

# Application of acoustic microscopy technique for the bulk visualization and elasticity measurement of nanocomposites

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**Abstract.** The impulse acoustic microscopy (AM) has been applied to study 3D microstructure and local mechanical properties of carbon nanocomposites. The particles of exfoliated graphite, graphite nanoplatelets, carbon nanoflakes, and carbon nanotubes have been used as a nanofiller. The AM technique shows the tendency of carbon nanoparticles to clusterization and formation of fractal micron-sized structures. Nanoparticle aggregates are visible on acoustic images for all types of carbon nanocomposites at arbitrary depth of their bulk. The elastic measurement demonstrates a weak dependence on type and content of carbon nanofiller. The impulse AM is the technique that provides direct data on bulk structure of a composite matter; it is characterized by combination of high efficiency and availability.

## 1. Introduction

The idea of nanocomposites implies that substantial changes in composite properties are realized at minimal content of nanofiller [1,2]. The changes stem from formation of extensive bulk networks of contacting nanoparticles and great value of contact interface of nanoparticles with polymer matrix. Highly dense distribution of contact interfaces results in restructuring polymer matrix and altering properties of the composite material. Therefore, nanoforms with big aspect ratios (nanotubes, nanoplatelets, and nanoflakes) are used as a filler to provide ramified interparticle contacts. Topology of nanofiller distribution is of great importance for nanocomposite properties. Uniform distribution of nanoparticles is needed to provide optimum conditions for forming the continuous clusters of nanoparticles and for maximal influence of nanofiller on composite properties.

The problem of the bulk structure of the filler in nanocomposites is the key for the purposeful creation of nanocomposite materials with desired properties. Progress in the field of nanocomposites is largely associated with the ability to characterize and control their integrated microstructure. In addition, there are new fundamental problems: identification of the variety of fractal structures formed by nanoobjects, the properties influence of these nanoobjects on the nanocomposite properties depending on the morphology of the fractal structure, etc.

Nowadays, the need to control microstructure of nanocomposites is underestimated. Publications on nanocomposites include structural studies using electron and probe microscopies to visualize only the sample surface or the small areas within a region of several microns that is associated with individual cluster of nanoparticles. Nevertheless, the presence of bulk microstructure in



nanocomposites was revealed by a small-angle scattering X-ray method. In Ref. [3], heterogeneous and multilevel distribution of nanoparticles in the form of fractal structures and conglomerates was demonstrated. This X-ray method allows measuring the fractal dimension of the structures that gives indirect characterization of the nanocomposite microstructure. The direct observation is possible by X-ray and acoustic microscopy (AM) only. Both techniques provide the same resolution; the acoustic imaging is simpler, safer and allows local measuring the elastic properties.

In the paper, the bulk mesostructure and local mechanical properties of epoxy nanocomposites with diverse carbon nanoforms (particles of exfoliated graphite, graphite nanoplatelets, carbon nanoflakes, and carbon nanotubes) have been studied by the impulse AM methods.

## 2. Experimental

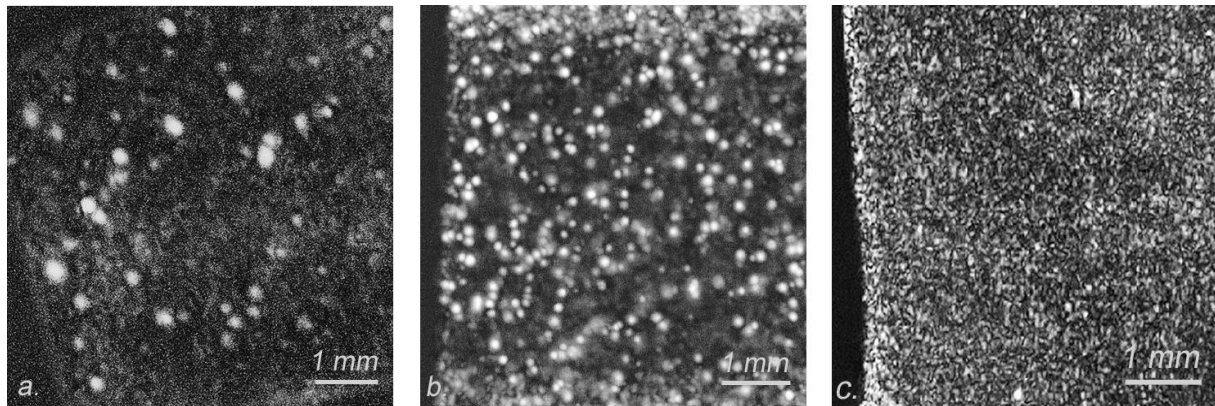
The impulse AM technique seems to be a powerful tool for visualizing cluster structure inside the nanocomposite bulk [4]. Moderate frequencies of 50-200 MHz provide spatial resolution of 15-60  $\mu\text{m}$  that is substantially bigger than characteristic sizes of carbon nanoparticles, so, the individual particles could not be resolved. But this frequency range is optimal to observe particles distribution, large-scale details of the nanofiller fractal structure, including zones of fractal agglomerations and discrete conglomerates. Visualization of nanofiller conglomerates is performed in the ultramicroscopical regime [5] that is an acoustical analogue of the dark-field light microscopy. Conglomerates generate scattered radiation similar to point sources. Focusing receiver collects the scattered radiation just at the position above the scatterer. Estimations show that fractal agglomerates of carbon nanoparticles could be observed in the images, if their sizes are not smaller than 0.5  $\mu\text{m}$  for the indicated frequency range. So, focused ultrasound is a sensitive instrument for evaluating distribution of carbon nanofiller over the composite bulk, revealing formation of aerogel conglomerates, and studying their fractal nature.

In the paper, epoxy-carbon nanocomposites were under investigation. The epoxy matrix was prepared from Epicote Resin 828 (Momentive Specialty Chemicals Inc.) with own curing agent (modified TEPA) [6,7]. Diverse kind of carbon particles was used for the nanocomposite fabrication. One type of them was so-called carbon nanoflakes (CNF) and graphite nanoplatelets (GNP) in the form of graphite stacks (30-40 atomic layers) manufactured by a fine milling of the exfoliated graphite accompanied by thermal treating. Thickness of CNF and GNP particles was in the range of 10-12 and 7-10 nm; their lateral size was in the range of 10-15 and 0.5-5  $\mu\text{m}$ , respectively. The other kind of filler was carbon nanotubes (CNT). Nanotubes were 20-40 nm in diameter with length of 0.5-20  $\mu\text{m}$ . Filler content was 0.5-1.5 weight % for CNF and GNP epoxy nanocomposites and 0.05-0.1 weight % for the CNT nanocomposite. The procedure included vacuum degassing of liquid matrix, preparation of graphite nanofiller suspension, mixing the liquid matrix and graphite particle suspension in alcohol, its evaporating and degassing the new mixture, adding curing agent and mixing it with the graphite-epoxy suspension, and curing the suspension at normal conditions and at 80°C. Plane-parallel specimens of 1.0-1.6 mm thick have been employed in experiments.

## 3. Results and discussion

### 3.1. Imaging of nanocomposites bulk structure with AM technique

The experimental results are represented as microstructural images at the specimen depth (C-scans) and the cross-sections (B-scans). In Figure 1 in-depth acoustic images are shown. The bright spots inside the material bulk are seen in the Figures 1a, 1b for CNF and GNP fillers. Brightness of the spots is caused by high efficiency of ultrasonic scattering at the obstacles, which are caused by nanoparticles agglomeration to the micron-sized fractal conglomerates. The effectiveness is caused by the fact that conglomerates include air and constitute aerogel particles. According to our estimation, such micron-sized conglomerates can be visible. Figure 1c represents the bulk microstructure for specimen with CNT filler. The microstructure demonstrates non-uniform distribution of CNT local density, as it has been shown in our previous studying by scanning electron microscopy [8]. Visible spots in acoustic image are the compact nanotube packages separated from each other and linked by single filaments.

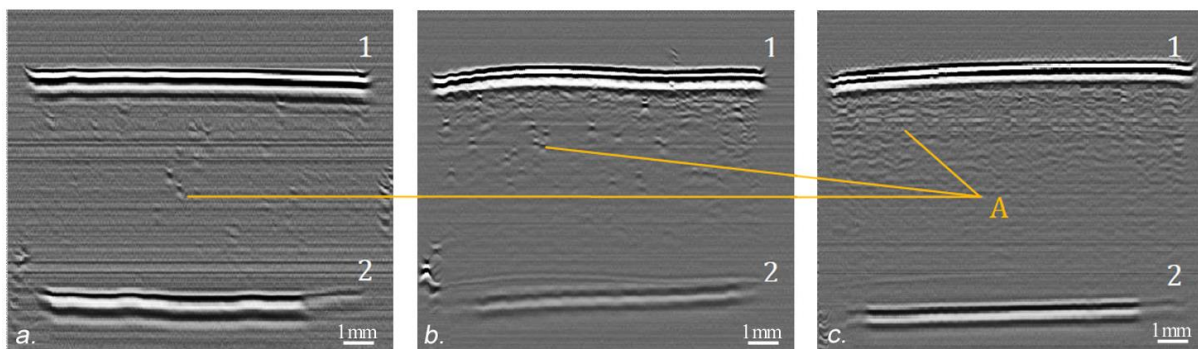


**Figure 1.** Acoustic imaging (C-scans) of carbon-epoxy nanocomposite with different contents and types of nanofiller at the depth of 0.5 mm: (a) epoxy+1.5 wt% CNF; (b) epoxy+0.75 wt% GNP; (c) epoxy+0.1 wt%.

The impulse AM technique was applied to evaluate homogeneity of elastic properties of the nanocomposites. For the goal, a set of B-scans was made (Fig. 2). The images show high-level elastic homogeneity for all nanocomposite samples. Small inclination of the bottom line in the B-scans is caused by geometry of the samples. The elastic homogeneity did not depend on filler content, at least, within the concentration range that has been employed in the current experiments.

### 3.2. Measuring the elastic properties of nanocomposites with AM technique

One of the essential goals of nanotechnology is developing nanomaterials with improved elastic and strength properties. Ultrasound is not suitable instrument for studying strength properties, but impulse AM is an efficient technique to study local elastic properties and their distribution over the material bulk by means of sonic velocity measurement. Data on the delay time between echoes reflected from the specimen face and bottom and the thickness measuring make it possible to find value of the sonic velocity inside the focal area of a probe beam. For epoxy-carbon nanocomposites, the longitudinal elastic wave velocity  $c_L$  was found (Table 1). Data on the material density  $\rho$  have been obtained by hydrostatic (Archimedes) weighing. These data on sonic velocity and density have been used to find longitudinal elastic modulus  $C = \rho c_L^2$ .



**Figure 2.** Acoustic imaging transverse cross-sections (B-scans) of carbon-epoxy nanocomposite with different contents and types of nanofiller: (a) epoxy + 1.5 wt % CNF (thickness of 1.42 mm); (b) epoxy + 0.75 % wt GNP (1.33 mm thick); (c) epoxy + 0.1 wt % CNT (1.39 mm thick). 1 – echo-line from the specimen top; 2 – echo-trace from the bottom; A – echoes from the structural elements inside the specimen bulk. Length of the scanning area is 12 mm.

**Table 1.** Measured longitudinal sonic velocity  $c_L$ , material density  $\rho$ , and longitudinal elastic modulus  $C$  in carbon-epoxy nanocomposites with various types and concentrations of nanofiller.

| Material   |        | $c_L$ , km/s | $\rho$ , g/cm <sup>3</sup> | $C$ , GPa |
|------------|--------|--------------|----------------------------|-----------|
| pure epoxy |        | 2.90         | 1.170                      | 9,8       |
| TG         | 0.25 % | 2.97         | 1.180                      | 11        |
|            | 0.5 %  | 3.00         | 1.186                      | 11        |
|            | 1.0 %  | 3.05         | 1.180                      | 11        |
|            | 1.5 %  | 2.97         | 1.189                      | 11        |
| GNP        | 0,5 %  | 2.87         | 1.179                      | 9,9       |
|            | 0.75 % | 2.88         | 1.186                      | 10        |
|            | 1.0 %  | 2.86         | 1.186                      | 10        |
| CNT        | 0.05 % | 2.73         | 1.156                      | 8,4       |
|            | 0.1 %  | 2.80         | 1.180                      | 9,3       |

Microacoustical measurements have revealed a weak influence of the nanocarbon filler on elastic properties of the composites. In spite of the observed bulk mesostructure including rather large-scaled particles or nanoparticle conglomerates, contribution of the carbon nanofiller in elastic properties is so small that its spatial non-uniform distribution does not induce any inhomogeneity of the material elasticity. The measured sonic velocity values are closed to the measurements for pure epoxy.

In literature, there are evidences of the elastic modulus increment in a polymer material as a result of its transformation into the nanocomposite state [9-12]. Our results are in a contradiction with them, which is caused by diversity in measuring technique and treating the elastic properties concept.

#### 4. Conclusion

The experimental results demonstrate that the pulse acoustic microscopy is a powerful technique for bulk microstructure visualization and local elastic measuring of nanocomposite material. The occurrence of complicated fractal microstructure in the bulk of nanocomposites has been shown. Efficient agglomeration of carbon nanofiller has been demonstrated. Local elastic measurements demonstrate elastic homogeneity of the studied nanocomposites despite the bulk microstructure presents. Ultrasonic elastic measurements demonstrate minimal influence of filler on nanocomposite elasticity.

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