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Bulk Microstructure and Local Elastic Properties of Carbon Nanocomposites studied by Impulse Acoustic Microscopy Technique

- **V. Levin, Yu. Petronyuk, E. Morokov**

Emanuel’s Institute of Biochemical Physique, Russian Academy of Sciences, Moscow, Russia

- **A. Shubin, D. Vinogradov**

Ostec-ArtTool, Moscow, Russia

- **S. Bellucci**

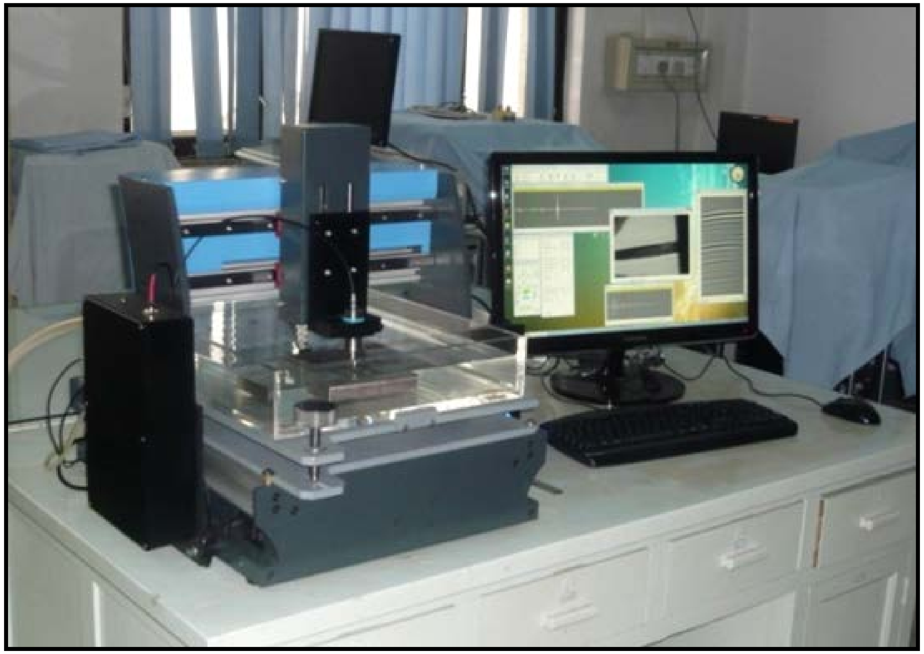
National Institute of Nuclear Physics, Frascati National Laboratory, Frascati (Roma), Italy

Scanning Impulse Acoustic Microscopy

Experimental unit

Scanning impulse acoustic microscope (SIAM),
Institute of Biochemical Physics, RAS, 2011

- Operation frequency: 50 - 200 MHz
- Immersion: water
- Scanning step: Z=15 μm
- Scanning field: up to 360 × 450 mm

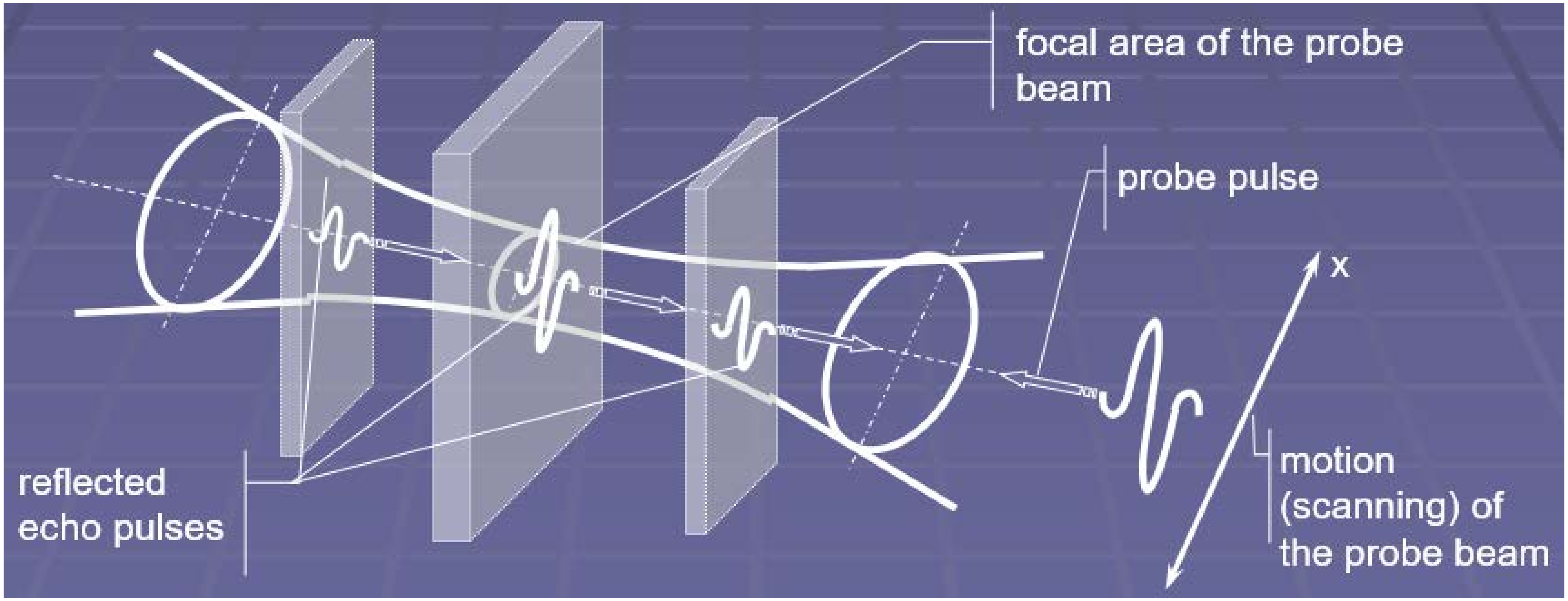


Modes:

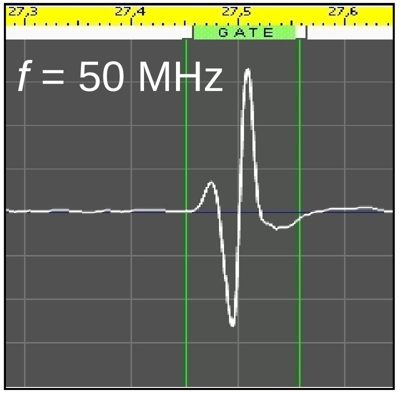
- 3D visualization (tomography)
- A, B and C-scans

Principles of acoustical bulk imaging

1. Reflection mode;
2. Impulse probe signals;
3. Time resolution of echo signals coming from different depth inside the specimen bulk
4. 1D or 2D probe beam scanning for image formation

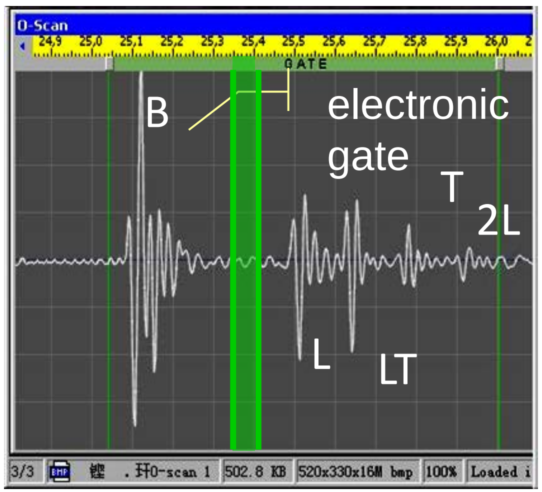


Basic modes of data representation

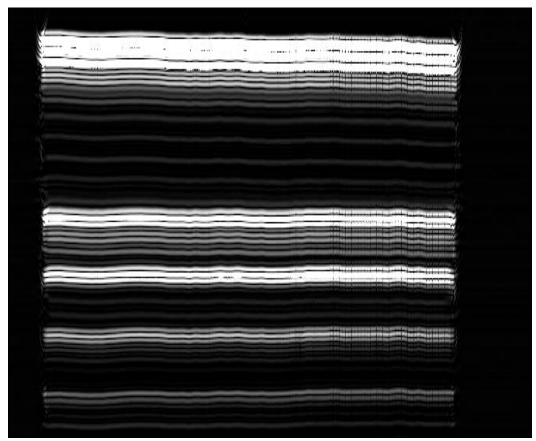


probe pulse

Electronic gate (given by green color) – technique of signal processing for displaying recorded signals as acoustical B- and C-scans.



Echo pattern - oscillogram of reflected signal



B-scan

sweep of echo signal within the electronic gate when 1D motion of the acoustic lens

C-scan

gray-scale displaying of echo-signal amplitude variations within electronic gate in 2D scanning of the acoustic lens

Idea of nanocomposites

1. routine **polymer** medium as binder (matrix material)
2. nanosized particles as filler
3. small content of nanofiller (**usually 0.05 ÷ 10 weight %**)
4. uniform distribution of nanofiller over the matrix material

Advantage of nanocomposite materials – new physical properties:

- DC electrical conductivity
- HF electromagnetic properties - effective EM absorption, resonance phenomena, shielding, screening, etc.
- high heat conductivity
- mechanical properties enhancing elastic moduli and strength

…

Graphite – Epoxy Nanocomposites

Binder: epoxi resin Epicote Resin 828

produced from Bisphenol A and Epichlorohydrin with a curing agent A1 (modified TEPA)

Nanofiller: diverse kinds of graphite nanoparticles

a. Exfoliated graphite (EG)
   Milled exfoliated graphite, particle sizes – (20 ÷ 500) µm

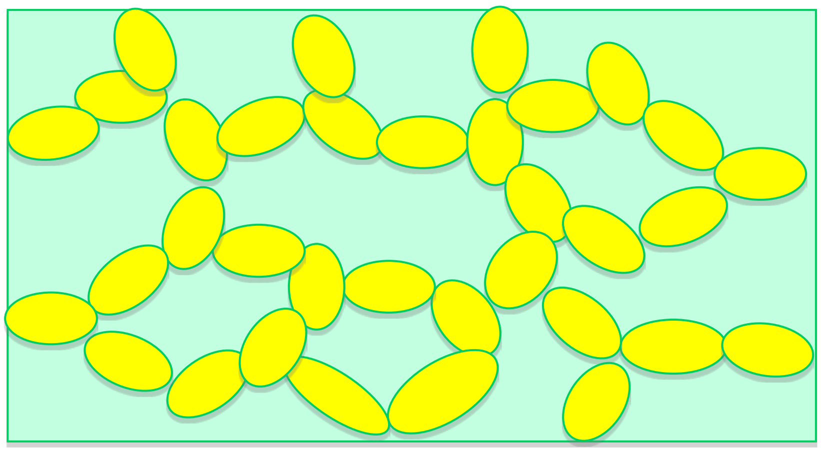
b. Flat micronic graphite (FMG)
   Fine milling and thermal treating of exfoliated graphite. Graphite stacks consisting of 30- 40 graphite atomic layers. Lateral sizes are not larger than 10-15 µm

d. Graphite nano-platelets (GNP)
   Intercalation / Pulverization / Additional milling
   Thickness ~10 nm, lateral sizes ~1 - 10 µm

c. Multiwall carbon nanotubes (MWCNT)
   CVD produced carbon multiwall nanotubes, Ø 20 – 40 nm, 5 - 12 µm long

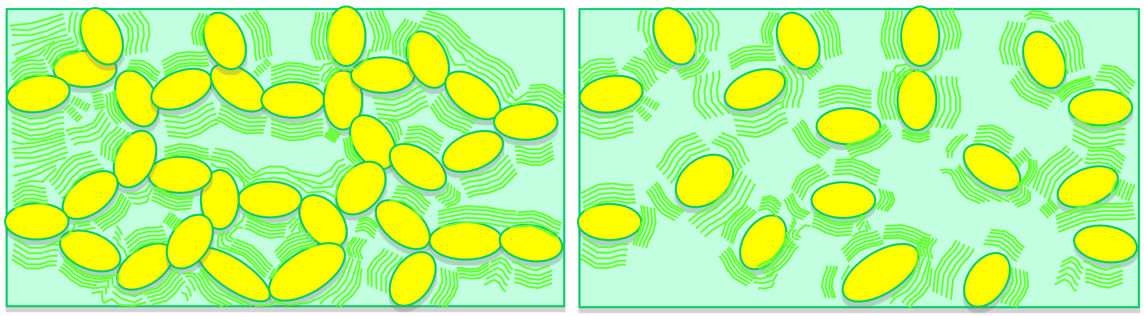
Possible mechanisms of properties enhancement

1. Formation of fractal clusters of contacting nanoparticles in polymer matrix: formation of conductive nets and islands



⇨ electrical and heat conductivity; electromagnetic properties

2. Restructuring polymeric matrix by ordering of macromolecules in the vicinity carbon nanoparticles



⇨ elastic and strength properties

The paper goals

Application of the high-resolution acoustic vision technique for studying fundamental problems of nanocomposite material science:

- uniformity of nanoparticle distribution over the composite bulk for nanocomposite with different types of carbon nanofiller;
- what elastic properties– enhanced or worsened ones comparing with properties of the neat polymer binding; are realized in nanocomposites with different carbon nanofiller;

Applied method:
Scanning Impulse Acoustic Microscopy

Investigated materials:
Epoxy + different carbon nanoforms

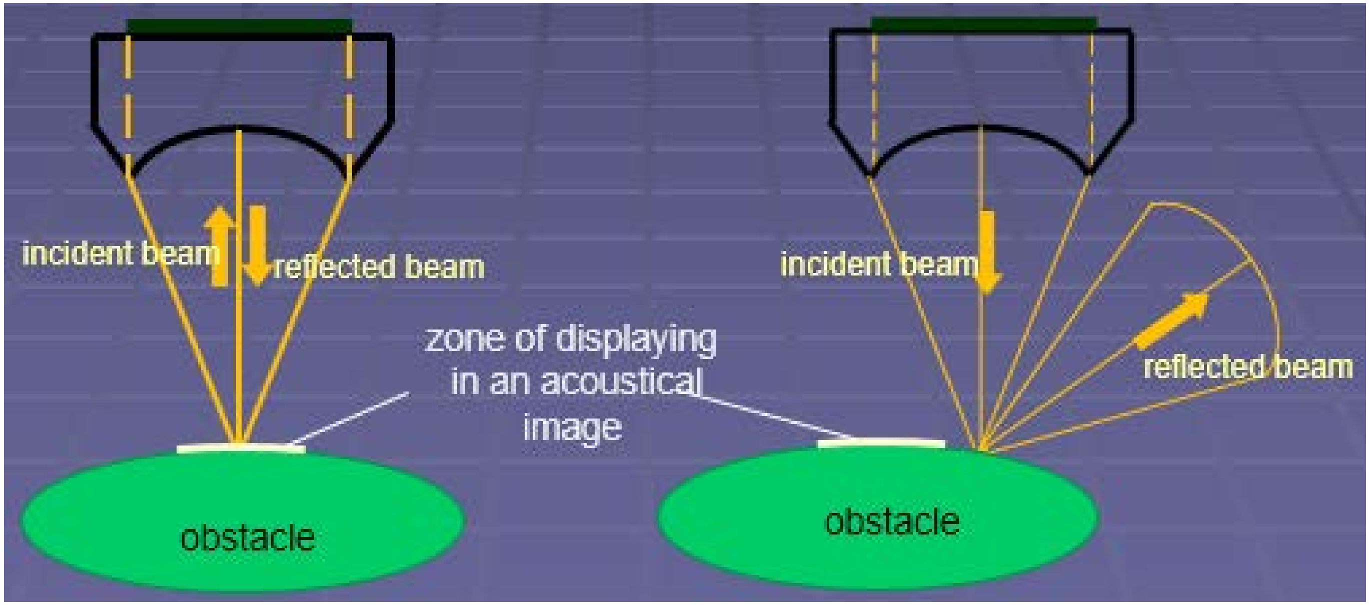
Mechanisms
of acoustical contrast
in carbon nanocomposites

1. Acoustical imaging in epoxy + exfoliated graphite (EG) composites

reflection or scattering of the probe beam at EG particles

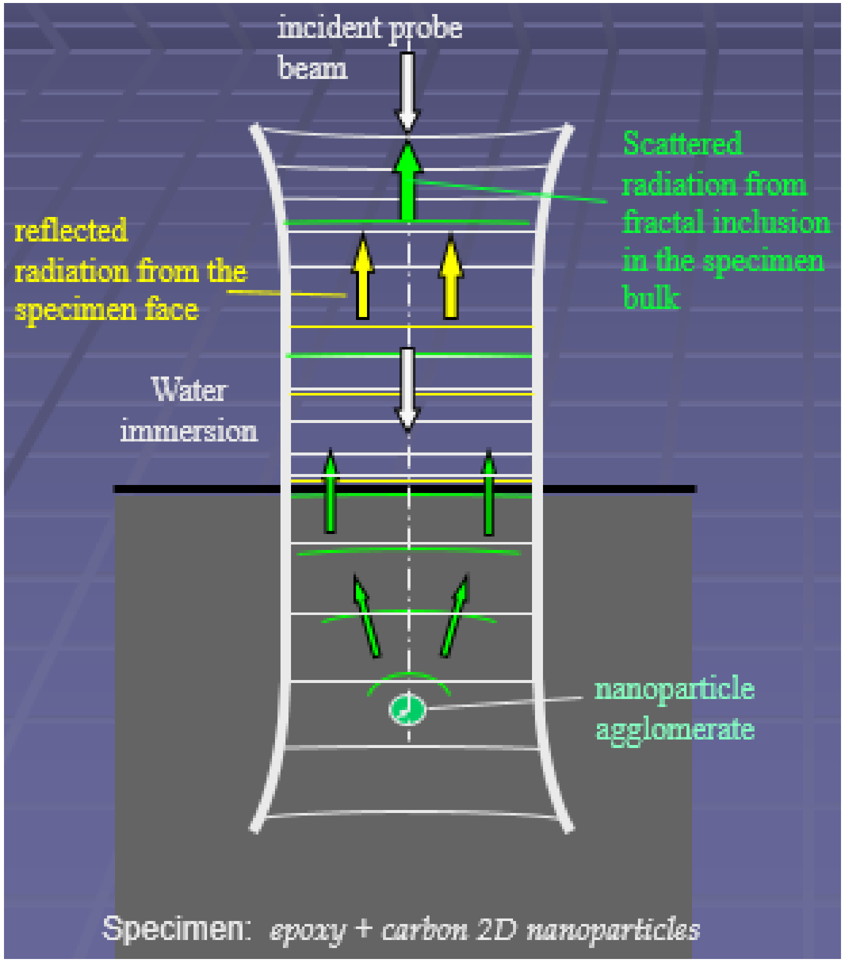
Tops of EG particles only are displayed in acoustical images

radiation reflected from other parts of the particle surface does not get into aperture of the acoustic objective



Acoustical images of epoxy + EG composites represent only occurrence of EG particles and their position in the specimen bulk. They give no information on particle sizes and shape.

2. Acoustical imaging in epoxy + 2D nanocarbon (FMG and GNP) composites:



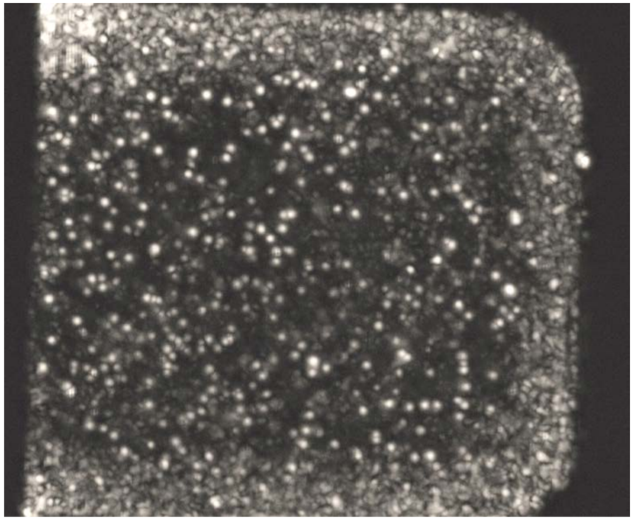
scattering at micronic 2D nanoparticle agglomerates filled by air (aerogels)

1. 2D nanoparticles agglomerate into micron-sized conglomerates because of their high affinity to each other (higher than their affinity to polymer binder).
2. Trapping air in interparticle space and aerogel formation
3. Ultramicroscopic mode of imaging - receiving radiation scattered at small obstacles inside the focal zone of the probe beam.
4. High efficiency of ultrasonic scattering at small acoustically soft obstacles (scatterers filled by air)

Ultramicroscopic mode is acoustical analog of the dark-field technique in optics

Acoustical images depict presence and position of scatterers, not their sizes and shape

What minimal objects could be see with impulse acoustic microscope in the specimen bulk



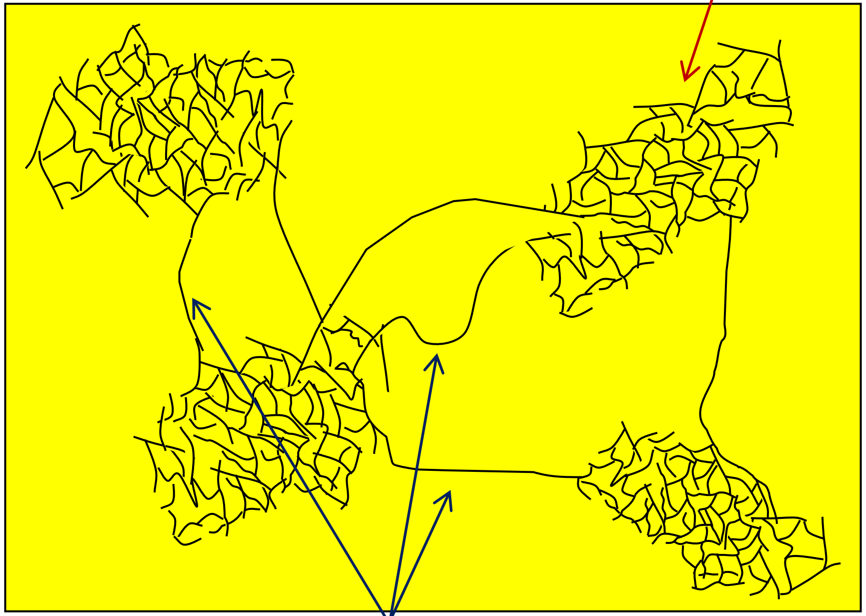
It is seen in the acoustic image:

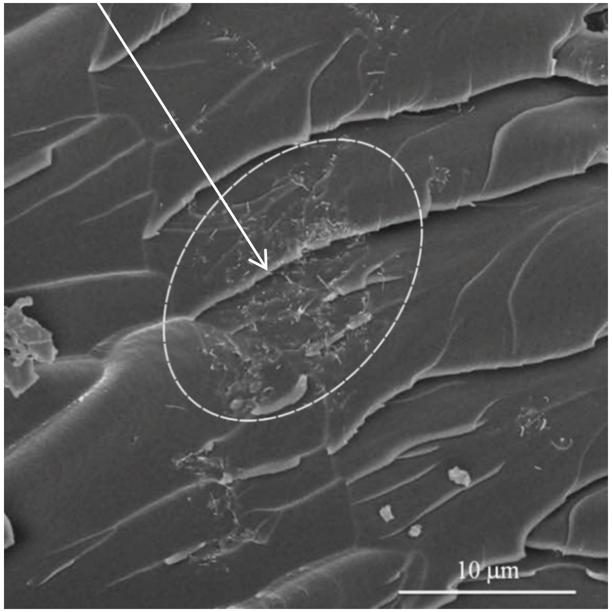
- air-filled fractal conglomerations with sizes ≥ 1÷2 μm
- stiff inclusions with sizes exceeded 20÷30 μm

3. Acoustical imaging in composites with carbon nanotubes (epoxy + MWCNT)

Acoustic contrast as a result of non-uniform distribution of nanotubes and corresponding spatial variations of local elasticity.

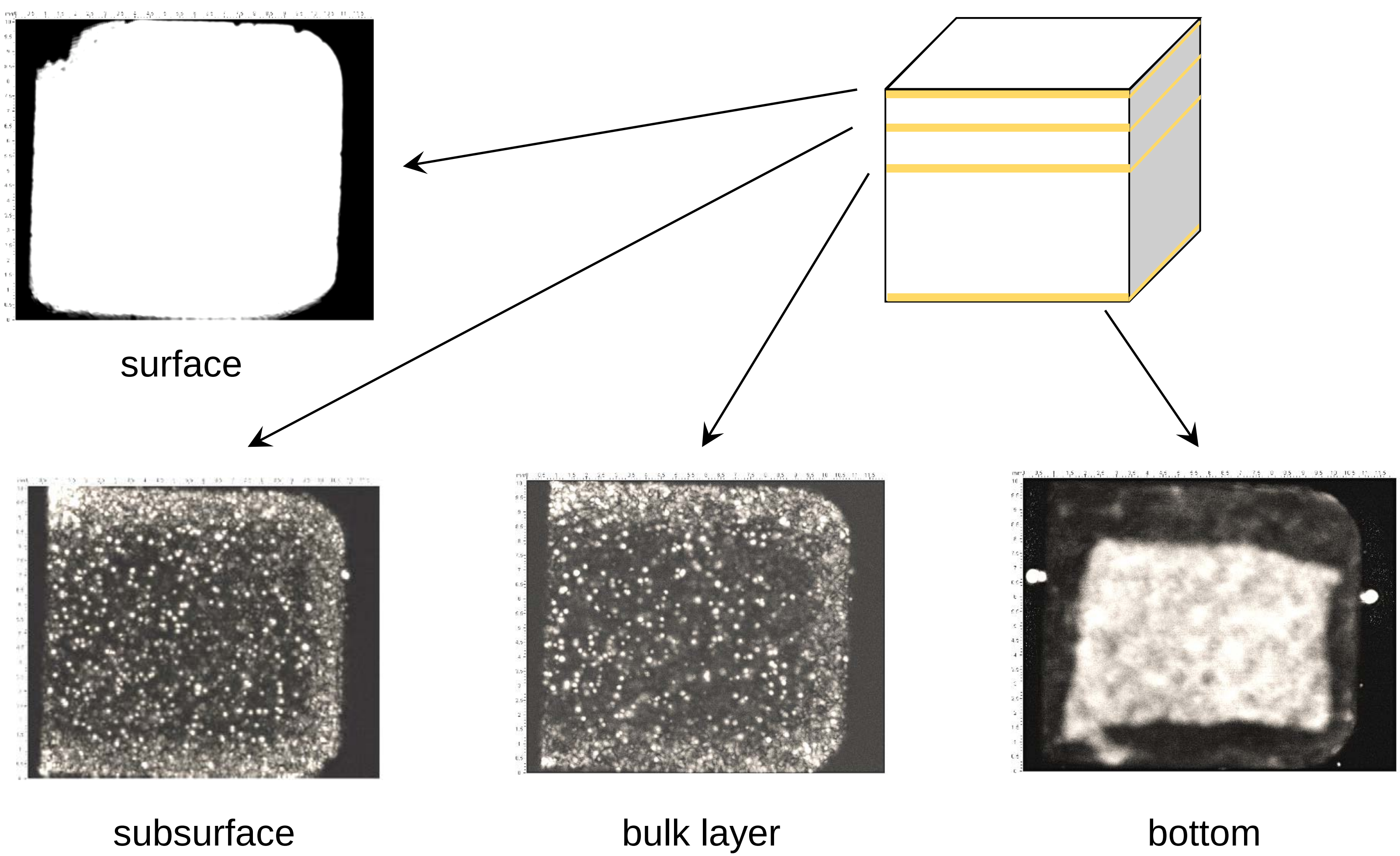
Areas of nanotube concentration



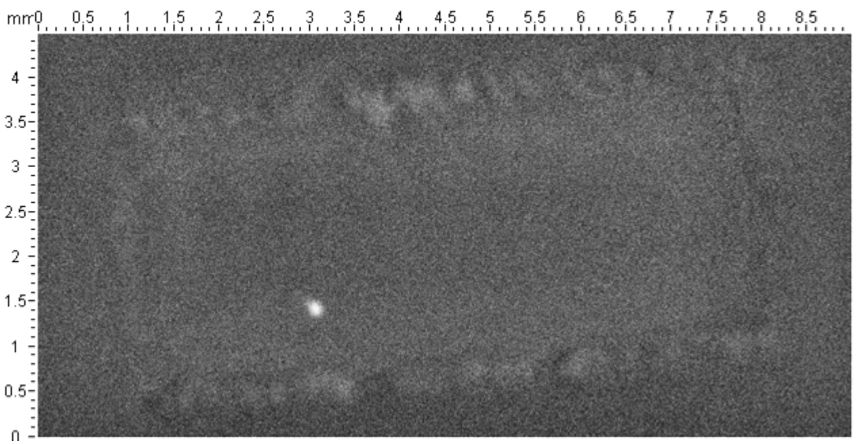


Individual nanotubes

3D imaging of carbon nanocomposites
Bulk microstructure



Interior structure in the pristine epoxy resin



Acoustic image (C-scan) of interior structure in the middle of the specimen thickness.

Specimen thickness d = 1.74 mm
Operation frequency - 50 MHz

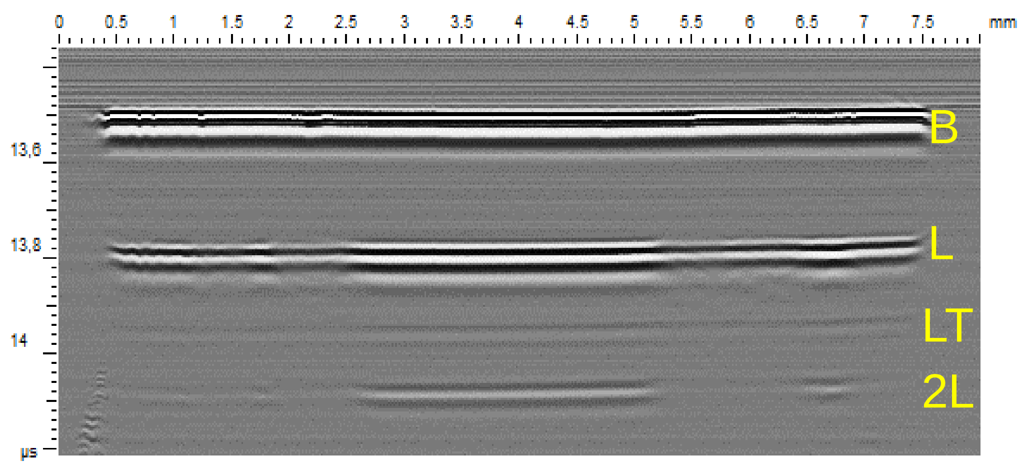
Imaging layer 120 µm thick is inside the specimen at the depth of 400 µm

Acoustic image of the specimen bulk structure in a transverse section (B-scan)

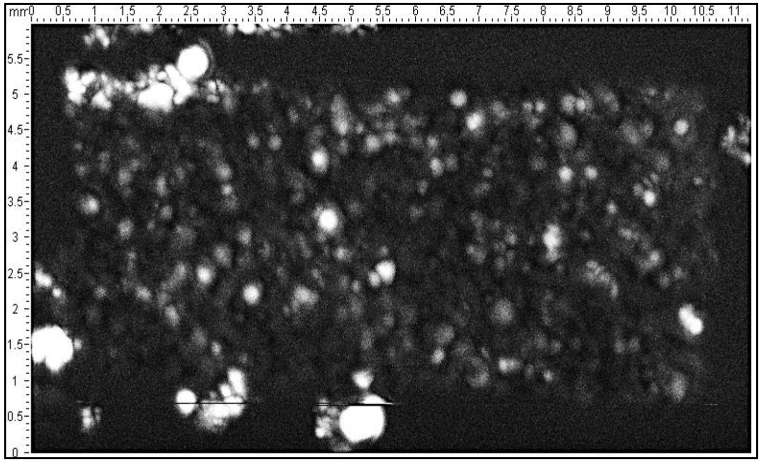
Specimen thickness d = 400 µm
Operation frequency - 100 MHz

specimen face

specimen bottom



Bulk microstructure of the (epoxy + 1.5 w% EG) specimen



Acoustic image (C-scan) of interior structure in the middle of the specimen thickness.

Specimen thickness d = 1.35 mm
Operation frequency - 50 MHz

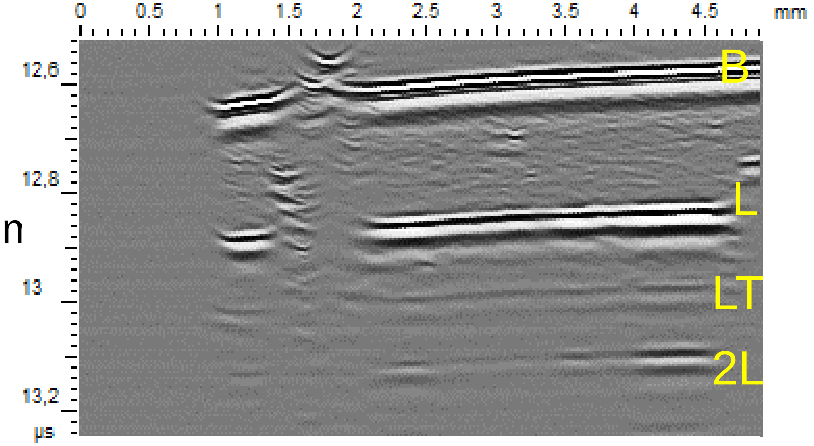
Imaging layer 200 μm thick is inside the specimen at the depth of 405 μm.

Acoustic image of the specimen bulk structure in a transverse section (B-scan)

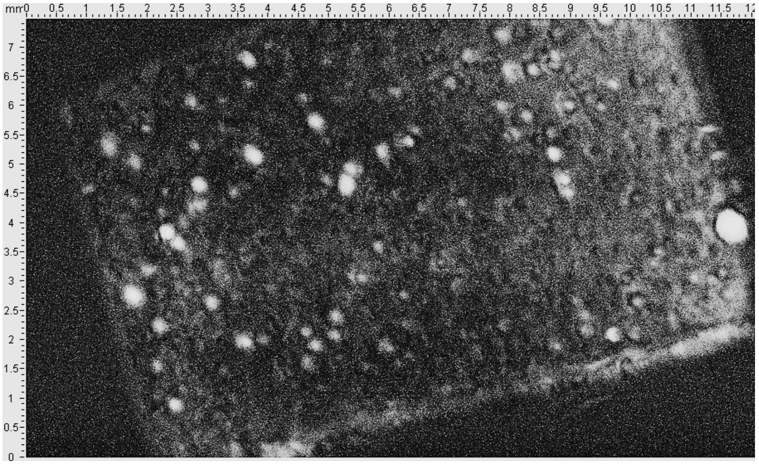
Specimen thickness d = 420 μm
Operation frequency - 100 MHz

specimen face

specimen botton



Bulk microstructure of the (epoxy + 1.5 w% FMG) specimen



Acoustic image (C-scan) of interior structure in the middle of the specimen thickness.

Specimen thickness d = 1.42 mm
Operation frequency - 50 MHz

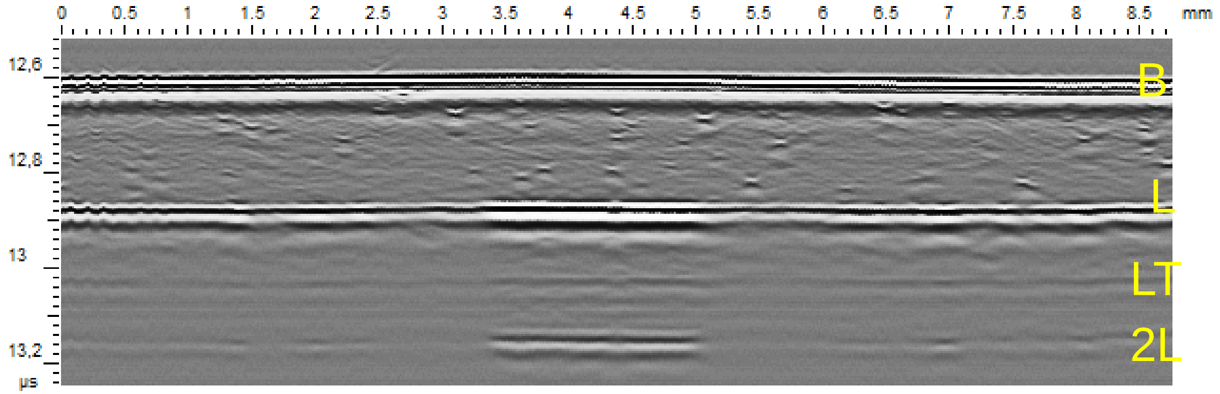
Imaging layer 120 µm thick is inside the specimen at the depth of 310 µm.

Acoustic image of the specimen bulk structure in a transverse section (B-scan)

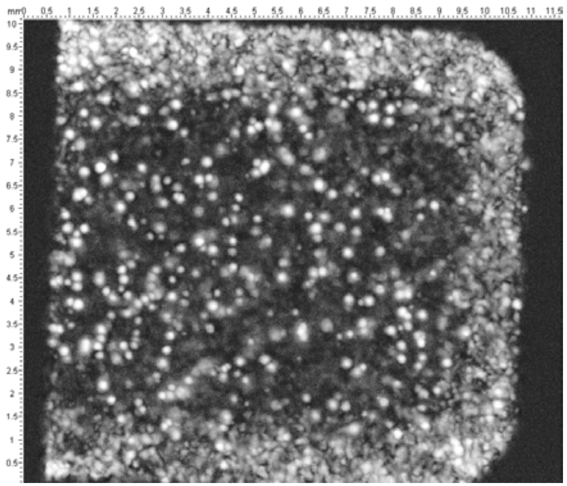
Specimen thickness d = 430 µm
Operation frequency - 100 MHz

specimen face

specimen bottom



Bulk microstructure of the (epoxy + 0.75 w% GNP) specimen



Acoustic image (C-scan) of interior structure in the middle of the specimen thickness.

Specimen thickness d = 1.56 mm
Operation frequency - 50 MHz

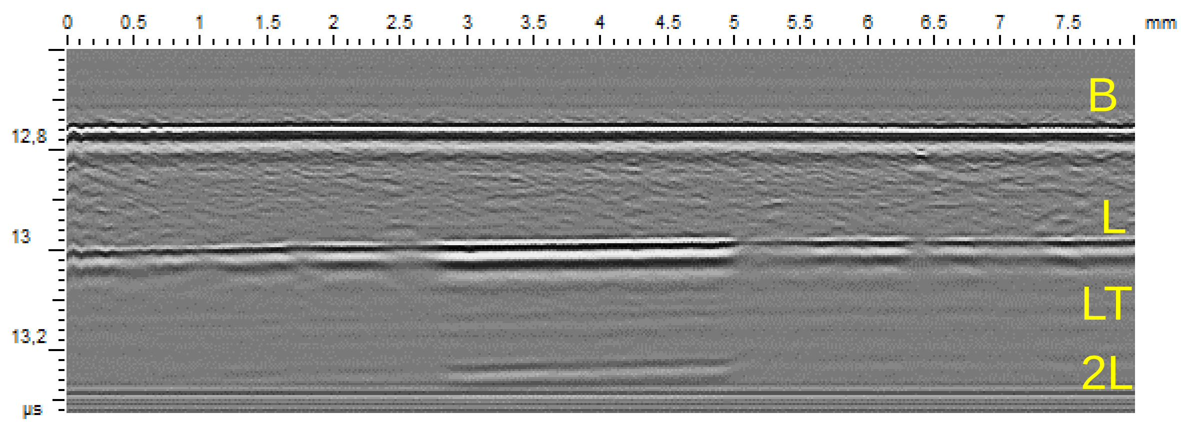
Imaging layer 130 μm thick is inside the specimen at the depth of 400 μm.

Acoustic image of the specimen bulk structure in a transverse section (B-scan)

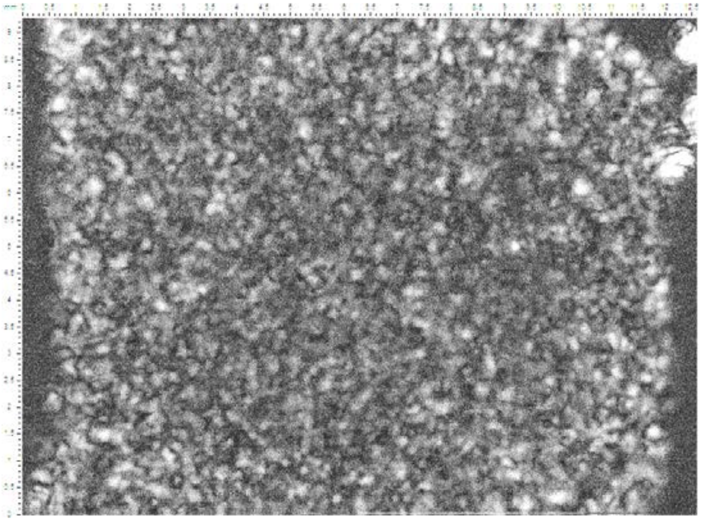
Specimen thickness d = 360 μm
Operation frequency - 100 MHz

specimen face

specimen bottom



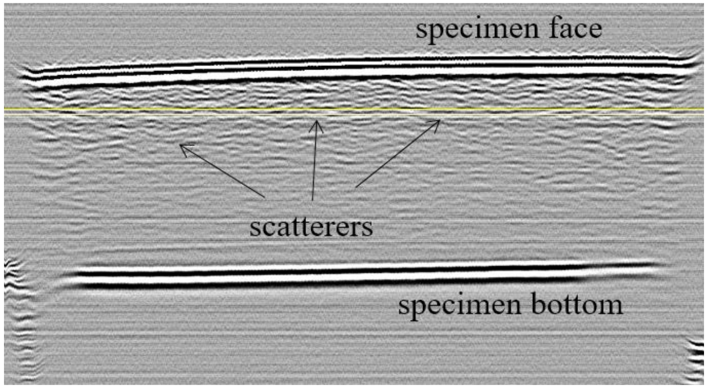
Bulk microstructure of the (epoxy + 0.1 w% MWCNT) specimen



Acoustic image (C-scan) of interior structure in the middle of the specimen depth.

Specimen thickness   d = 1.39 mm
Operation frequency - 100 MHz

Imaging layer 60 µm thick is inside the specimen at the depth of 280 µm.



Imaging layer

Acoustic image of bulk microstructure in a transverse section (B-scan) of the same specimen

Material	Specimen thickness d, mm	Longitudinal sound velocity c_L, km/sec	Transverse sound velocity c_T, km/sec	Density ρ, g/cm^3
Epoxy 100%	0.40	2.88	1.37	1.170
	1.74	2.90	-	-
Epoxy+1 w % EG	0.36	3.00	1.40	1.186
	1.58	2.86	-	-
Epoxy+1 w %GNP	0.43	2.99	1.41	1.182
	0.93	3.05	-	-
Epoxy+1 w %TG	1.60	3.04	-	1.135
Epoxy+ 0,1 w % MWCNT	1.39	2.80	-	1.180
Average		**2.99**	**1.39**	**1.171**

Comparison of non-destructive techniques for 3D visualization of bulk microstructure in nanocomposites

Available techniques of bulk microstructure visualization:

- **High –resolution X-ray tomography**

Spatial resolution is given by the thickness of the X-ray probe beam.

Micron-scale resolution is implemented by synchrotron radiation or application of special high-power X-ray tubes.

- **Impulse scanning acoustic microscopy**

Spatial resolution is given by the wavelength (15 – 60 μm) of the probe ultrasound.

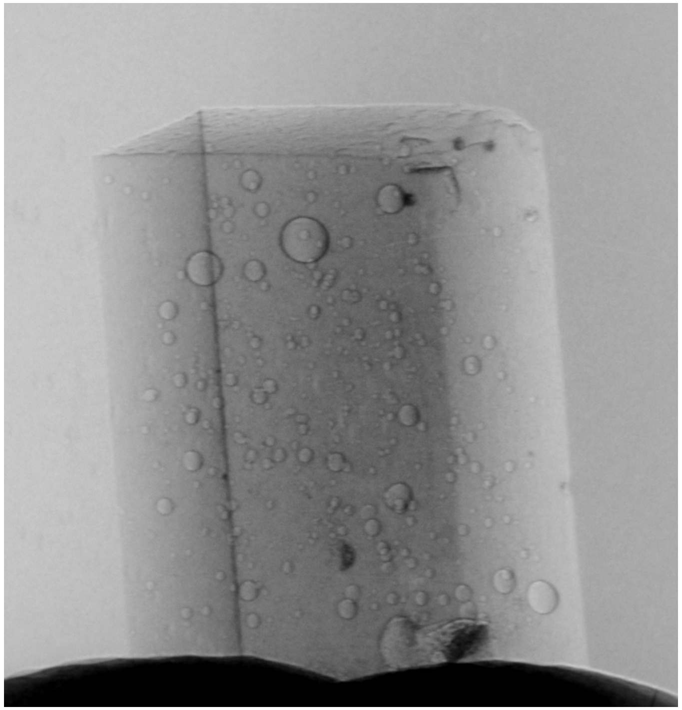
Ultramicroscopic mode provides micron resolution of 3D imaging of the bulk microstructure.

Bulk microstructure of the (epoxy + 1.5 w% exfoliated graphite) specimen (thickness d = 1.44 mm)

as seen by

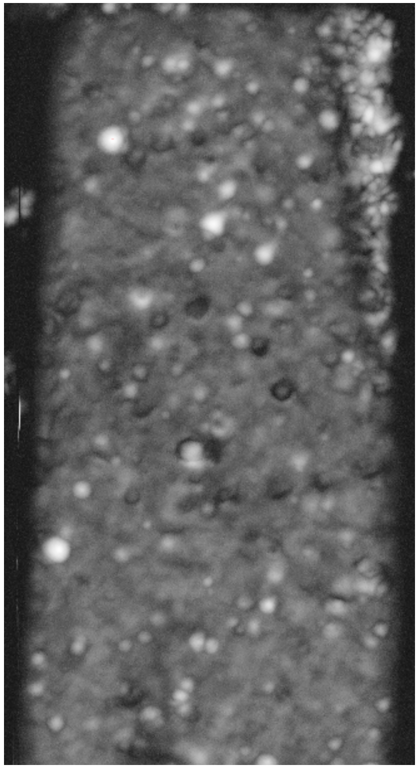
synchrotron radiation;

probe beam ∅ 20 μm



focused ultrasound,

f = 50 MHz, λ = 30 μm

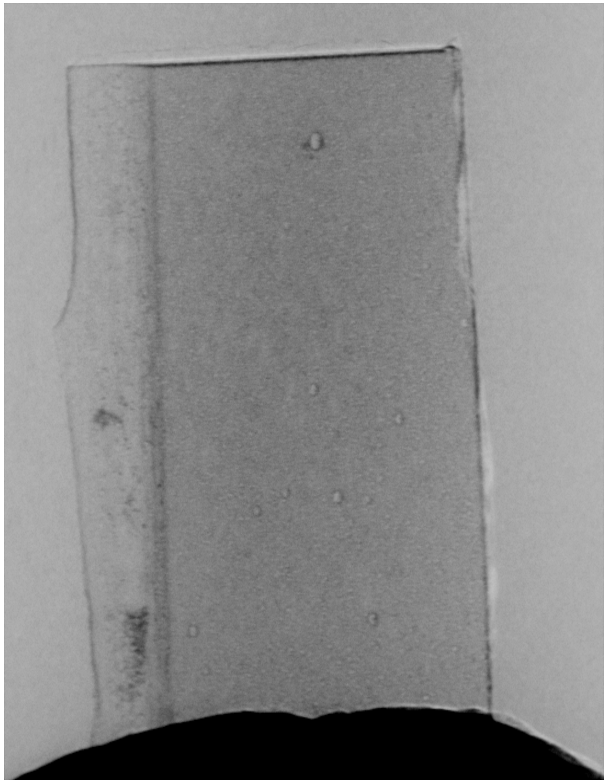


Bulk microstructure of the (epoxy + 0.1 w% MWCNT) specimen (thickness d = 1.4 mm)

as seen by

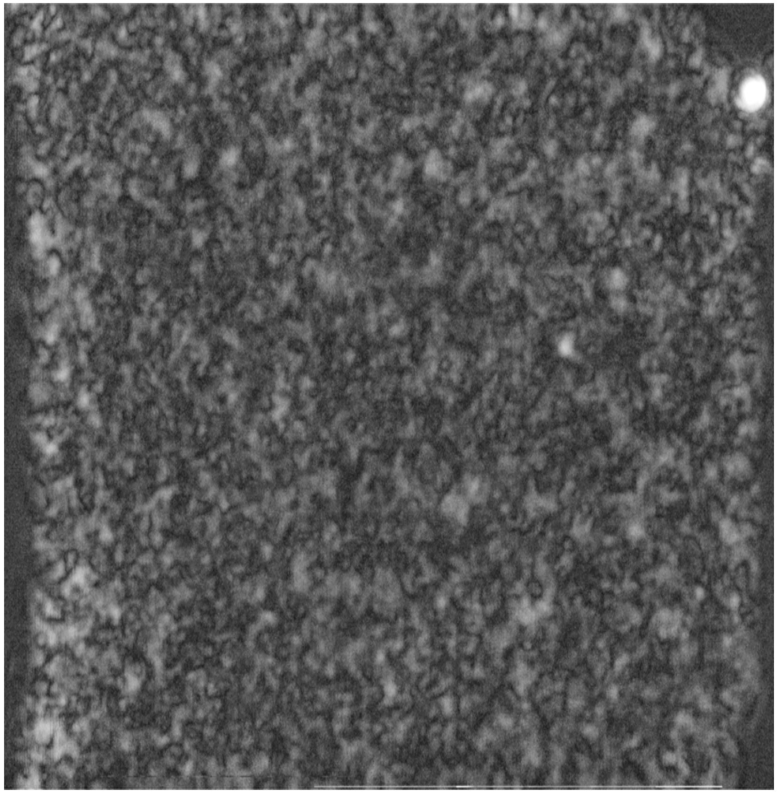
synchrotron radiation;

probe beam ∅ 20 μm



focused ultrasound,

f = 50 MHz, λ = 30 μm



Conclusions

1. It was shown the impulse acoustic microscopy is a powerful technique for studying internal microstructure and local elastic measuring in the bulk of nanocomposite materials.
2. It was the first time when occurrence of complicated fractal mesostructure in the bulk of nanocomposites has been shown.
3. Efficient agglomeration of carbon nanofiller in the bulk of carbon nanocomposites has been demonstrated for 2D carbon nanoforms.
4. Local elastic measurements demonstrated sufficient elastic homogeneity of carbon nanocomposites despite occurrence of bulk mesostructure.

Ultrasonic elastic measurements demonstrate minimal influence of nanofiller on elasticity of carbon nanocomposites for wide spectrum of carbon nanoforms being used as nanofiller – from exfoliated graphite up to carbon nanotubes and thick grapheme stacks.

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Thank you!