Characterisation of Compounding Methods for Graphene-Based Thermoplastic Composites using 2D Microwave Imaging Technique

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Outline

1. Motivation and background.
2. Materials of interest – thermoplastic polymer composite (ABS/GNP)*.
3. Microwave intrument: 2D Scanner based on 10GHz iSiPDR.
4. Results and discussion.
5. Conclusions.

**Thermoplastic polymer composites*

based on: *acrylonitrile−butadiene−styrene (ABS)*

inclusions: *graphene nanoplatelet (GNP)*

Motivation - bridging the gaps

Multiphysics Computational Modeling

Focus on Materials Characterisation

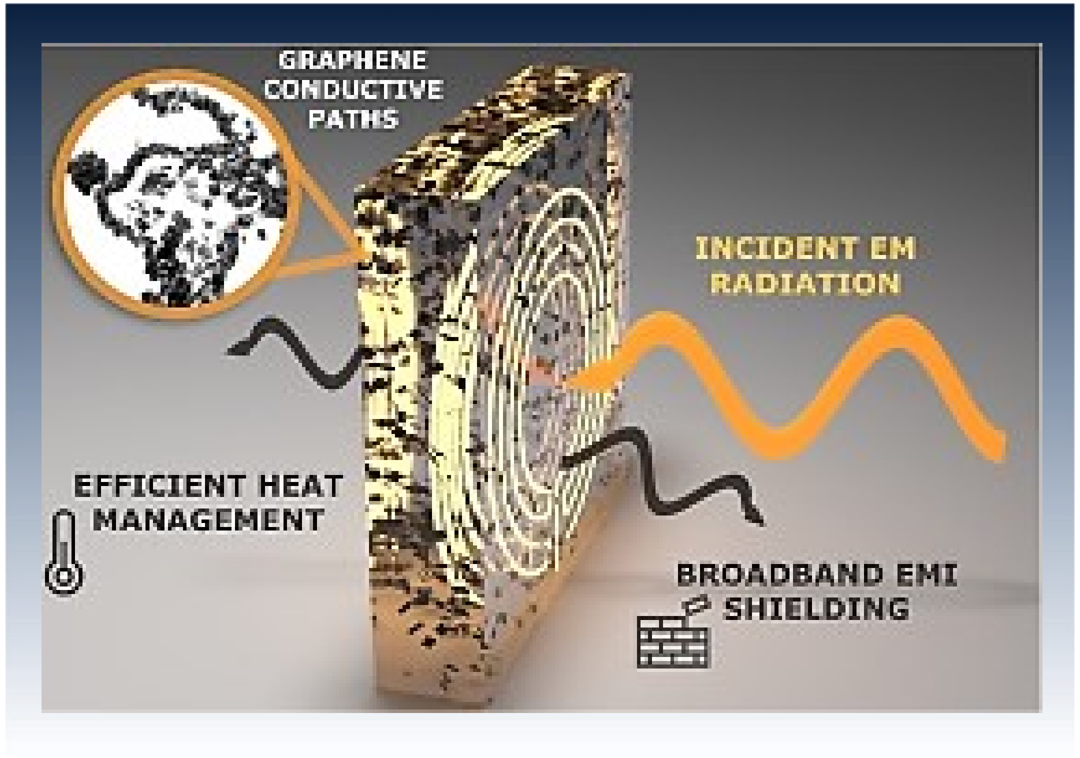
Multifunctional Materials

Focus on EMI Applications

GHz Imaging of Graphene-Based Panels

Materials of Interest

Thermoplastic polymer composites
based on: acrylonitrile−butadiene−styrene (ABS)
inclusions: graphene nanoplatelet (GNP)



advantages:

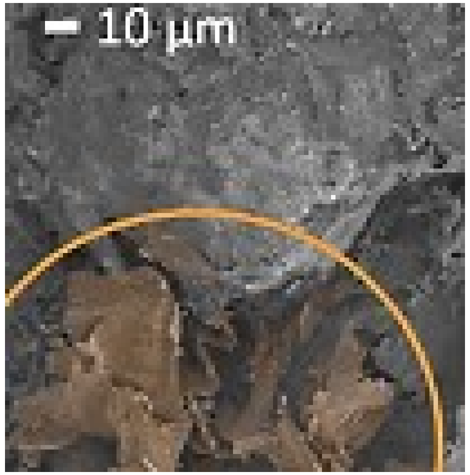
- reduction of weight
- no interfacial mismatches

allow for:

- miniaturization,
- low weight
- high functionality

targeted applications in:

- aerospace
- wearable electronics



targeted functionality: EMI shielding from MHz to GHz
primary mechanism: EM absorption
required paramaters:

- high electrical conductivity (order of 100-200 S/m)
- high thermal conductivity (order of 1-2 W/mK)

→ **the future of modern electronics**

K. Żerańska-Chudek, K. Filak, K. Wilczyński, A. Siemion, N. Pałka, K.Godziszewski, Y. Yashchyshyn, and M. Zdrojek, ” Graphene-Based Thermoplastic Composites as Extremely Broadband and Frequency-Dependent EMI Absorbers for Multifunctional Applications”, *ACS Appl. Electron. Mater.* 2022, 4, 4463−4470

Materials Developement

Thermoplastic polimer composite

Acrylonitrile−butadiene−styrene (ABS) with graphene nanoplatelet (GNP)

- Resinex Poland supplied ABS in a powder form that had a melt flow rate of 43 g/10 min (220 °C/10 kg) and a density of 1.04 g/cm^3 , according to the provided technical datasheet.
- Sigma-Aldrich provided GNPs in the form of a powder with an average lateral dimension of 25 μm and a surface area of 120-150 m^2/g.
- The graphene powder was first mixed with ABS using different concentration ratios of 0.5, 1, 2, 5 and 10 wt%.
- Different mixing methods are used.
  In all cases a hydraulic press is used at the last step, to fabricate flat samples.

Sample Preparation

Thermoplastic polimer composite

Acrylonitrile−butadiene−styrene (ABS) with graphene nanoplatelet (GNP)

Four methods of sample preparation:

1. **Simple dry mixing process via a three-dimensional mixer:** Both components in powder form were dryly mixed using a three-dimensional (3D) mixing process with a 3D mixer. The resulting mixture was then compressed using a hydraulic hot press at the polymer's softening temperature and under constant pressure (mold temperature was set at 290 °C, and a pressure of 20 MPa was applied).

2. **Twin-screw extrusion mixing process:** First, a pre-mixture of the materials was prepared using a 3D mixer, which was then fed into a twin-screw extruder. Both components were homogenised in the twin-screw extruder at the flow temperature, resulting in a filament. The filament was pelletised.

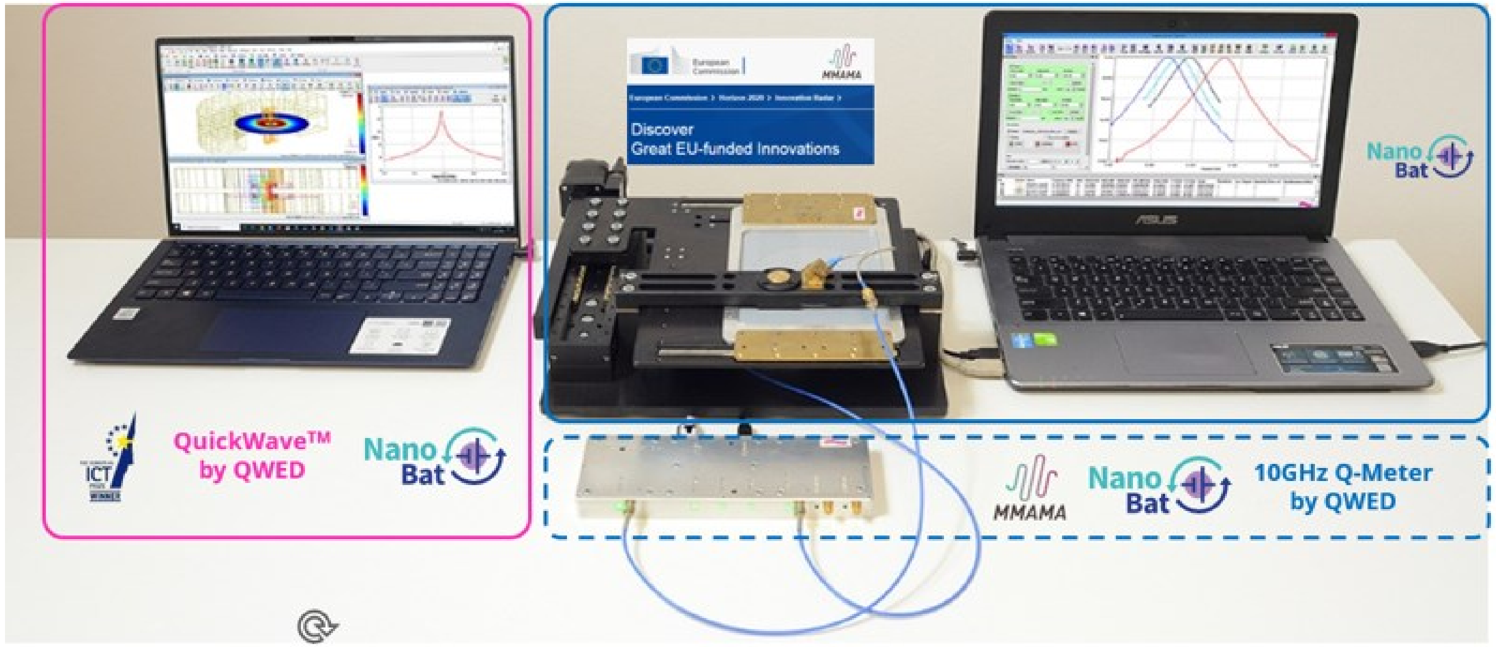
2a: **single crossing**: the pelletised filament was compressed into plates using a hydraulic hot press.

2b: **double-crossing:** The obtained pellets were fed back into the extruder to obtain another filament, which was then cut into pellets again. The doubly extruded and cut material was compressed using a hydraulic hot press.

4. **The solution mixing process** involved dissolving the polymer (ABS) using a solvent (acetone) and mixing graphene in the dissolved ABS suspension. The material was then evaporated from the solvent and compressed into thin plates using a hydraulic hot press.

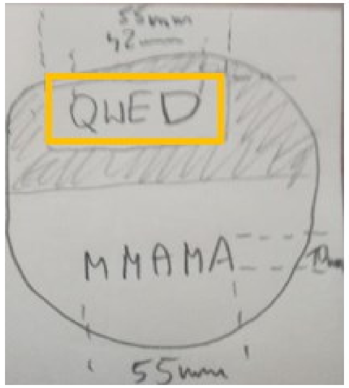
Characterisation Concept (1)

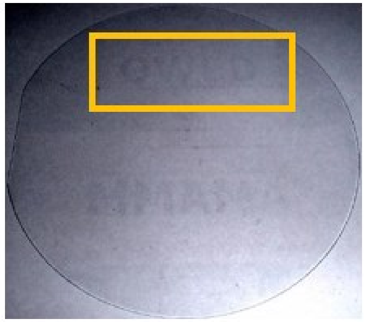
Modelling-Based Materials' Characterisation Setup



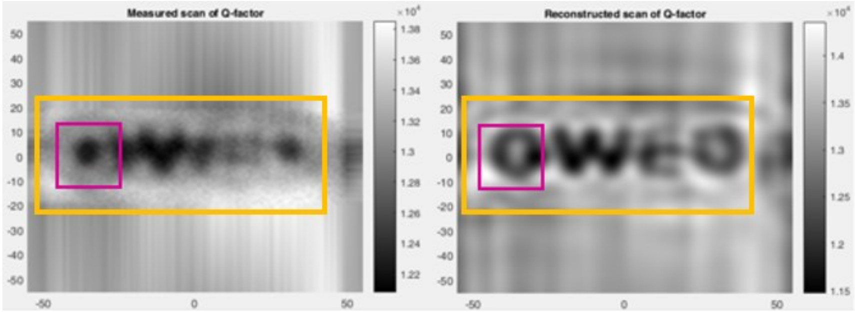
2D scanner designed with a modified 10 GHz SPDR

Finalist of the European Innovation Radar Prize 2021





Patterned PEDOT:PSS sample
courtesy MateriaNova, Belgium



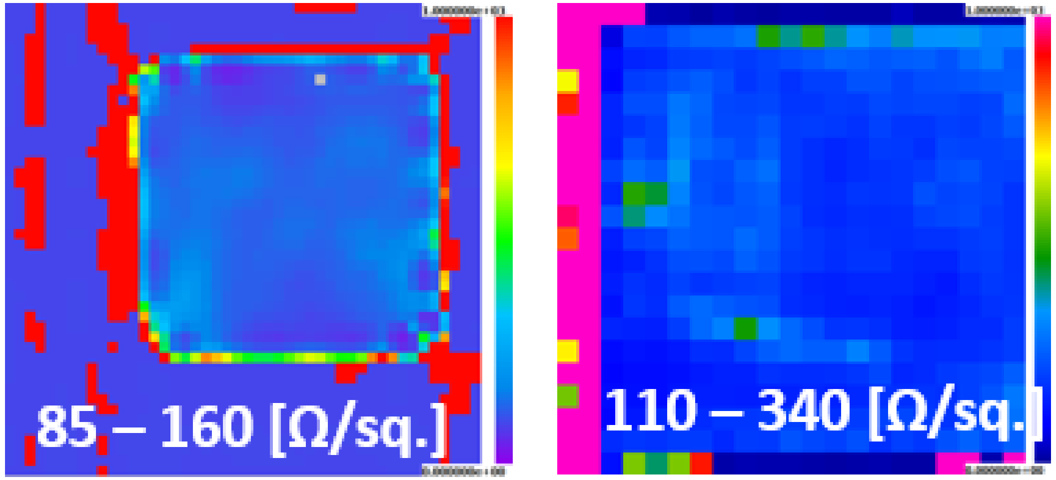
applicable to high-resistivity materials

new version later developed for conductive sheets…

Characterization Concept (2)

Modelling-Based Materials' Characterisation Setup

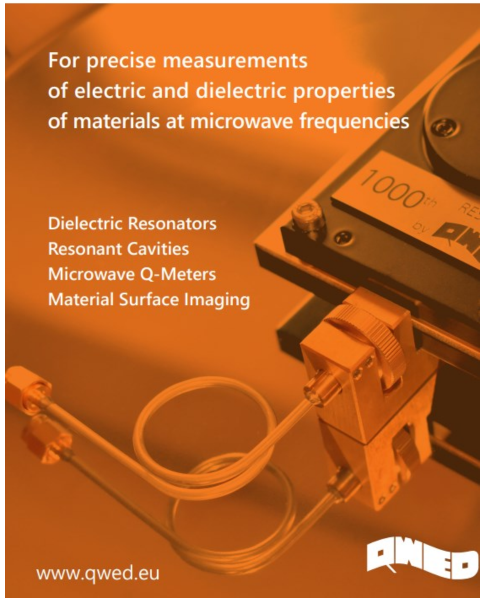
2D iSiPDR scanner based on inverted 10 GHz SiPDR

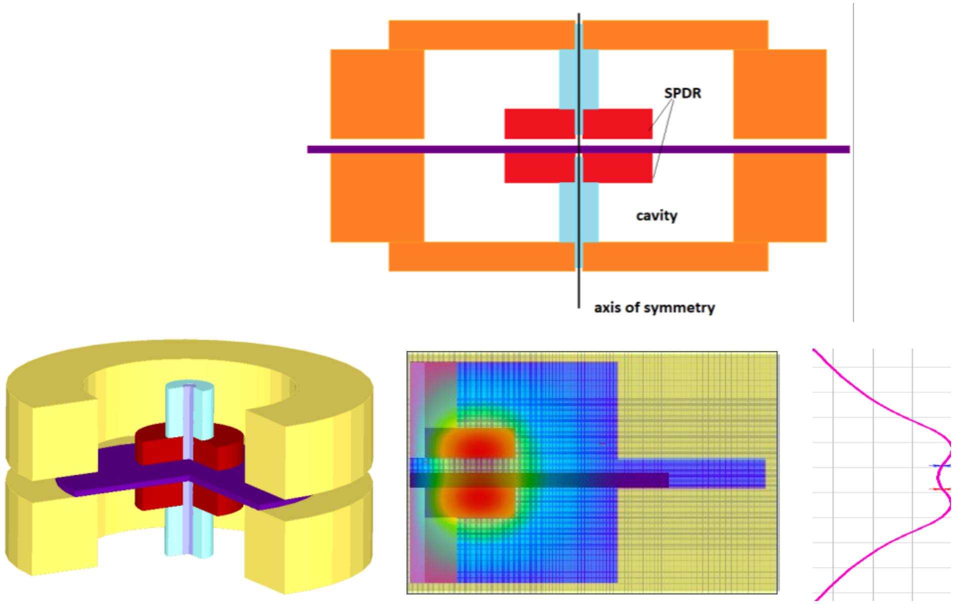


Example application:
battery anodes before & after cycling (SEI formation).

Which Scanner: SPDR or iSiPDR

Test Fixtures and Setups





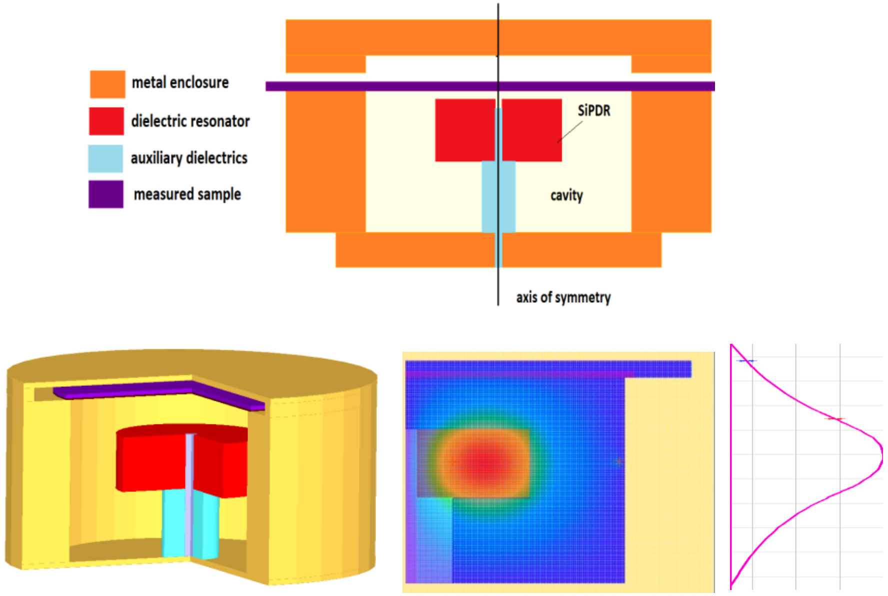


Table 2. Typical ranges of applications of SPDRs and SiPDRs			
	Conductivity [1/(Ωm)]	Resistivity [Ω cm]	Surface resistivity [Ω/sq]
Range od SPDR applications	$2\ 10^{-3}$ to 0.5	from $2\ 10^{2}$ to $5\ 10^{4}$	from $2\ 10^{3}$ to 10^{7}
Range of SiPDR applications	0.1 to 10^{6}	from 10^{-4} (*) to 10^{3}	from 10^{-1} to $2\ 10^{4}$

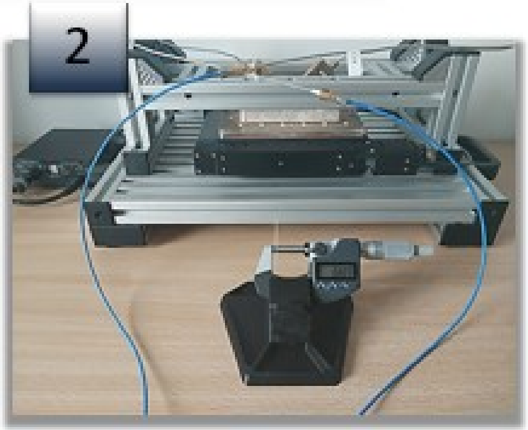
Resonator designs after:

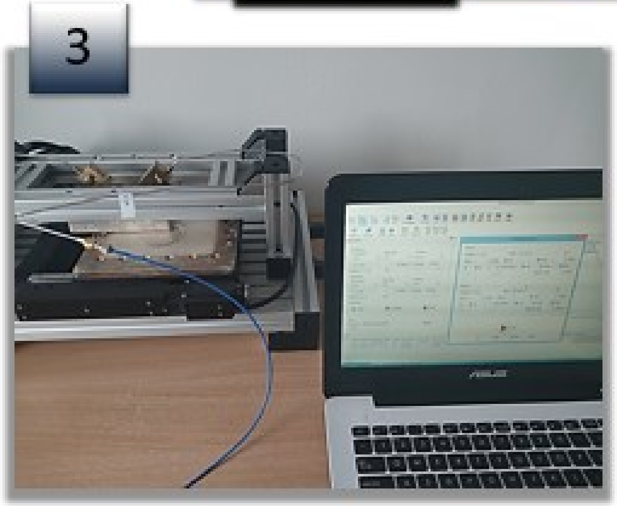
J. Krupka and J. Mazierska, *IEEE Trans. Instr. Meas.*, 2007, doi: 10.1109/TIM.2007.903647

CAD models and EM field distribution:

QuickWave^{TM} software by QWED

Measurement Procedure





0. Connect the iSiPDR to Q-Meter using SMA cables Connect Q-Meter and STANDA Motor to PC using USB cable.

1. Measure "empty" iSiPDR - app invoked measurement.
2. Measure thickness of the sample.
3. Insert the sample into iSiPDR.
4. Insert the sample thickness into the PC app.
5. Material parameters are extracted automatically with each step.

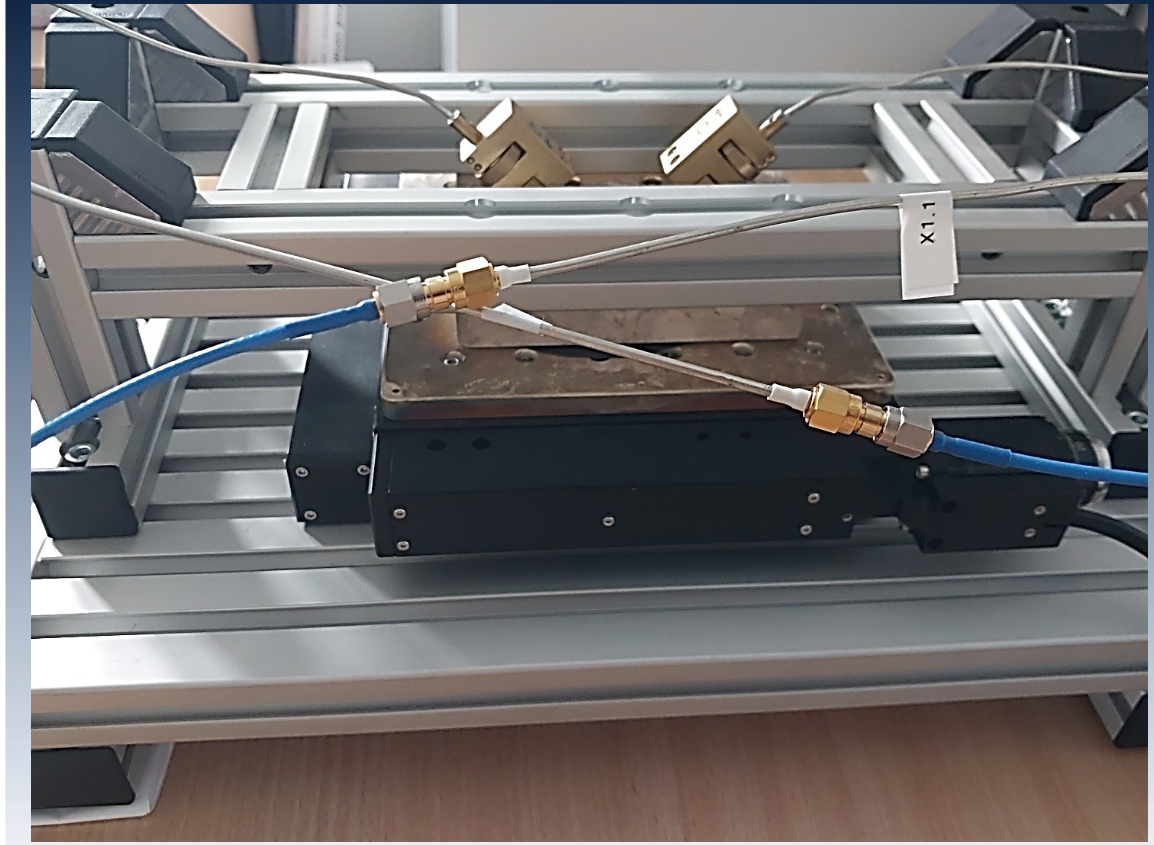
Measurement Procedure – Steps 2,3

Example of "1st attempt" sample obtained by simple dry mixing

ABS/GNP

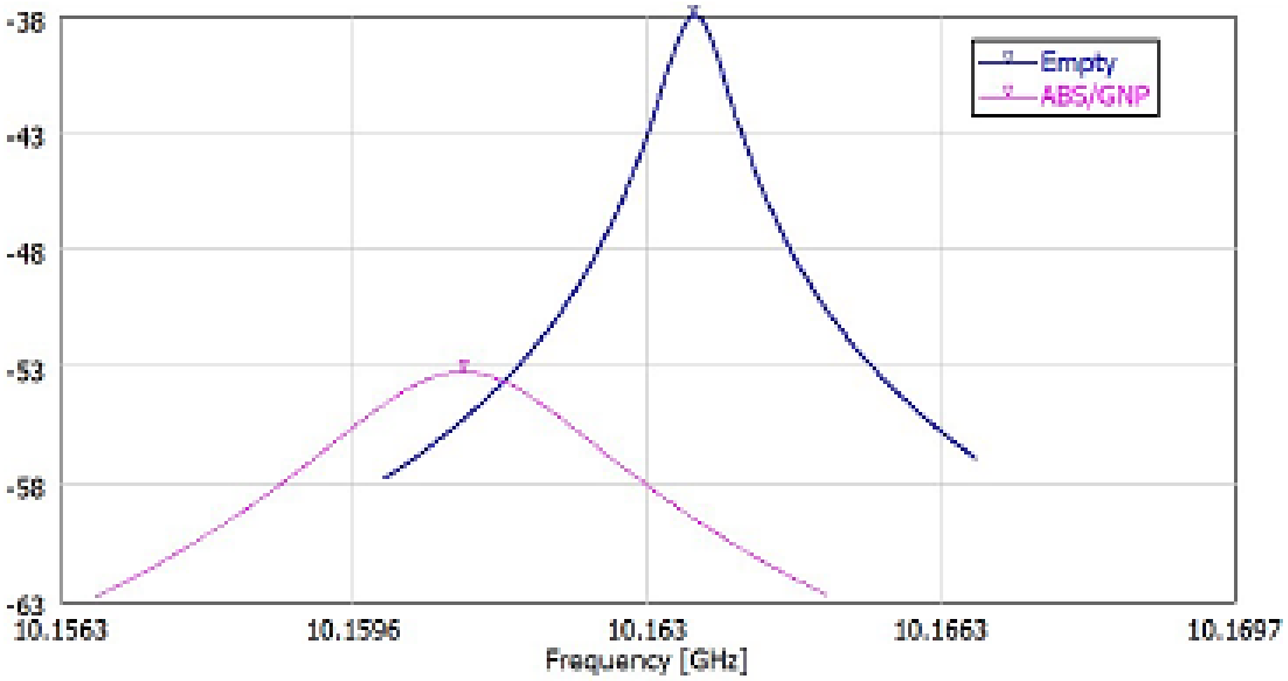
Average thickness: 429.9 [µm]
Maximum: 480 [µm]
Minimum: 362 [µm]

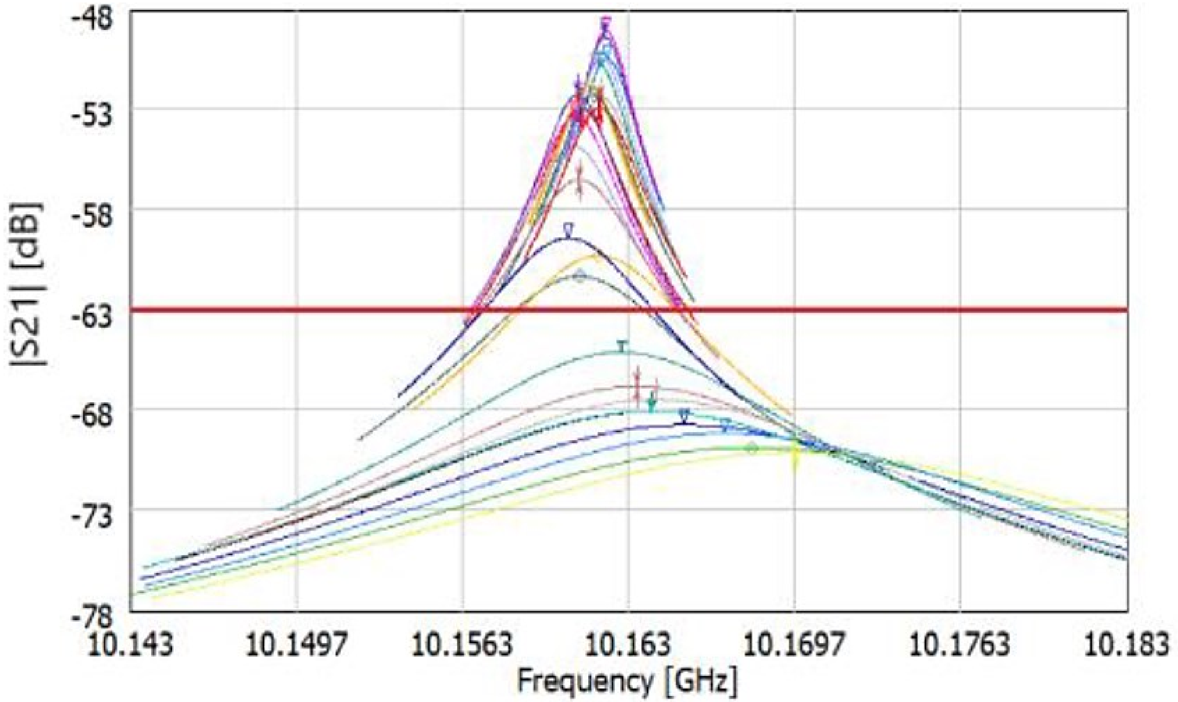
Insert the sample into iSiPDR



Measurement setup for 2D imaging of GBPC panels

Results and discussion

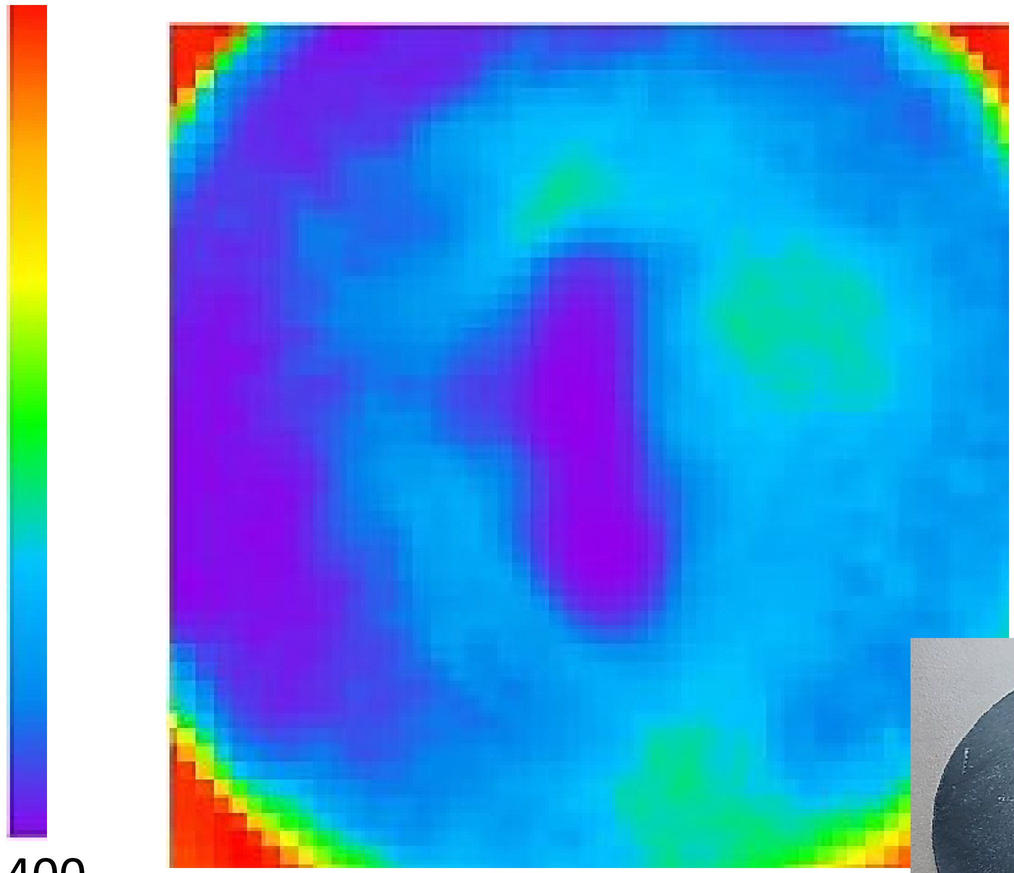




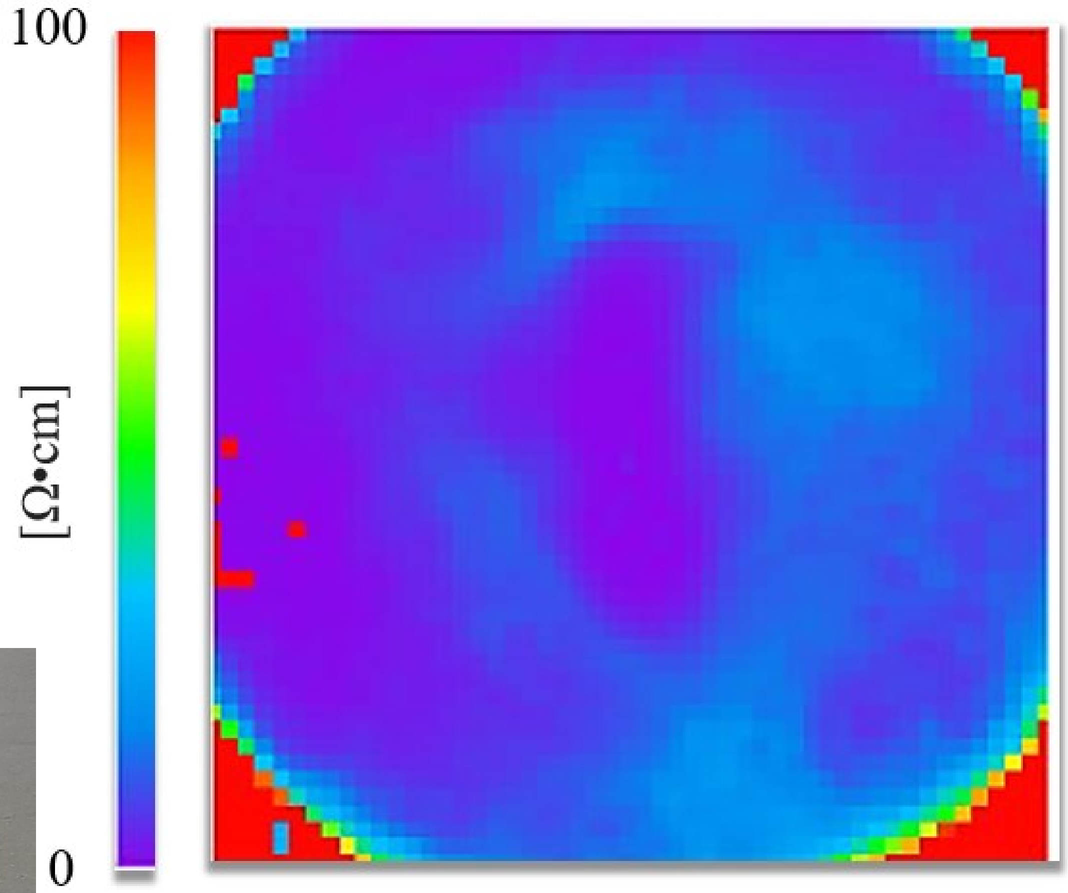
Transmission (abs (S21)) through the 10 GHz iSiPDR mounted in the scanner
and placed at two selected positions:
over an empty region (blue) and at a selected point over the ABS/GNP sample (pink).
The sample introduces losses, decreasing the transmission and damping the resonant curve.

Results and discussion

Q-Factor map of iSiPDR over the sample



Resistivity map of ABS/GNP sample



samples ca. 2x thicker than the ”1st attempt”

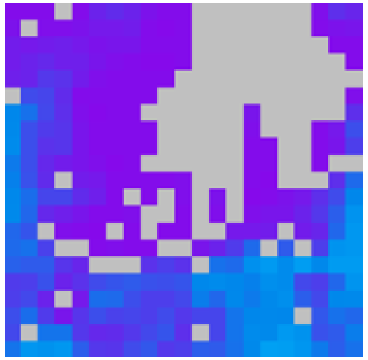
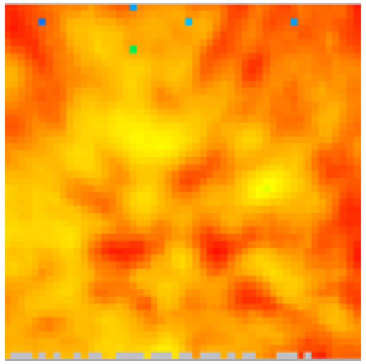
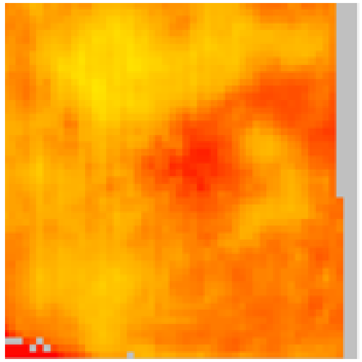
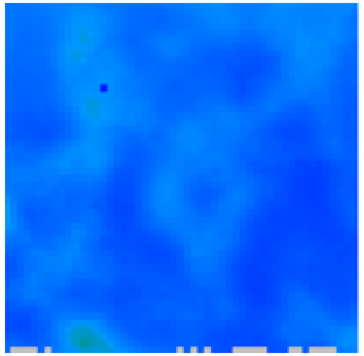
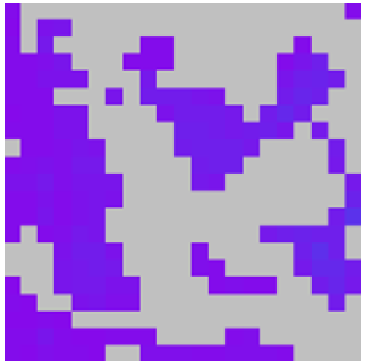
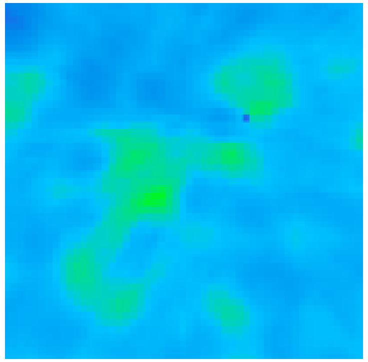
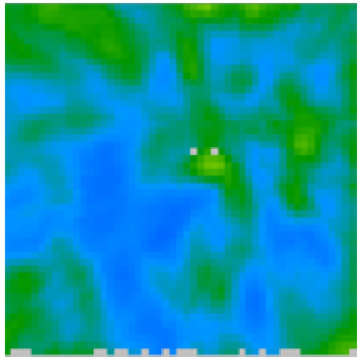
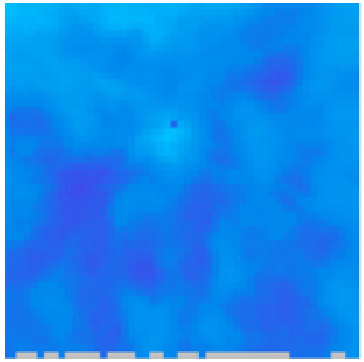
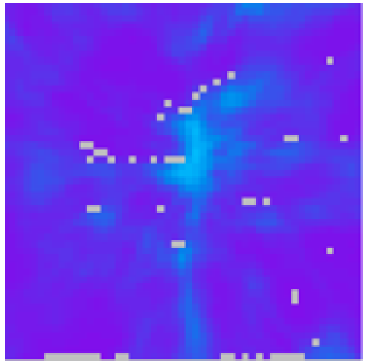
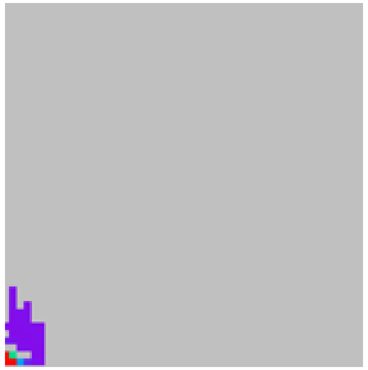
Concentration of GNP in ABS	Simple dry mixing process via three dimensional mixer	Twin-screw extrusion mixing process		Solution mixing process
		Single crossing	Double crossing	
5%				
10%				
15%				

Results and discussion

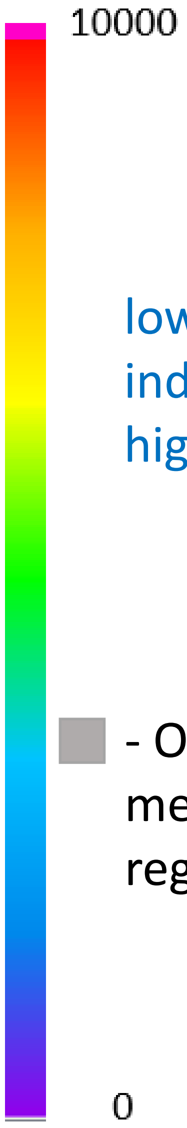
Average thickness of samples

Concentration of GNP in ABS	Simple dry mixing process via three dimensional mixer	Twin-screw extrusion mixing process		Solution mixing process
		Single crossing	Double crossing	
5%	NE- 1 **0.8514 mm**	NE – 4 **0.8124 mm**	NE – 7 **0.814 mm**	NE – 10 **0.8179 mm**
10%	NE – 2 **0.8365 mm**	NE – 5 **0.8148 mm**	NE – 8 **0.8118 mm**	NE – 11 **0.808 mm**
15%	NE – 3 **0.8344 mm**	NE – 6 **0.8156 mm**	NE – 9 **0.8234 mm**	NE – 12 **0.8266 mm**

The results were averaged by measuring the thickness of the sample at 10 locations using a micrometer.

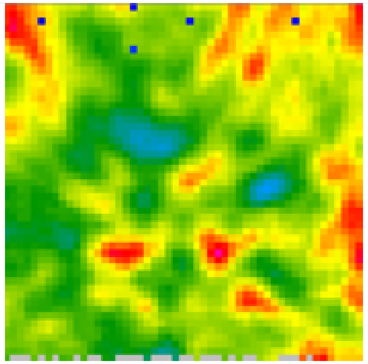
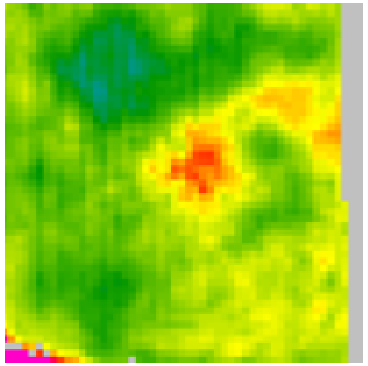
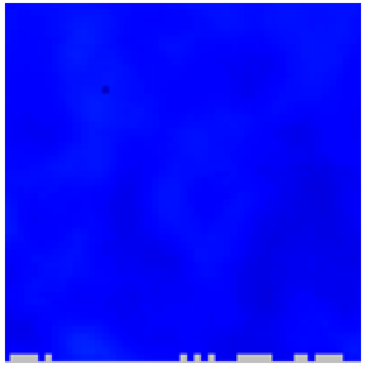
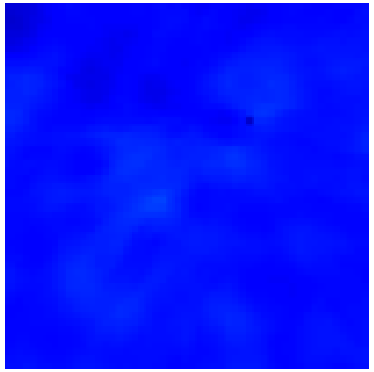
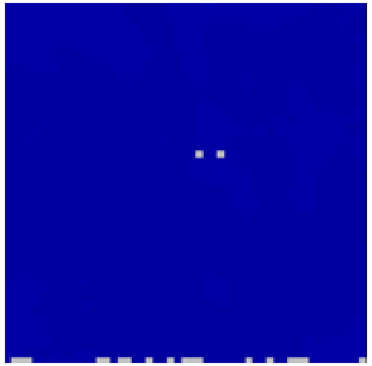
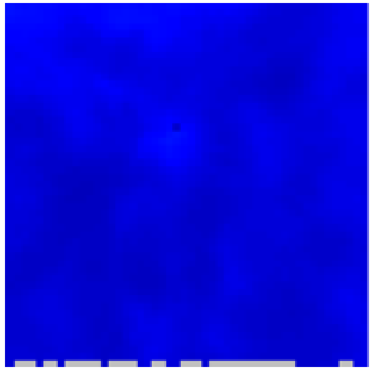
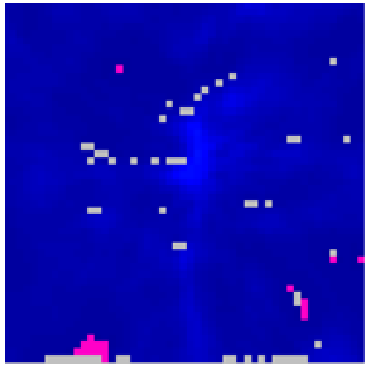
Concentration of GNP in ABS	Simple dry mixing process via three dimensional mixer	Twin-screw extrusion mixing process		Solution mixing process
		Single crossing	Double crossing	
5%				
10%				
15%				

Q–Factor

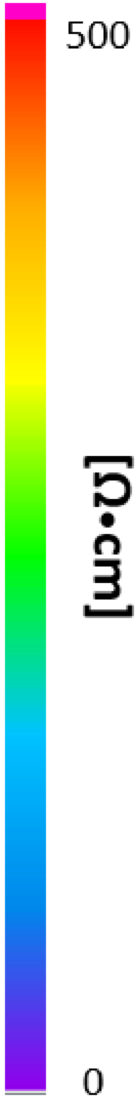


lower Q indicates higher loss

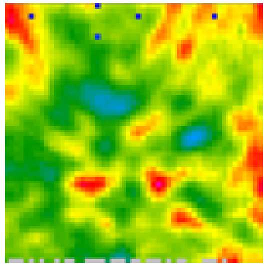
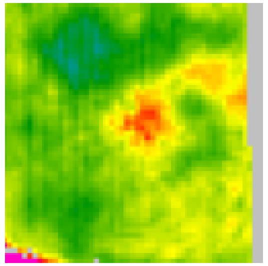
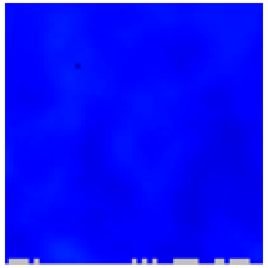
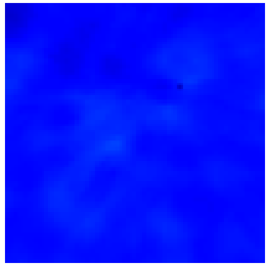
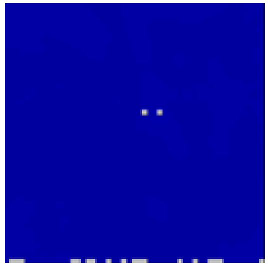
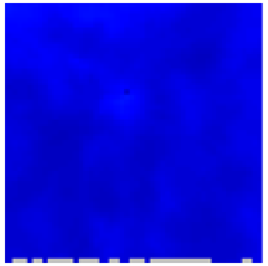
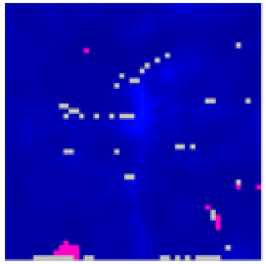
- Outside of measurement region

Concentration of GNP in ABS	Simple dry mixing process via three dimensional mixer	Twin-screw extrusion mixing process		Solution mixing process
		Single crossing	Double crossing	
5%	**Not Applied!**			
10%	**Not Applied!**			**Not Applied!**
15%	**Not Applied!**			**Not Applied!**

Effective Resistivity



Effective Resistivity

Concentration of GNP in ABS	Twin-screw extrusion mixing process		Solution mixing process
	Single crossing	Double crossing	
5%	 295.15±62.72 [Ω•cm]	 276.47±89.69 [Ω•cm]	 45.26±8.46 [Ω•cm]
10%	 54.39±10.61 [Ω•cm]	 69.75±14.81 [Ω•cm]	Not Applied!
15%	 27.37±7.93 [Ω•cm]	 8.49±6.39 [Ω•cm]	Not Applied!

Conclusions

QWED's new instrument for materials' characterisation (2D 10 GHz iSiPDR scanner) has been successfully applied for the testing of novel materials (graphene-based polymer composites) developed at the Warsaw University of Technology.

The applied characterisation method is a merger of QWED's competencies in materials' measurement (GHz resonator-based instruments) and computational modelling (QuickWave simulation software). In particular ultra-fast BoR FDTD EM simulation with advanced QProny signal post-processing is used to convert the measured resonant frequencies and Q-factors to the material-under-test resistivity.

The characterisation results are qualitatively and quantitatively appealing.

The initial samples of ABS/GNP showed significant surface inhomogeneities, sometimes beyond the measurement range of the applied instrument.

The work is ongoing on:

- improvements in the material fabrication process, for better spatial uniformity,
- extending the instrument's measurement range (material resistivity and resistivity variations) .

Acknowledgement

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and is currrently co-funded by the Polish National Centre for Research and Development under contracts M-ERA.NET2/2020/1/2021 (**ULTCC6G_Epac**) and M-ERA.NET3/2021/83/**I4BAGS**/2022.

ULTCC6G_EPac