Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 70 (2015) 703 – 706

Physics Procedia

2015 International Congress on Ultrasonics, 2015 ICU Metz

What does see the impulse acoustic microscopy inside nanocomposites?

V.M. Levin[a,b,*], Y.S. Petronyuk[a,b], E.S. Morokov[a,b], A. Celzard[c], S. Bellucci[d], P.P. Kuzhir[e]

[a]*Emanuel Institute of Biochemical Physics Russian Academy of sciences, 4 Kosygin st., Moscow, 119334, Russia*
[b]*Scientific and Technological Center of Unique Instrumentation, Russian Academy of sciences, 15 Butlerov st., Moscow, 117342, Russia*
[c]*Institut Jean Lamour – UMR Université de Lorraine – CNRS 7198, France*
[d]*INFN-Laboratori Nazionali di Frascati, Via E. Fermi 40, Frascati, 00044, Italy*
[e]*Research Institute for Nuclear Problems, Belarusian State University, 11 Bobruiskaya st., Minsk, 220030, Belarus*

Abstract

The paper presents results of studying bulk microstructure in carbon nanocomposites by impulse acoustic microscopy technique. Nanocomposite materials are in the focus of interest because of their outstanding properties in minimal nanofiller content. Large surface area and high superficial activity cause strong interaction between nanoparticles that can result in formation of fractal conglomerates. This paper involves results of the first direct observation of nanoparticle conglomerates inside the bulk of epoxy-carbon nanocomposites. Diverse types of carbon nanofiller have been under investigation. The impulse acoustic microscope SIAM-1 (Acoustic Microscopy Lab, IBCP RAS) has been employed for 3D imaging bulk microstructure and measuring elastic properties of the nanocomposite specimens. The range of 50-200 MHz allows observing microstructure inside the entire specimen bulk. Acoustic images are obtained in the ultramicroscopic regime; they are formed by the Rayleigh type scattered radiation. It has been found the high-resolution acoustic vision (impulse acoustic microscopy) is an efficient technique to observe mesostructure formed by fractal cluster inside nanocomposites. The clusterization takes its utmost form in nanocomposites with graphite nanoplatelets as nanofiller. The nanoparticles agglomerate into micron-sized conglomerates distributed randomly over the material. Mesostructure in nanocomposites filled with carbon nanotubes is alternation of regions with diverse density of nanotube packing. Regions with alternative density of CNT packing are clearly seen in acoustical images as neighboring pixels of various brightness.

Peer-review under responsibility of the Scientific Committee of ICU 2015

Keywords: ultrasonic imaging; impulse acoustic microscopy; microstructure; nanocomposite

* Corresponding author. Tel.: +7-499-137-83-47; fax: +7-499-137-41-01.
E-mail address: levin1943@gmail.com

Peer-review under responsibility of the Scientific Committee of ICU 2015
doi:10.1016/j.phpro.2015.08.094

1. Introduction

Nanocomposites, their properties and their possible applications attract high scientific interest [1-10]. The publications touch upon the problem of nanocomposite structure at the nanoscale level only. Electron or probe microscopy is employed to display spatial distribution of nanofiller particles within small, micron-sized area of the specimen surface. The areas are chosen rich in nanoparticle content; spaces between clusters are not interesting for visualization. For the first time occurrence of the fractal cluster microstructure in nanocomposites was shown by indirect methods with using small-angle X-ray scattering [11, 12].

The impulse acoustic microscopy technique seems to be a powerful instrument for visualizing cluster structure inside the nanocomposite bulk. Moderate frequencies of 50-200 MHz provide spatial resolution of the order of some tens of micrometers (15-60 µm). These values are substantially higher than characteristic sizes of carbon nanoparticles. The probe ultrasound could not resolve individual particles of carbon nanofiller – their uniform distribution does not result in any contrast details in acoustical images. But this frequency range is optimum to observe large-scale details of the nanofiller fractal structure, including zones of fractal agglomerations, discrete conglomerates and aerogel particles.

There are two possible scenarios for the interaction ultrasound with such structures. In the case of uniform nanofiller distribution nanocomposite materials are taken by ultrasound as homogeneous structured media. Presence of the filler induces only changing elastic property of the media. The other scenario is proper to nanocomposites with particle agglomeration. Conglomerates, likely, contain air in the space between nanosheets or inside nanotubes; so they are excellent scatterers of ultrasonic radiation at frequencies being in use. Visualization of nanofiller conglomerates is performed in the ultramicroscopical regime that is an acoustical analog of the dark-field light microscopy. Conglomerates generate scattered radiation similar to point sources. The ultrasonic focusing receiver is able to perceive the scattered radiation only at its position against such a scatterer. Outside it the receiver does not feel any scattered radiation. So, results of nanofiller agglomeration in the bulk of a nanocomposite should be seen in acoustic images as distribution of small bright spots against the dark background. These pictures, similar to optical images in the dark-field light microscopy, demonstrate only presence of small particles and give their distribution over the specimen bulk; they do not display real sizes and shape of particles. Occurrence of individual scatterers in acoustic images is determined by amplitudes of echo pulses V_{sc} – to be displayed the amplitudes should surpass the noise level V_n in the electronic system of the focusing ultrasonic receiver: $V_{sc} / V_n > 1$.

Scattering by small particles is known as Rayleigh scattering; its efficiency falls as the particle size a decreases. In the case of ultrasonic scattering at small soft particles, for which the inequality $(\rho{\cdot}c)_{sc} << (\rho{\cdot}c)_{matrix}$ is valid, the total cross-section of scattering coincides with the geometric cross-section of the scatterer: $\sigma \sim \pi{\cdot}a^2$. For air-filled fractal particles their echo signals are $V_{sc} = B{\cdot}a$, here B – value that does not depend on properties and sizes of scatterers. Experimental data on dynamic range (40 dB) of the acoustic microscope being in use in our experiments make it possible to estimate critical sizes of scatterers that give them a chance to be displayed in acoustic images. The estimations have shown gas-filled fractal agglomerates of carbon nanoparticles could be observed in the images if their sizes are not smaller than 0.5 µm. Respectively, ultramicroscopic regime provides observation micron- and submicron-sized agglomerates that are much smaller than the ultrasonic wavelength. So, high-frequency ultrasound seems to be a sensitive instrument for evaluating distribution of carbon nanofiller over the composite bulk, for revealing formation of aerogel conglomerates and studying their fractal nature. The ascertained features of acoustical contrast formation will be applied to treat experimental results presented below.

2. Experiments

2.1. Specimen description

The epoxy resin Epicote Resin 828, a medium viscosity resin produced from bisphenol A and Epichlorohydrin (Momentive Specialty Chemicals Inc.) with own curing agent called A1 (being a modified TEPA), has been employed as a matrix material [13-15]. Various kinds of small carbon particles have been used as nanofiller. For one series of specimens graphite nanoplatelets (GNP) have been used to form a composite. They possess approximately the same small thickness of 7-10 nm and extensive lateral sizes up to 0.5-5 µm. Other types of carbon epoxy nanocomposites have been produced with using multiwall carbon nanotubes (MWCNT). Nanotubes are of 20-40 nm in diameter; this value is much smaller than nanotube length (0.5-20 μm).

Filler content value in our experiments does not surpass 1.5 wt% for both types of the carbon nanofiller. The weight content of 0.75 and 1.5 wt%, have been used in GNP-epoxy nanocomposite; for MWCNT-based nanocomposite the carbon content has been much smaller – 0.05 and 0.1 wt%. Estimations show that shuch content provides formation of continuous cluster occupying the entire volume of nanocomposite. The real distribution of nanocarbon is a goal of the present investigation.

2.2. Instrumentation

Impulse acoustic microscopes SIAM, designed by the Emanuel Institute of Biochemical Physics, RAS, have been applied for studying internal microstructure of carbon-epoxy nanocomposites. Long-focus (low-aperture) objectives at operation frequencies of 50 and 100 MHz with a half angle aperture of 11° and focal distance of 13.33 and 3.75 mm in water immersion, correspondently, have been employed. The parameters are suitable to visualize the bulk microstructure inside epoxy specimens a few millimetres thick. Principles of the imaging technique are described clearly in [16-18].

2D scanning of the specimen in the focal plane is applied to produce gray-scale images (C-scans) that display structure within the layers located at diverse depth inside the specimen bulk. The depth position of each layer is given by its delay time regarding to the reference signal reflected from specimen surface. In modern acoustic microscopes the reflected echo signal entirely are saved in digital form over the scanning area; the compiled data file is stored as a 3D image of the object. The specimen bulk microstructure is represented as a set of layer-by-layer images (C-scans) at any depth inside the specimen bulk, or as a distribution of reflecting interfaces and scattering centers at any specimen cross section (B-scans) and as an echo patterns of output signal at any point of scanning area.

3. Results and discussion

Image in Fig.1 depict bulk microstructure of epoxy-carbon nanocomposites with (a) 0.75 wt% of graphite nanoplatelets and (b) 0.1 wt% of carbon nanotubes (MWCNT) as filler. Inside the nanocomposite bulk, distribution of numerous bright points appears in acoustic images (Fig.1a, b). Brightness of the spots in the images is evidence of high efficiency of ultrasonic scattering at these obstacles. The nature of the scatterers is an agglomeration of low-dimentional nanocarbon particles and formation micron-sized fractal conglomerates. Presence of air in fractal structure of the conglomerates can be a reasonable explanation of high efficiency of the ultrasonic scattering. According to previous estimations such particles are able to be effective scatterers up to their submicron sizes. As seen from image of GNP nanofilled composite (fig.1a), acoustic microscopy demonstrates an assured tendency of the carbon 2D nanoforms to agglomeration and formation of micron-sized aerogel fractal conglomerates.

Essentially different picture of the internal structure is characteristic for nanocomposite with MWCNT addition. It seems the main mechanism of acoustic contrast in the image (Fig.1b) is variations of CNT local density. Multiwall nanotubes are extensive hollow tubular elements, considerable part of whose volume is hollow or filled by air. Variations in density of nanotubes package induce variations in ultrasonic reflection power. So, in MWCNT nanocomposite agglomeration of nanoparticles is not observed; large-scaled fractal conglomerates are not inherent to this type of the carbon nanoforms. Nevertheless, high-resolution acoustical vision technique is useful for assessing features of nanotube distribution over the material.

4. Conclusion

Methods of impulse acoustic microscopy were applied to observe bulk microstructure of carbon-epoxy nanocomposites. In the frequency range of 50-100 MHz the technique makes it possible to reveal cluster architecture of carbon nanoplatelets and nanotubes in the material. Tendency to form micron-sized fractal conglomerates has been found for nanoplatelets. Carbon nanotubes form regions of alternative density of their packing.

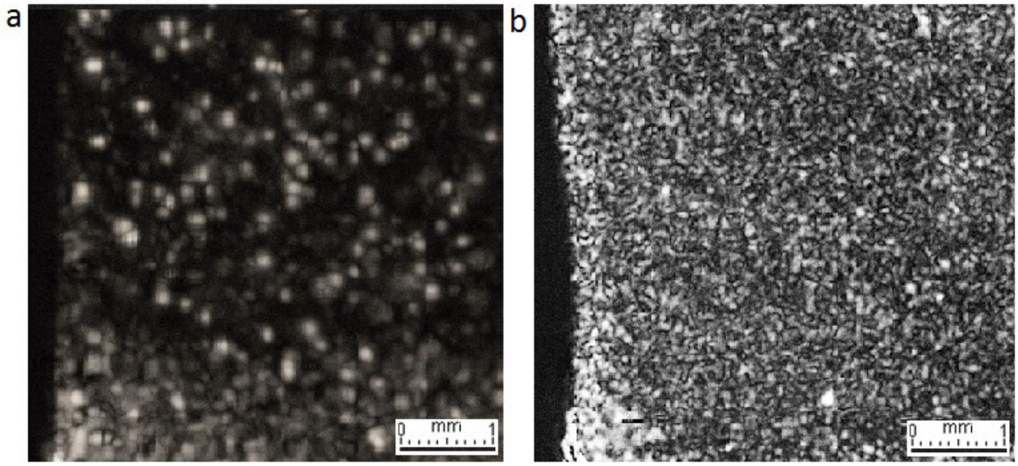

Fig.1 (a) Acoustic imaging the bulk conglomerate microstructure of carbon-epoxy nanocomposite filled with graphite nanoplanelets (**epoxy + 0.75 wt% GNP**). Image are given at depth of 750 µm; (b) Acoustic imaging the bulk microstructure of carbon-epoxy nanocomposite filled with nanotubes (**epoxy + 0.1wt% MWCNT**). Images are given at depth of 320 µm. Operation frequency is 50 MHz.

Acknowledgements

This work was supported in part by PIRSES-2012-318617 FAEMCAR, FP7-PEOPLE-2013-IRSES-610875 NAmiceMC, grant of Russian Foundation of Basic Research (project A-15-02-04994), the grant of Russian Scientific Foundation (project No.15-12-00057) and Belarus-CNRS project BRFFI F13F-004.

References

1. Paul D.R., Robeson L.M., 2008. Polymer nanotechnology. Nanocomposites. Polymer. 49(15), 3187-3204.
2. Stankovich S., et al, 2006. Graphene-based composite materials. Nature, 442, 282-285.
3. Kuilla T. et al, 2010. Recent advances in graphene based polymer composites. Progr. in Polymer Science, 35, 1350–1375.
5. Kim H., Abdala A.A., Macosko Ch.W., 2010. Graphene-polymer nanocomposites. Macromolecules, 43, 6515–6530.
6. Potts J.R., Dreyer D.R., Bielawski Ch.W., Ruoff R.S., 2011. Graphene-based polymer nanocomposites. Polymer, 52, 5-25.
7. Li B., Zhong W.-H., 2011. Review on polymer/graphite nanoplatelet nanocomposites. J Material Science, 46, 5595–5614.
8. Mittal G.,et al, 2015. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. J. Industr. Eng. Chem., 21, 11-25.
9. Gao J.-S., Shiu S.-Ch., Tsai J.-L., 2013. Mechanical properties of polymer near graphite sheet. J. Composite Materials, 47(4), 449-458.
10. Coleman J.N., et al, 2006. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. Carbon, 44(9), 1624-1652.
11. Schaefer D.W., et al., 2000. Multilevel structure of reinforcing silica and carbon. J. Appl. Crystallogr., 33, 587-591.
12. Schaefer D.W., Justice R.S., 2007. How Nano Are Nanocomposites? Macromolecules, 40(24), 8501-8517.
13. Kuzhir P., et al., 2011. Microwave probing of nanocarbon based epoxy resin composite films: Toward electromagnetic shielding. Thin Solid Films, 519, 4114–4118.
14. Macutkevic J., et al., 2012. Terahertz time domain spectroscopy of epoxy resin composite with various carbon inclusions. Chem. Phys., 404, 129-135.
15. Kuzhir P., et al., 2013. Epoxy composites filled with high surface area-carbon fillers: Optimization of electromagnetic shielding, electrical, mechanical, and thermal properties. J. Appl. Phys., 114, 164304.
16. Zakutailov K.V., Levin V.M., Petronyuk Yu.S., 2010. High-resolution ultrasound methods: Microstructure visualization and diagnostics of elastic properties of modern materials (Review). Inorganic Materials, v.46, №15, 1635-1661.
17. Liu S., et al., 2006. Application of pulse acoustic microscopy technique for 3D imaging bulk microstructure of carbon fiber-reinforced composites. Ultrasonics, 44(Supp.L), e1037–1044.
18. Petronyuk Yu.S., et al, 2005. Measuring elastic properties and anisotropy of microstructural units of laminate composite materials by microacoustical technique. J Materials Science & Engg.-A, 412(1-2), 93-96.