Proceedings of the III National Conference on Nanotechnology *NANO 2009*

Utilization of the Electrostatic Force Microscopy for Detection Filler Grains in Nanocomposites

A. Sikora*

Electrotechnical Institute, Division of Electrotechnology and Materials Science

M. Skłodowskiej-Curie 55/61, 50-369 Wrocław, Poland

In this article the utilization of electrostatic force microscopy for grains detection of silica nanofiller in epoxy matrix composite is presented. By observation of long-range electrostatic interaction it is possible to reveal the particles inaccessible for the scanning tip.

PACS numbers: 07.79.–v, 68.37.–d, 68.55.aj, 68.55.Nq

1. Introduction

Dynamic development of new class of the materials opens the opportunity to introduce breaking-through technologies in the industry. Specific properties of such material are connected to the nanometer-size objects or features. Their development is possible due to high resolution diagnostic techniques. In many investigations, the application of specific measurement method is vital for obtaining specific information. Therefore one can still observe progress in that field [1–3]. One of interesting materials is the epoxy matrix with the silica filler of nanometer size (typically 10–30 nm of diameter). It can be used as a new generation dielectric material. Its permittivity and dissipation factor can be much better than in products present on the market [4]. The devices made of such material can be more resistive for wear and climatic conditions and require lower energy consumption during production process. In order to correlate the technology and macroscopic measurement results [5], one should know the nanofiller distribution.

2. Material diagnostic problems

To provide information about nanoparticles presence and their distribution in the matrix, high-resolution imaging methods are desired. The atomic force microscopy (AFM) method proved its efficiency in various applications including dielectric materials investigations. Although this technique generally delivers the information only about the surface properties, one can use the modes which can detect interaction of few tens of nanometers range, therefore insight into the bulk can be obtained. As shown in Fig. 1a, the short-distance interaction cannot reveal presence of the objects, if at least partially they are not above the surface. If the interaction has a range of few tens of nanometers (Fig. 1b), there is a possibility of detection of the particles buried not deeper than at that range. One can conclude that the topography information as well as the phase imaging [6, 7] available during the intermittent mode measurement [8] are not sufficient for that purpose. Also the contact mode and lateral force detection [9] cannot provide necessary information. The force modulation mode [10] allows us detecting the local stiffness of the surface, which sometimes is related to presence of particles located shallowly under the surface. In this case however it appeared to be useless.

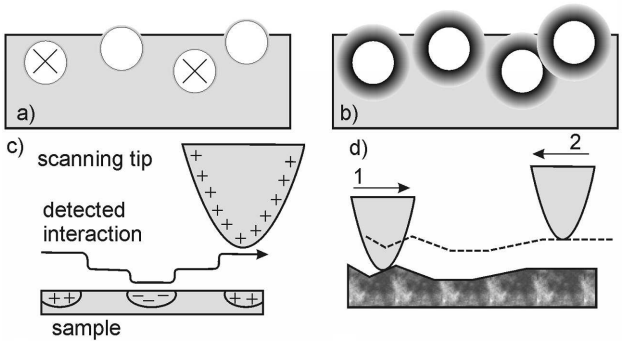

Fig. 1. The detection possibility of the nanoparticles using short-distance interactions (a) and long-distance interactions (b). The electrostatic force detection (c) bases on moving biased tip over the surface. The scheme shows paths during two-pass surface scanning (lift-mode) (d).

Therefore the other mode which could reveal presence of the particles is desired. It is known that the tested material should be able to gather electrical charge in grain–matrix interface. Therefore after introducing the charge into the volume of the material, one could ex-

* corresponding author; e-mail: sikora@iel.wroc.pl

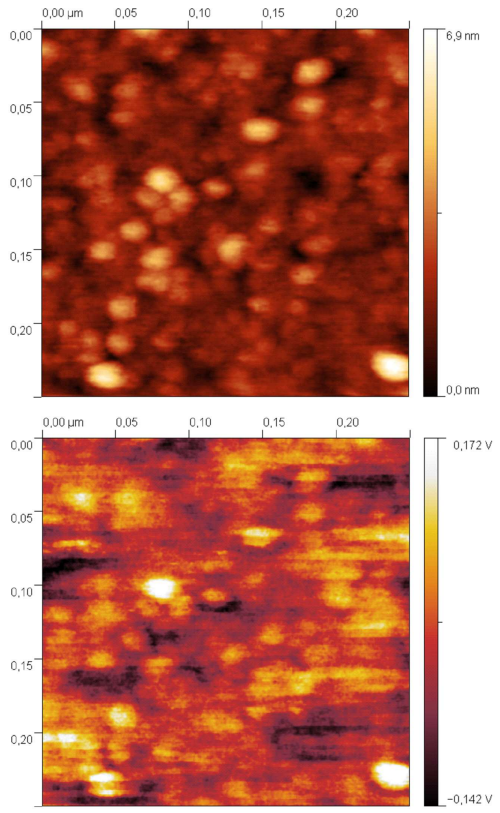

Fig. 2. Topography (top) and the EFM imaging (bottom) of the sample. Scanning field 250 nm × 250 nm.

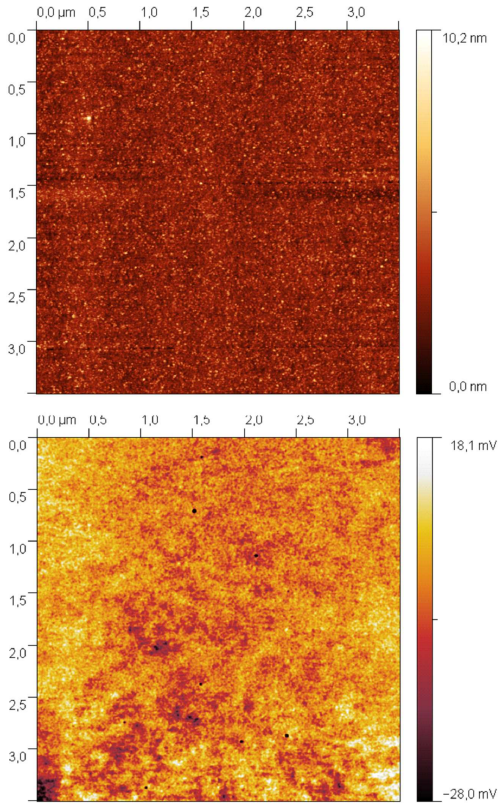

Fig. 3. Topography (top) and the EFM imaging (bottom) of the sample. Scanning field 3.5 μm × 3.5 μm.

pect the electrostatic field presence over the surface. The measurement mode electrostatic force microscopy (EFM) [11, 12] can be used to detect such phenomena. The tip covered with conductive film moves over the surface twice (Fig. 1c): first, in intermittent contact, provides the information about the surface's profile. The second pass is performed along this profile, but few tens of nanometers above the surface in order to detect long-distance interaction with biased tip (Fig. 1d).

3. Sample preparation and measurement

One of the crucial problems is the preparation of the sample. One should scan very flat surface in order to avoid presence of the artifacts caused by steep structures. The process was carried in two steps. Pre-preparation was performed with Target Surfacing System EM TXP (Leica Microsystems), where a tungsten carbide miller was used to create a block-face. Then the final surface was prepared using the EM UC6 ultramicrotome (Leica Microsystems). The 35° diamond knife (Diatome) for AFM samples sectioning was used. The section thickness was 30 nm and the speed 0.4 mm/s. After the preparation the roughness parameters of the surface were as follows: $R_{\mathrm{a}} = 0.481$ nm, $R_{\mathrm{ms}} = 0.631$ nm, skew 1.08, kurtosis 2.66. One should be aware that due to different mechanical properties of the filler and epoxy matrix, some particles could be removed from the surface instead of cutting by the diamond knife.

The measurement was performed with Innova instrument from Veeco. EFM mode (30 nm lift mode) allowed obtaining: topography, electrostatic interaction map and phase imaging map (phase shift during first pass) in order to check the correlation between the viscoelastic interaction and EFM signal. Typical Pt–Ir tip coated cantilevers with typical spring constant about 1 N/m and the resonance frequency 60 kHz were used.

4. Experimental results

The experimental results are shown in Figs. 2 and 3. One can see clearly that the EFM map contains plenty of visible objects as hills (filler particles) on the topography picture. That proves the presence of the electrical charge particle–matrix interface. However there are also revealed other objects invisible on topography. This correlated to presence of the charge on filler particles under the surface. The equipotential surfaces of the electrostatic field from different grains can overlap and create larger area sometimes recognizable as multi-circle shape. The interpretation of such shapes would require more complicated analysis tool than grain analysis functions. The larger field scan (Fig. 3) shows quite homogeneous distribution of the filler, however some local irregularities can be seen.

5. Conclusions

In this article the EFM method of nanofiller grains detection was presented. The long-range electrostatic interaction allowed to reveal the presence of the grains placed below the surface of the sample. This solution gave better insight into the material composition and its properties than only topography shape analysis. One must be very careful when such data is interpreted. Some simulation work should be performed in order to understand the way the electrical fields of certain charges trapped in interfaces of the grains interact with each other and how the matrix material convolutes electrical field distribution. It should be mentioned that the results were compared with theoretical estimation of density and average particle–particle distance of the nanofiller grains and the EFM map delivered coherent data. Also the particle's size estimation based on AFM measurement was correct.

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