06

Features of visualization of the carbon nanotubes distribution in polymer media using atomic force microscopy

© S.M. Khantimerov, R.R. Garipov, D.A. Bizyaev, N.M. Lyadov, N.M. Suleimanov

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Kazan, Russia
E-mail: gari_rtrf@mail.ru

Received May 22, 2025
Revised July 31, 2025
Accepted August 18, 2025

In this work, the electrical methods of atomic force microscopy were used to visualize the distribution of carbon nanotubes in polymethyl methacrylate, and the true location of the nanotubes was revealed without the influence of roughness or local surface irregularities of the polymer matrix. It was shown that the atomic force microscopy method, which is a non-destructive research method, can be used to study the distribution of carbon nanotubes in a polymer matrix.

Keywords: carbon nanotubes, polymers, composite materials, atomic force microscopy.

DOI: 10.61011/TPL.2025.11.62215.20379

Polymer-based composite materials with finely dispersed fillers hold promise for application in various fields of industry [1,2]. The most promising fillers are carbon nanotubes (CNTs) [3,4] and graphene [5,6], which offer unique physical, mechanical, and electrophysical properties. The key factor determining the effectiveness of material modification in production of polymer composites is a uniform distribution of the filler in a polymer matrix. Therefore, the study of filler distribution in a polymer matrix is crucial in composite material engineering. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used widely for this purpose. Specifically, the distribution of carbon nanotubes in nylon and polytetrafluoroethylene was studied in [7] by SEM. SEM and TEM were used in [8] to characterize the distribution of CNTs and nanodiamonds in epoxy resin.

Alongside with SEM and TEM studies of composite materials, atomic force microscopy (AFM) presents exceptional opportunities for examining carbon nanotubes positioned on the surface of conductive substrates [9–12]. The conductive properties of CNTs were studied in [9] by AFM in the contact mode (with the probe always remaining in contact with the surface) via spreading resistance measurements. The advantages of this method are its fine resolution and sensitivity, since the probe is in direct contact with carbon nanotubes. However, it is not suitable for examination of CNTs in the bulk of a polymer or composite substrate. With this CNT positioning, the probe does not come into contact with nanotubes, and an electric current is not recorded. Owing to the long-range nature of interaction, electrical semi-contact AFM methods [10–12] may be used to study the distribution of carbon nanomaterials in a polymer matrix. The conductive probe oscillates in this case at a specific frequency. The Kelvin probe force microscopy (KPFM) method was found to be the most sensitive one. It allows one to measure the potential generated in CNTs. However, the resolution of this method decreases with increasing probe–CNT distance due to the long-range nature of interaction between the potentials at the probe and CNTs. Therefore, virtually all electrical AFM techniques are better suited for thin films than for bulk samples. A KPFM technique allowing one to measure the gradient of capacitance formed between several CNTs or a conductive surface and CNTs with a dielectric medium in the form of a polymer [11,12] or a composite [10] between them is used to raise the sensitivity. However, capacitance gradient measurements require two independent lock-in amplifiers, which increases the equipment cost.

All the semi-contact double-pass electrical modes of operation of a scanning probe microscope (SPM) mentioned above have limitations regarding the surface quality of the samples being studied; specifically, we will show below that the surface roughness is critical in this case. In double-pass measurement techniques, of which KPFM is an example, irregularities introduce distortions associated with the topographic relief into the received signal.

The present study reveals the possibility and features of application of electrical atomic force microscopy methods in the examination of distribution of carbon nanotubes in a polymer matrix. Polymethyl methacrylate (PMMA) (Acros Organics, Belgium) was the polymer material, and LUCAN BT 1001M (LG) multi-walled carbon nanotubes processed in accordance with the procedure outlined earlier in [13] served as the dopant. A composite was prepared by dissolving PMMA in chlorobenzene to a concentration of 0.5 wt.% and dispersing pre-processed CNTs in this solution in a concentration of 1 wt.% relative to the polymer mass.

Composite material samples were thin films formed on the surface of a single-crystal silicon (KDB-0.1) substrate. Since a conductive coating is needed for electrical AFM measurements, a silver film was deposited onto the substrate before the composite. After that, the solution of PMMA with CNTs was applied to the stationary substrate, which

was then rotated at speeds up to 3000 rpm for 5 s. Following drying at room temperature, PMMA films with a thickness of approximately 50 nm were formed on the substrate surfaces.

The distribution of carbon nanotubes in the polymer matrix was examined with an EVO 50 XVP scanning electron microscope (Carl Zeiss) and a Solver Smane-A atomic force microscope (NT-MDT, Zelenograd, Russia). Standard silicon NSG-11 cantilevers with force constant $k = 5$ N/m and a resonance frequency of 160 kHz (NT-MDT) were used to investigate the morphology of the samples in AFM measurements. DCP-11 cantilevers (NT-MDT) with a diamond-like conductive coating, a probe tip radius of 100 nm, $k = 6$ N/m, and a resonance frequency of 165 kHz were applied in electrical measurements. Semi-contact double-pass KPFM and single- and double-pass electrostatic force microscopy (EFM) were used for CNT imaging.

A SEM image of the composite material sample with a CNT concentration of 1 wt.% is shown in Fig. 1.

It can be seen that the method for carbon nanotube processing developed earlier allows one to obtain a uniform distribution of CNTs throughout the PMMA volume.

In order to visualize carbon nanotubes by electrical AFM methods, the conductive silver film on the silicon substrate was grounded, and the polymer matrix surface was scanned to find a suitable region. The surface in this region should be as smooth as possible (Fig. 2, *a*). The chosen region featured protrusions with a height no greater than 4 nm. The surface roughness was on the order of 0.34 nm (Fig. 2, *b*). The double-pass KPFM method was applied first (Fig. 2, *b*). A 30–35 mV signal in the region of protrusions found in the topographic map is seen in the figure. The positive potential follows the outline of these protrusions accurately, while the negative potential is larger in area. It may be assumed that the positive potential is due to topographical interference or an artifact. Therefore, the negative potential stems from the interaction between a carbon nanotube embedded in the polymer matrix and the probe. Single- and double-pass EFM was then used to verify this hypothesis. It is assumed that double-pass EFM should yield a similar result: the image will contain both positive and negative responses. At the same time, since the surface relief is not processed in single-pass scanning, the signal associated with surface roughness should vanish.

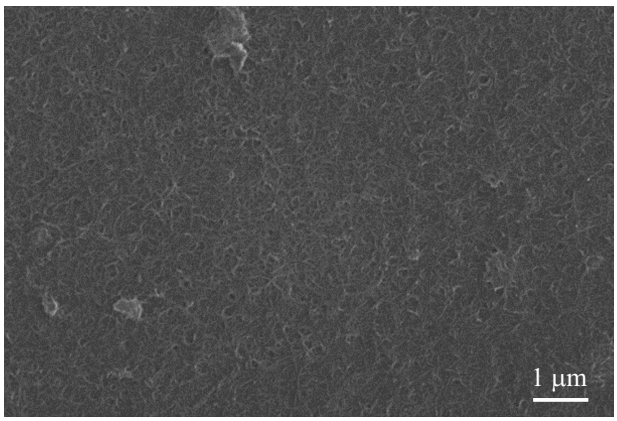

Figure 1. SEM image of a composite material based on CNTs functionalized in accordance with the procedure detailed in [13]. The CNT concentration is 1 wt.%.

The double-pass scanning mode was used first. We failed to obtain an image of this region in the standard configuration programmed into the microscope's control software. A voltage of +1 V was applied to the probe in this case.

It was assumed based on the previous KPFM measurement that the potential in the observed region is negative; therefore, negative voltage was applied to the probe instead of positive one. This was done so that the response in the form of a phase shift of cantilever oscillations would be positive rather than negative and would replicate the image obtained earlier. Interacting like-sign charges repel each other, producing light contrast in the image (Fig. 2, *c*). The voltage applied to the probe was −6 V. This image is an inversion of the one obtained in the KPFM mode. It also contains an element of topography in the form of black depressions next to light protrusions. Certain differences may be noted as well. Since the probe voltage may be varied in this method, a response from a larger number of CNTs was obtained, which is evident when one compares the upper parts of images. As expected, topographic irregularities induce artifacts in the electrical images obtained in double-pass scanning modes. To eliminate this problem, one needs either to perform appropriate image processing and exclude distortions associated with topographic irregularities or to apply scanning methods or modes that do not replicate the surface relief in the measurement process. The latter category includes semi-contact methods with single-pass scanning. Unfortunately, the used SPM and its software do not provide an opportunity to perform KPFM measurements, which ensure the best resolution, in the single-pass scanning mode.

The same region was then scanned using the single-pass EFM method at the same probe voltage (Fig. 2, *d*). It can be seen that the negative signal component, which was previously attributed to topographical interference, has vanished. It is fair to say that the obtained images characterize the arrangement of CNTs in the PMMA matrix. The preferential orientation of CNTs in the matrix is likely attributable to the specifics of sample preparation (namely, the use of pre-processed carbon nanotubes and the application of the CNT solution with sample rotation). If the sample is not rotated, the surface is rougher. In addition, non-functionalized CNTs form agglomerates (Fig. 3). The images presented were obtained by SPM using previously tested methods: the topographic AFM image was obtained in the semi-contact mode and was not used anywhere else (unlike the double-pass scanning mode); the EFM image was obtained in a single pass. It can be seen from Fig. 3, *a* that the surface has both protrusions and depressions. The height spread is 18 nm, while the height variation in Fig. 2, *a* is 4 nm. However, single-pass scanning did not produce

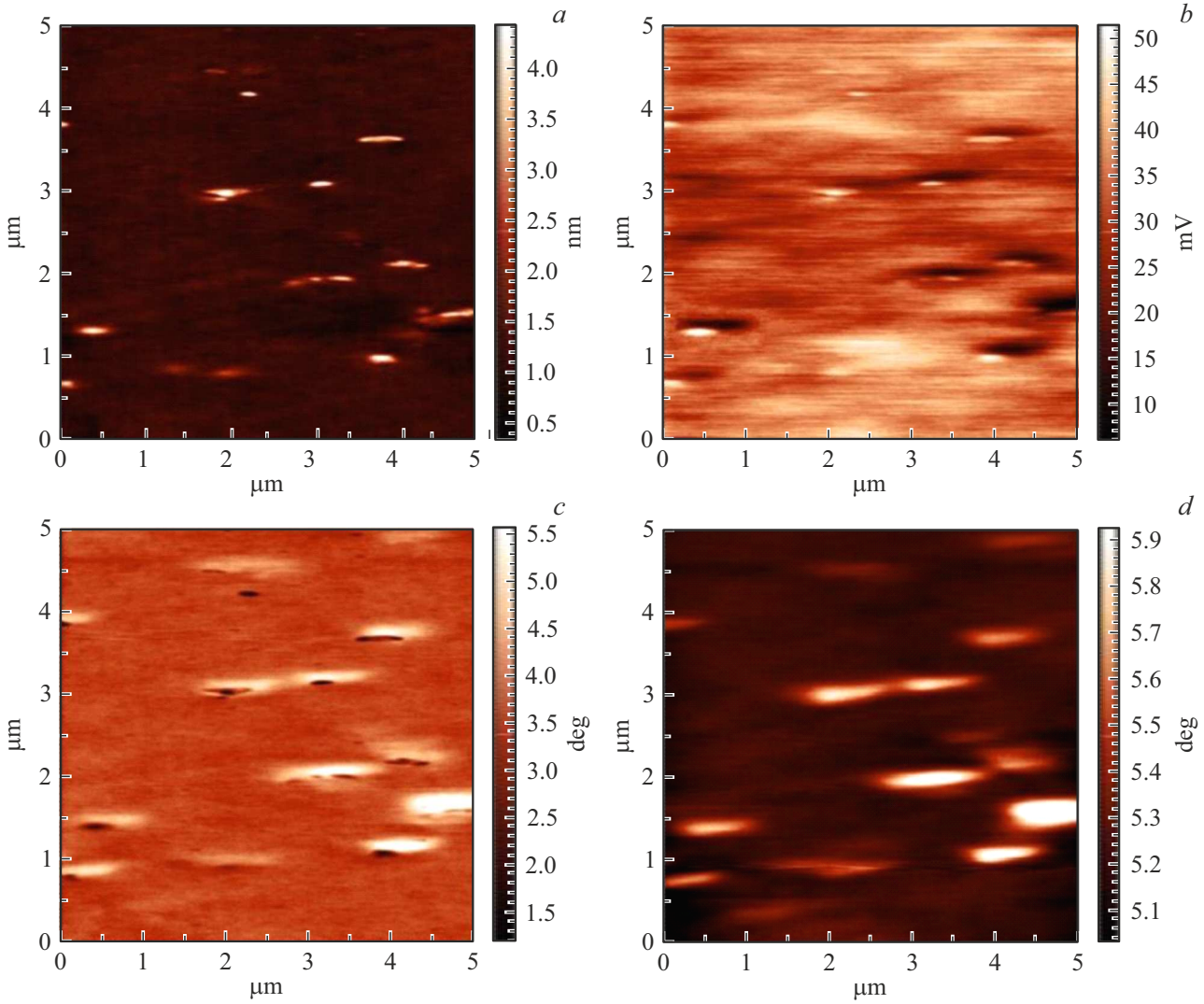

Figure 2. *a* — AFM image of the surface topography of PMMA with 1 wt.% of functionalized CNTs; *b* — KPFM image of the potential distribution within the chosen region; *c* — EFM image of the same region obtained using the double-pass method; *d* — EFM image of the same region obtained using the single-pass method.

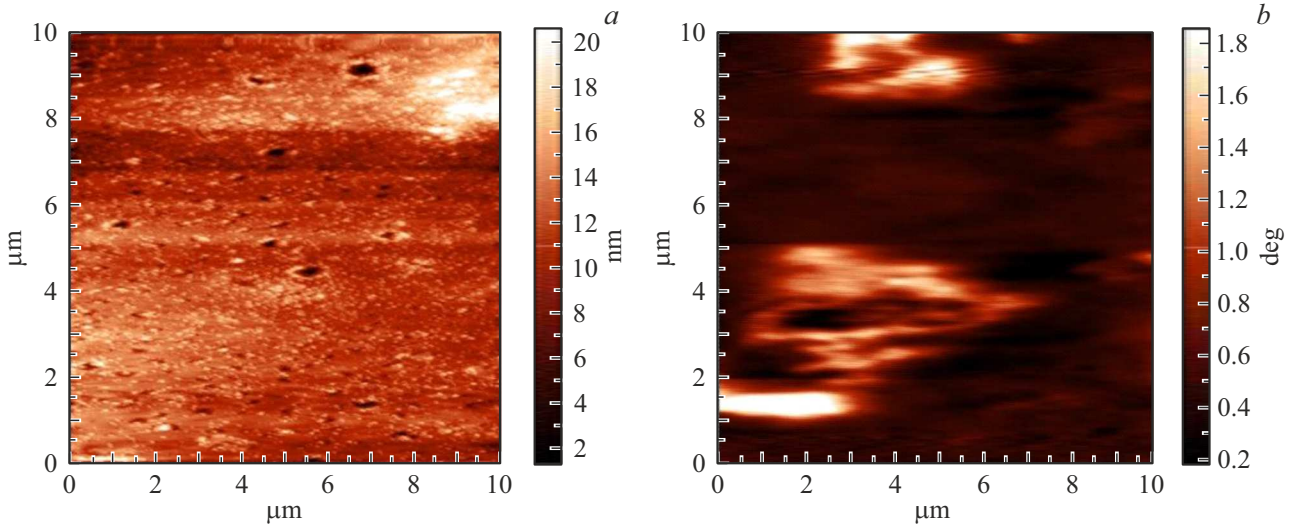

Figure 3. AFM image of the surface of PMMA with 1 wt.% of non-functionalized CNTs (*a*) and SEM image of the same region (*b*).

artifacts related to these surface irregularities. The signal was received only from CNT clusters (Fig. 3, *b*). The obtained results (Figs. 2, *d* and 3, *b*) reveal that single-pass imaging is free from the artifacts produced in double-pass scanning measurements (Figs. 2, *b*, *c*), allowing for a more accurate interpretation of data regardless of the degree of surface development.

Regions of positive and negative potential were observed when the surface of samples was scanned using electrostatic atomic force microscopy. The results of comparative analysis revealed that the regions of negative potential form due to the electrostatic interaction between a CNT embedded in the polymer matrix and the probe, while the regions of positive potential are artifacts associated with protrusions on the sample surface. The obtained images show clearly that CNT functionalization ensures the needed deagglomeration of CNTs, contributing to their uniform distribution in the polymethyl methacrylate matrix.

Thus, it was demonstrated experimentally that electrical AFM methods may be used to visualize the distribution of carbon nanotubes in a polymer matrix. The possibility of AFM measurements with less instrumentation than described in [11,12] was also demonstrated. Single-pass scanning modes provide reliable data on the distribution of carbon nanotubes in the polymer matrix regardless of surface roughness. The presented results may help advance the methods for research and quality control of composite materials.

Funding

This study was carried out under the state assignment of Federal Research Center „Kazan Scientific Center of Russian Academy of Sciences."

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y.J. Kim, H.J. Kang, C.T. Moerk, B.-T. Lee, J.S. Choi, J.-H. Yim, Sensors Actuators B, **344**, 130269 (2021). DOI: 10.1016/j.snb.2021.130269
[2] M.M. Harussani, S.M. Sapuan, G. Nadeem, T. Rafin, W. Kirubaanand, Def. Technol., **18**, 1281 (2022). DOI: 10.1016/j.dt.2022.03.006
[3] Z. Ali, S. Yaqoob, J Yu, A. D'Amore, Composites C, **13**, 100434 (2024). DOI: 10.1016/j.jcomc.2024.100434
[4] P. Parnian, Macromol. Symp., **405**, 2100339 (2022). DOI: 10.1002/masy.202100339
[5] W. Gao, N. Zhao, T. Yu, J. Xi, A. Mao, M. Yuan, H. Bai, C. Gao, Carbon, **157**, 570 (2020). DOI: 10.1039/D3RA07245B
[6] C. Feng, D. Zhu, Y. Wang, S. Jin, Materials, **13**, 528 (2020). DOI: 10.3390/ma13030528
[7] Y. Hashimoto, H. Ito, M. Sasajima, Microscopy, **69**, 167 (2020). DOI: 10.1093/JMICRO/DFAA006
[8] D. Zhang, Y. Huang, W. Xia, L. Xu, X. Wang, Polym. Compos., **45**, 398 (2024). DOI: 10.1002/pc.27785
[9] M. Toader, H. Fiedler, S. Hermann, S.E. Schulz, T. Gessner, M. Hietschold, Nanoscale Res. Lett., **8**, 24 (2013). DOI: 10.1186/1556-276X-8-24
[10] L. Liu, G. Li, Appl. Phys. Lett., **96**, 083302 (2010). DOI: 10.1063/1.3332489
[11] O.A. Castañeda-Uribe, R. Reifenberger, A. Raman, A. Avila, ACS Nano, **9**, 2938 (2015). DOI: 10.1021/nn507019c
[12] M.J. Cadena, R. Misiego, K.C. Smith, A. Avila, B. Pipes, R. Reifenberger, A. Raman, Nanotechnology, **24**, 135706 (2013). DOI: 10.1088/0957-4484/24/13/135706
[13] R.R. Garipov, S.M. Khantimerov, S.G. L'vov, V.A. Shustov, N.V. Kurbatova, N.M. Suleimanov, Fuller. Nanotub. Carbon Nanostruct., **29**, 251 (2021). DOI: 10.1080/1536383X.2020.1833191

Translated by D.Safin