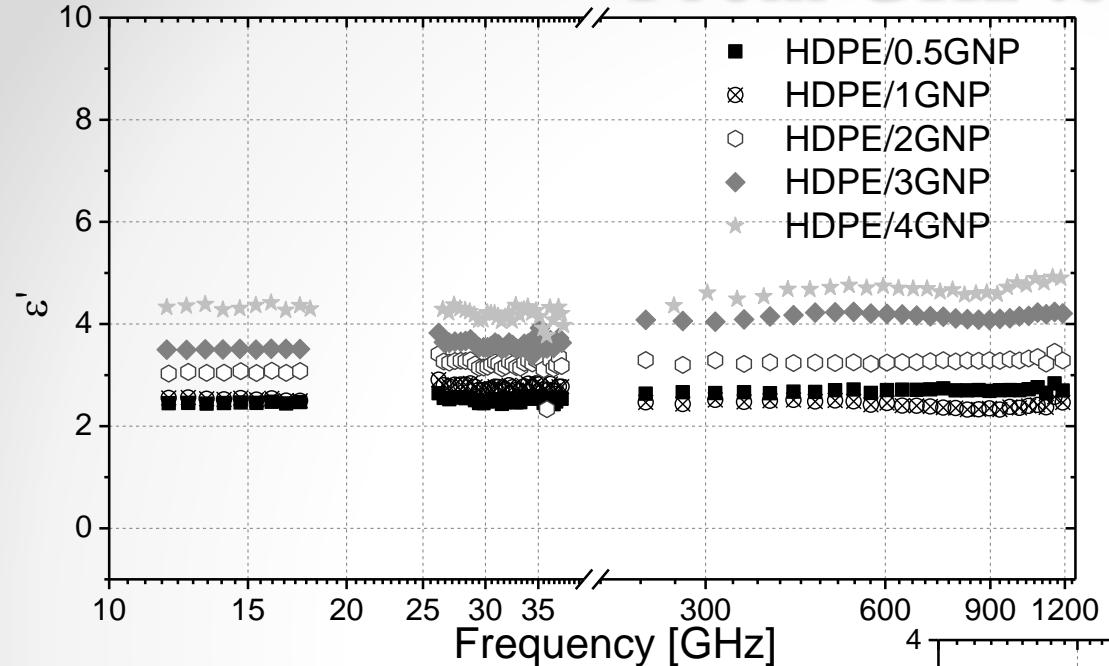
Percolation threshold:

- between 0.5 and 1wt% MWCNT
- 2wt% Bi-Filler



From GHz to THz

GRAPHENE
3D

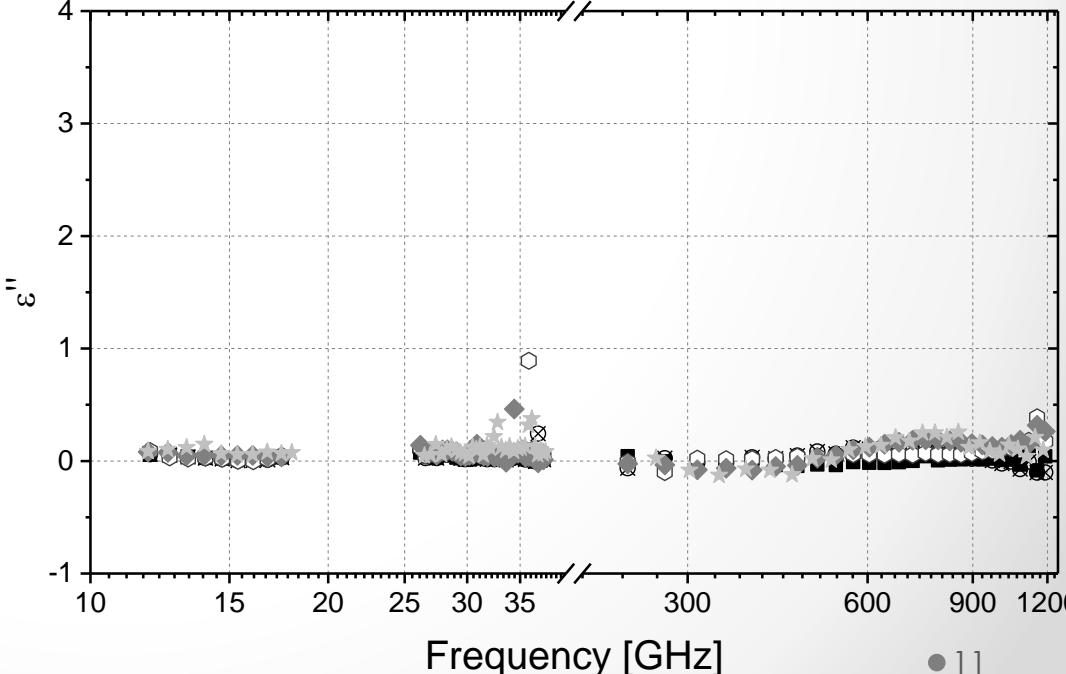


12 – 18 GHz

26 – 37 GHz

0.2 – 1 THz

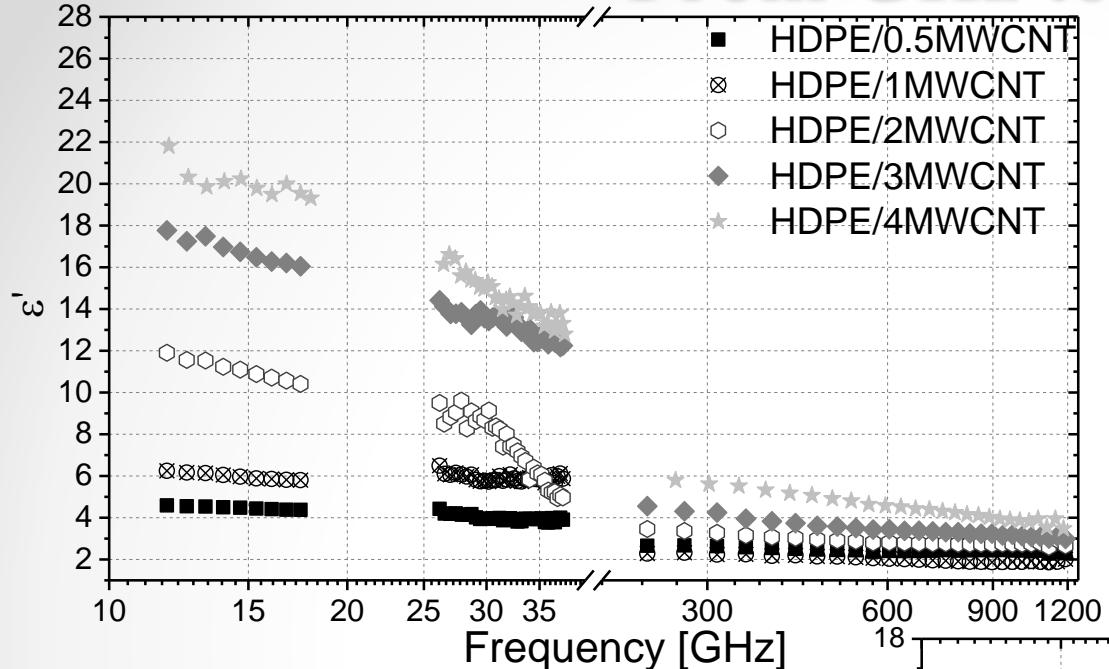
Slight effect on the dielectric permittivity



[3] J. Backer-Jarvis, R.G. Geyer, P. D. Domich, en, IEEE Transactions on Instrumentation and Measurement, Oct. 1992, 41, 646-652.

From GHz to THz

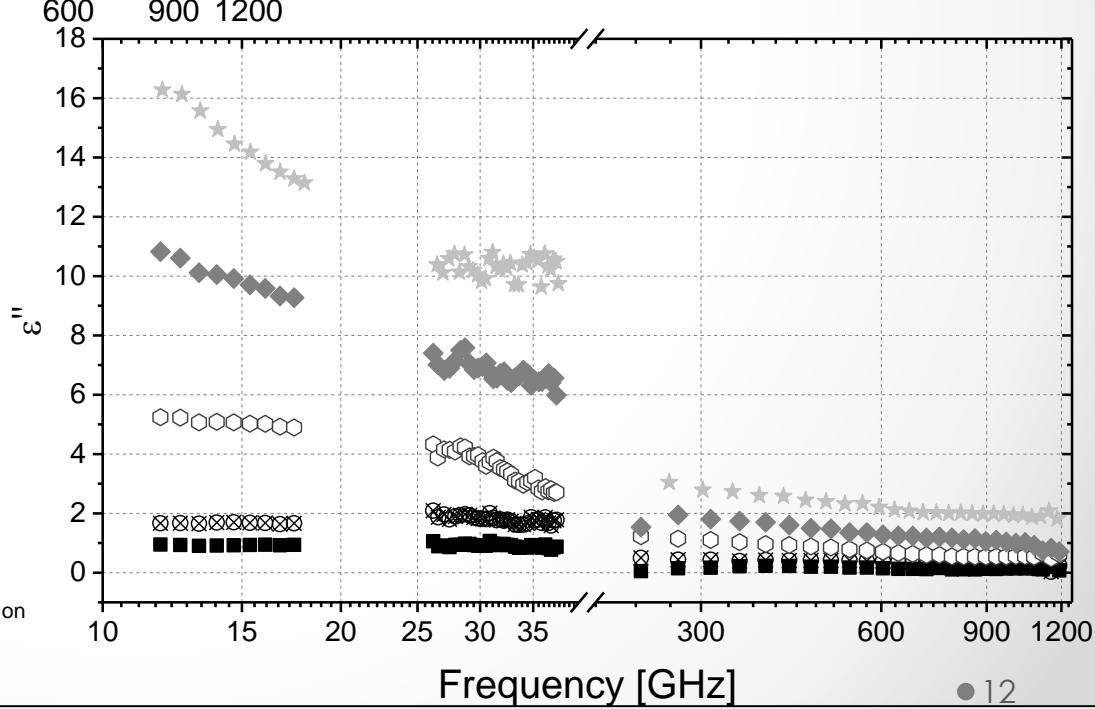
GRAPHENE
3D



12 – 18 GHz

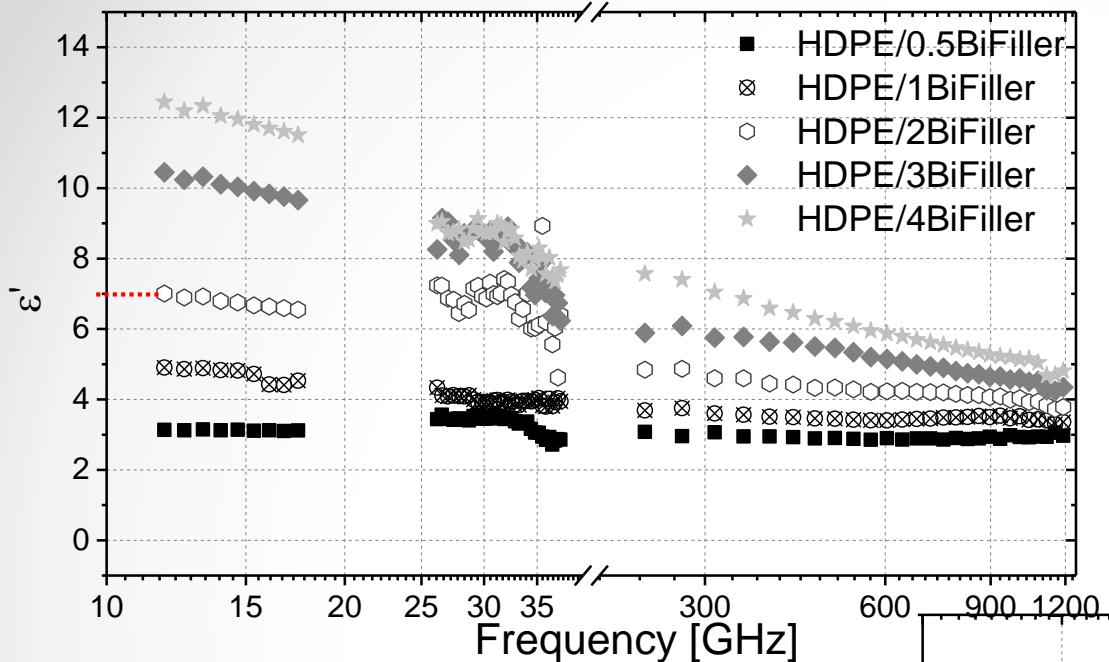
26 – 37 GHz

0.2 – 1 THz



[3] J. Backer-Jarvis, R.G. Geyer, P. D. Domich, en, IEEE Transactions on Instrumentation and Measurement, Oct. 1992, 41, 646-652.

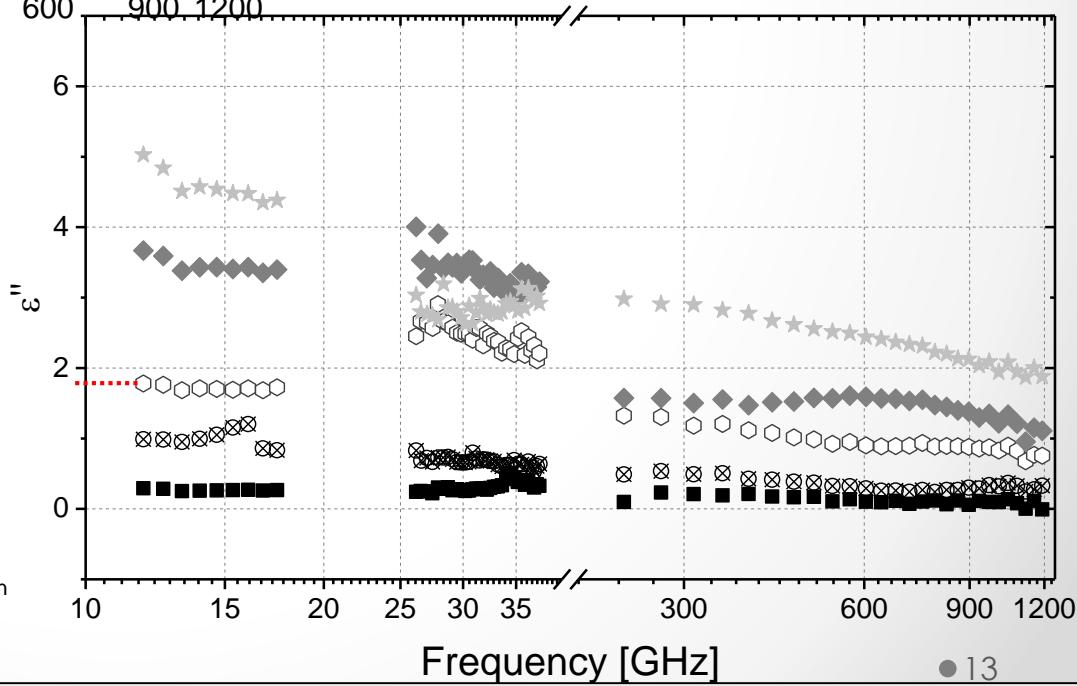
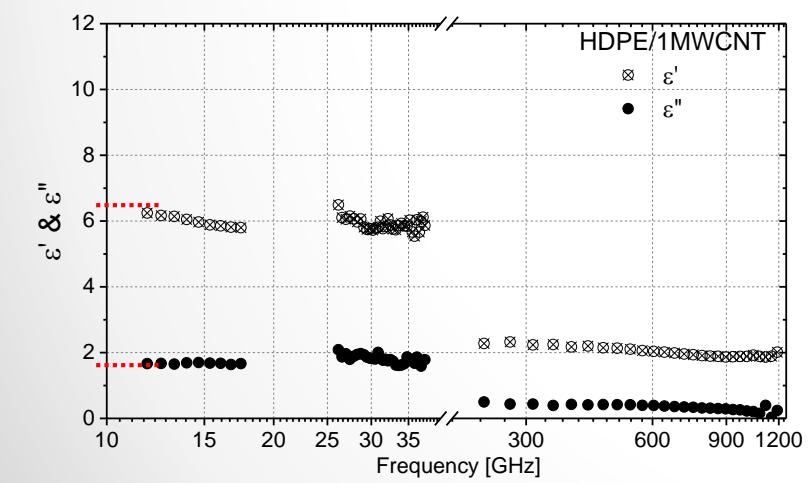
From GHz to THz



12 – 18 GHz

26 – 37 GHz

0.2 – 1 THz



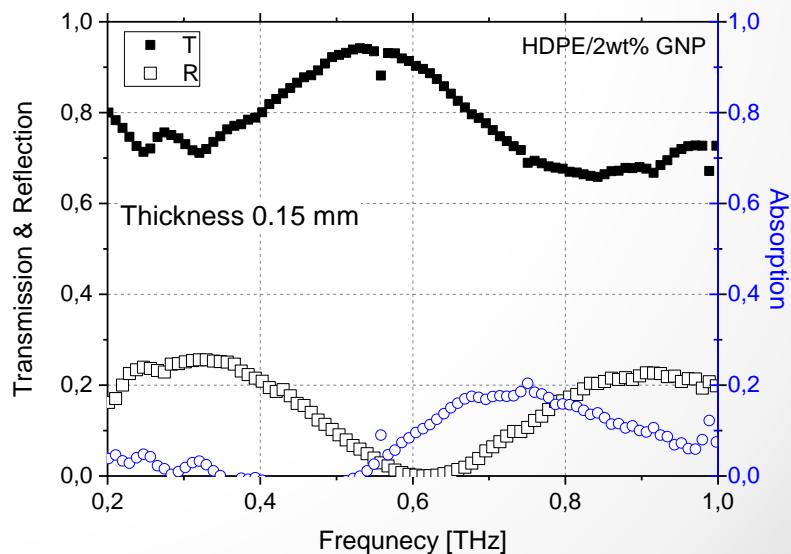
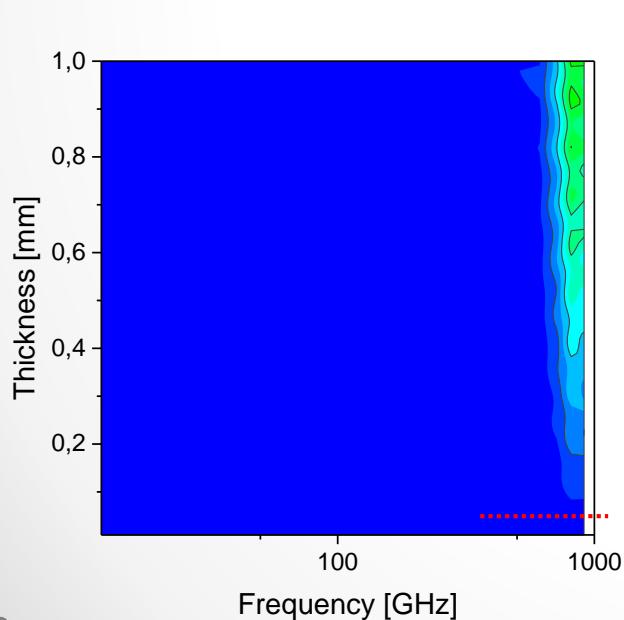
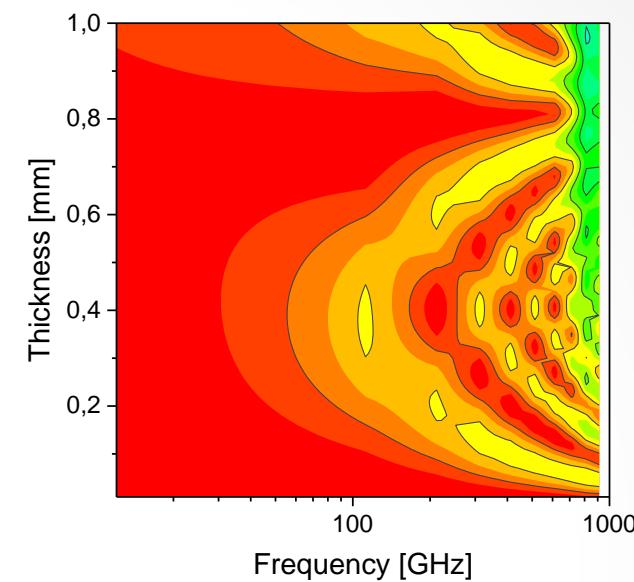
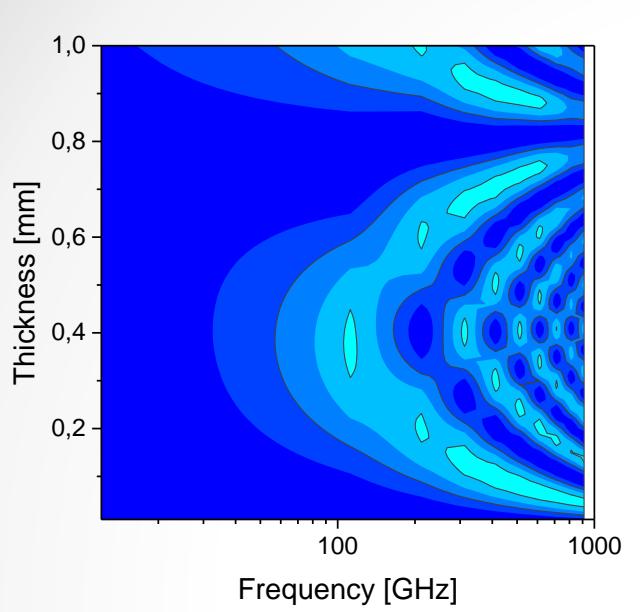
[3] J. Backer-Jarvis, R.G. Geyer, P. D. Domich, en, IEEE Transactions on Instrumentation and Measurement, Oct. 1992, 41, 646-652.

Frequency [GHz]

● 13

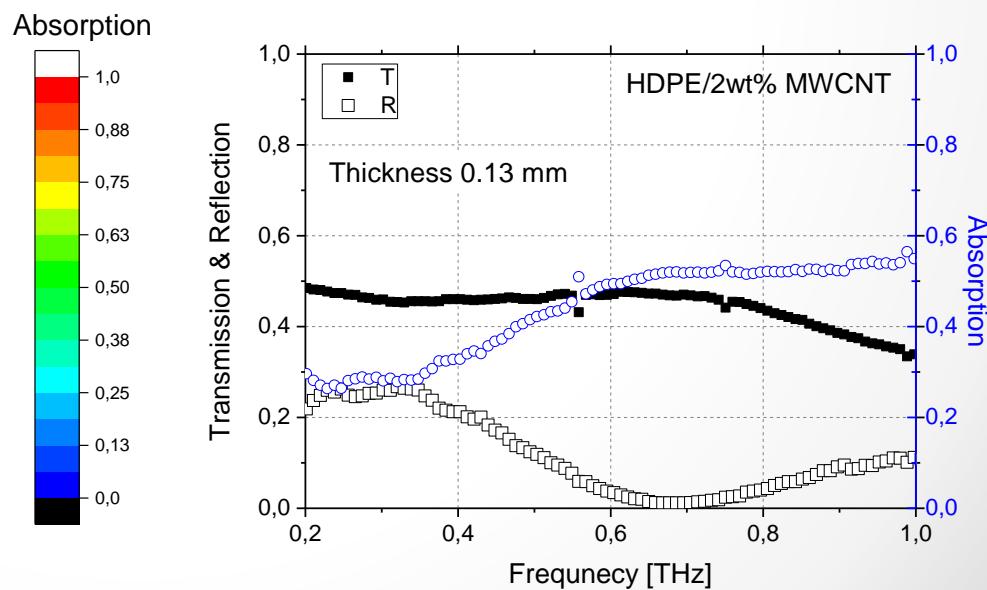
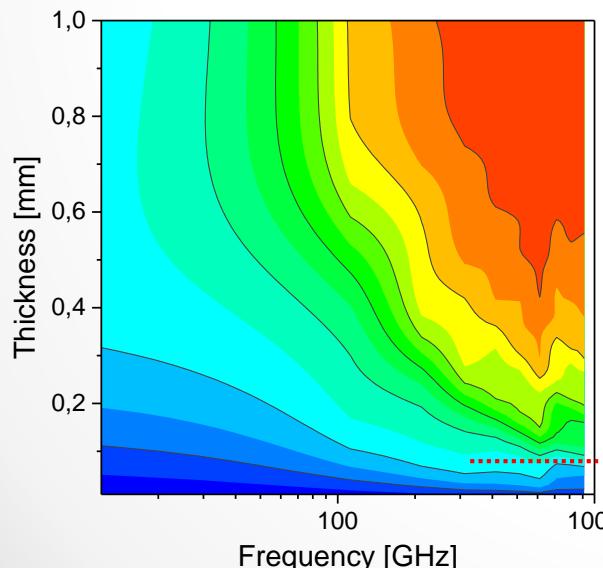
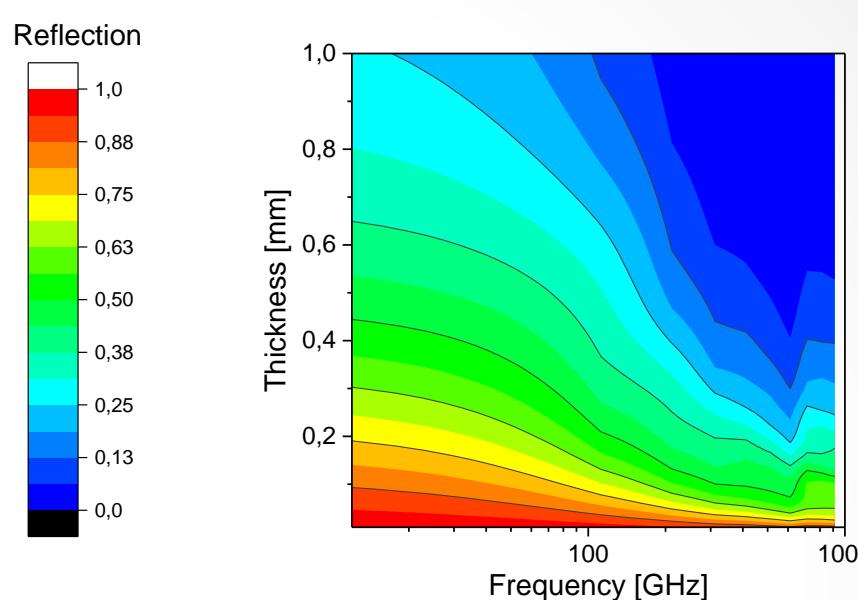
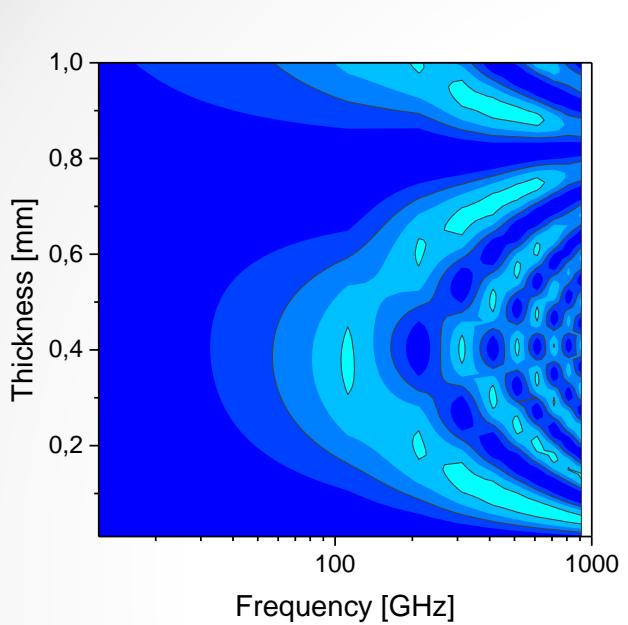
HDPE/2wt%GNP

GRAPHENE
3D



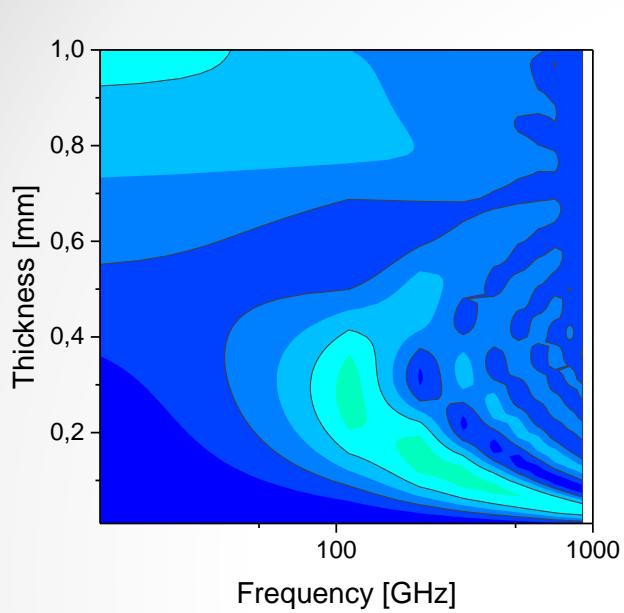
HDPE/2wt% MWCNT

GRAPHENE
3D

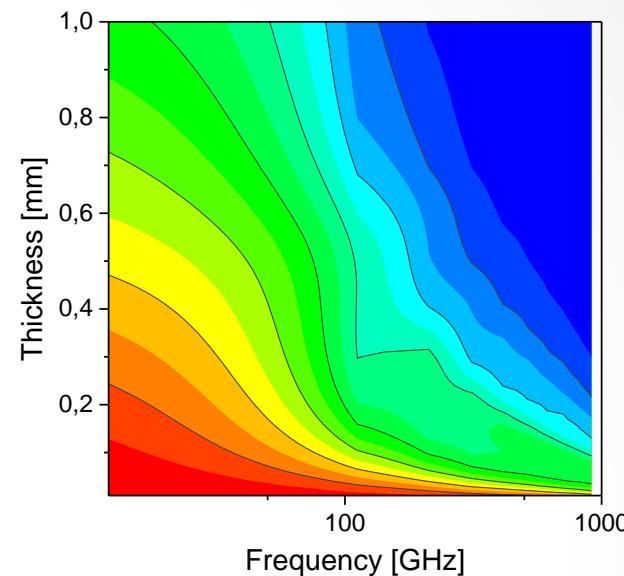
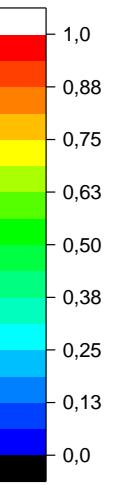


HDPE/2wt%Bi-Filler

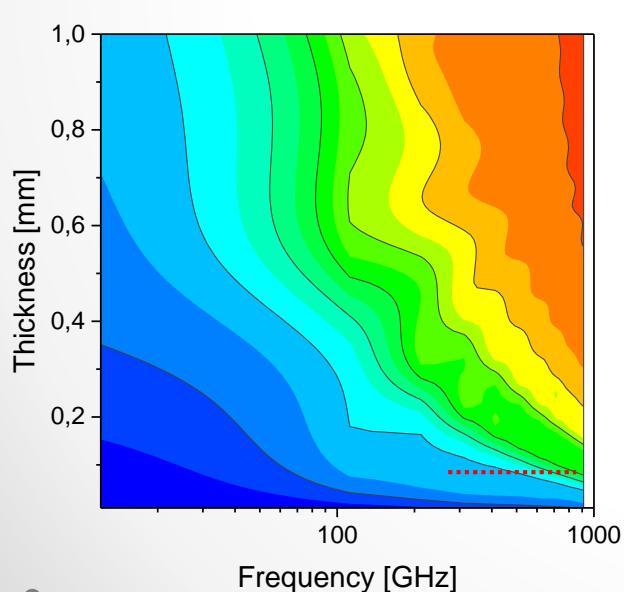
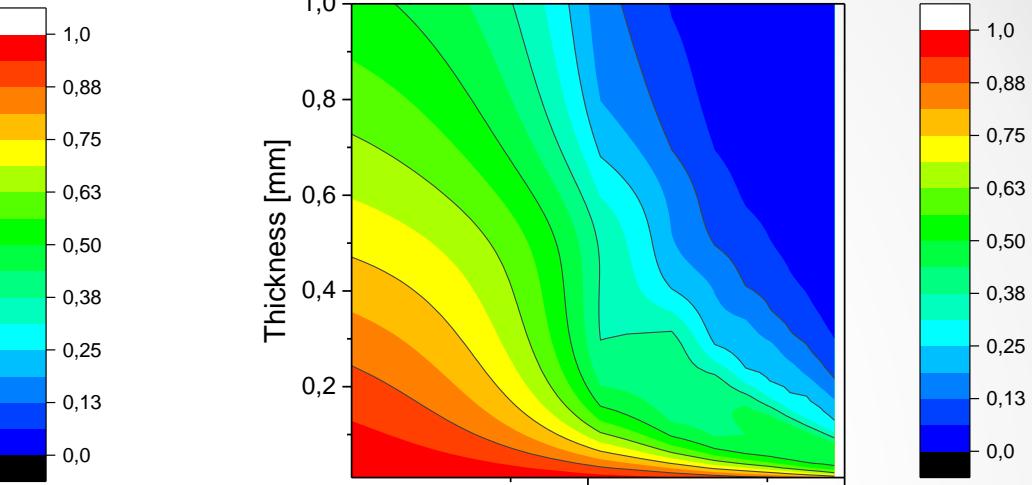
GRAPHENE
3D



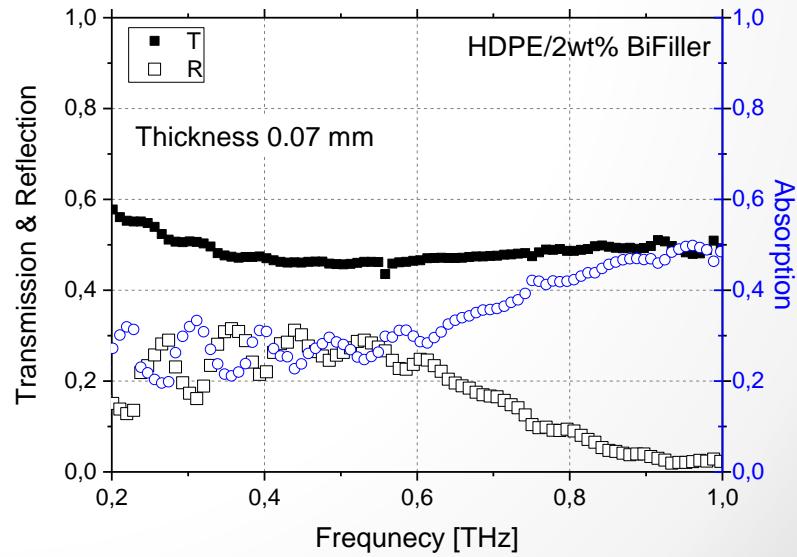
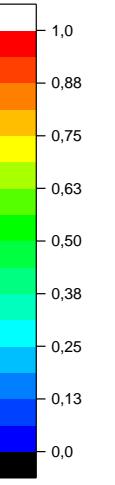
Reflection



Transmittance



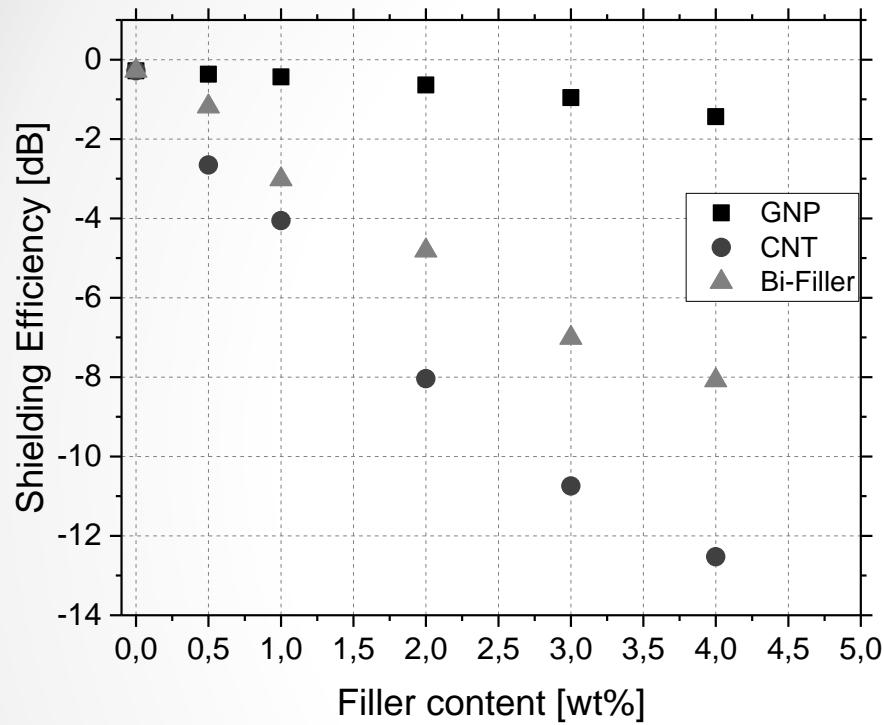
Absorption



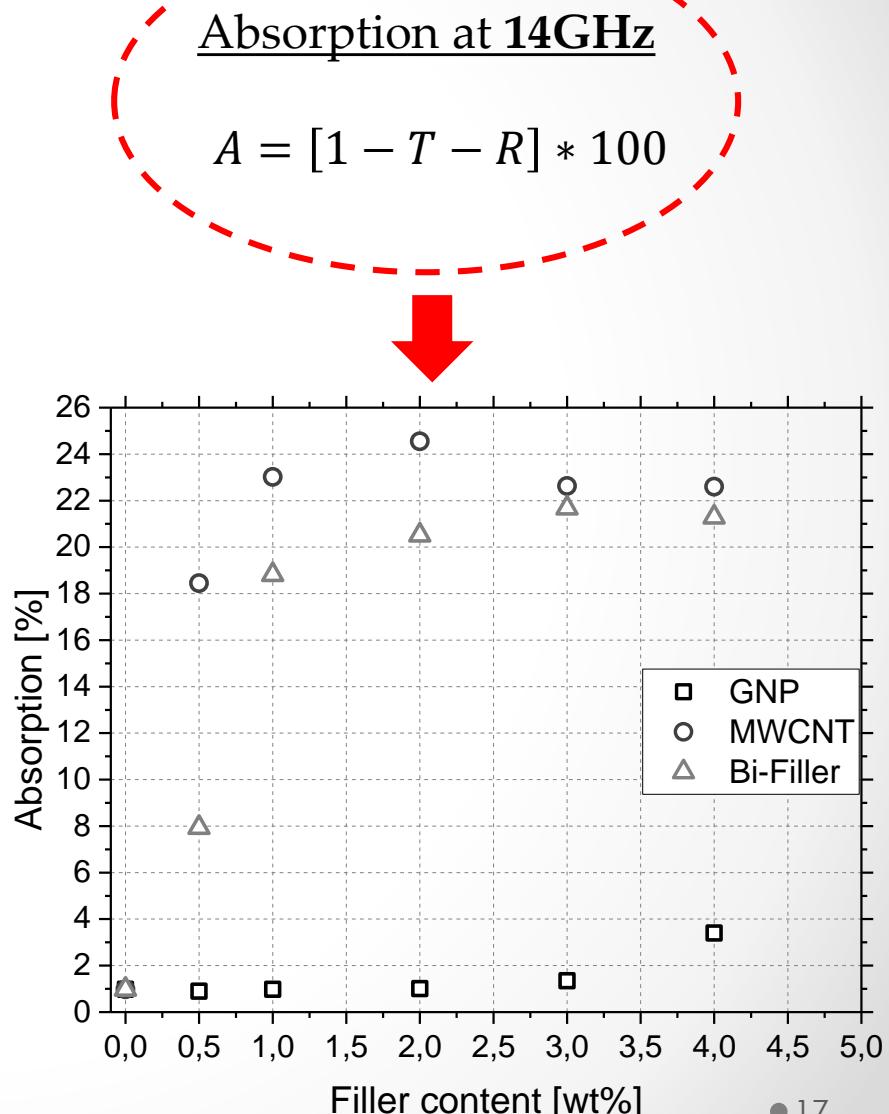
Shielding efficiency and Absorption

12 - 18 GHz

20Lg(S21lin)



Thickness ~1mm



Conclusion remarks

GNP composites

- Nucleation effect;
- Don't show significant effect on the dielectric permittivity;
- Not conductive;
- No dispersion at high frequency;
- Maximum absorption at 14GHz is ~4%;

MWCNT composites

- An efficient mix of CNTs in the polymer matrix;
- Conductivity percolation threshold between 0.5 and 1wt%;
- High dispersion at high frequency;
- ~90% absorption in THz for 2wt% filler with 1mm thickness;

Ternary composites

- Conductivity percolation threshold ~2wt%;
- ~80% absorption in THz for 2wt% Bi-filler system with 1mm thickness;
- Shielding efficiency for 4%Bi-Filler = 2%MWCNTs;



A large, colorful word cloud centered around the words "thank you" in various languages. The words are arranged in a circular pattern, with "thank" at the top and "you" at the bottom. The languages include German (danke), Chinese (謝謝), Swahili (ngiyabonga), Turkish (teşekkür ederim), Spanish (gracias), French (merci), English (thank you), Russian (спасибо), Polish (dziękuje), Portuguese (obrigado), Dutch (dank u), and many others like Korean (감사합니다), Indonesian (terima kasih), and Thai (شكرا). Each word is in a different color and font style, creating a diverse and vibrant visual effect.

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