Semicontact AFM Mode for Fast Determining the Subsurface Structure of Filled Elastomers

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Abstract. Using atomic force microscopy in the semicontact AFM mode, we examined the surface of the filled elastomer obtained by the rupture method. A feature of the material is that it consists of a soft binder and hard nanofiller particles. Filler particles are usually hidden by a binder layer. In our work, we have shown that the information on the phase shift obtained during scanning makes it possible to look into the subsurface layer and obtain more information about the geometry of the filler particles and their location in the nanocomposite. It is possible to make visible the fragments of particles immersed in the binder, which are almost invisible on the surface relief. This does not require the use of special modes of the atomic force microscope for analysis. It is enough to use the reliable and fast scanning method in semicontact mode.

1. Introduction

Since the invention of atomic force microscopy [1], a lot of research has been carried out, constantly expanding the range of its capabilities beyond topographic imaging. These studies made AFM capable of displaying material composition, magnetic or electrical properties, obtaining images of subsurface layers not only in air, but also in a liquid medium, and determining many other characteristics (local elastic moduli, hardening, creep parameters, residual stresses, the appearance of dislocations, phase transitions and other phenomena [2-4]).

Atomic force microscopy makes it possible to effectively investigate the microstructure of materials on the nanometer scale [5, 6]. It provides information on the mechanical properties of a material. Of great interest are the features of the mechanical properties of the matrix near the filler particles and the features of the mutual arrangement of nanoparticles in the binder. The progress of AFM since the 1980s has led to the development of a variety of modes and applications [7, 8]. The main directions of the AFM technique development can be distinguished: 1) Modifications of a simple single indentation. 2) Improvement of the semicontact method. In essence, these methods can be called discrete (measurements are taken from point to point of the surface) [9-11] and continuous (lateral movement of the cantilever is continuous, and the break occurs only when moving to a new line) [12-15]. Of great importance is obtaining maps of data on the mechanical characteristics of a material, known as nanomechanical mapping [5, 16, 17].

It should be noted the dynamic modes of materials research [18]. One of the most promising dynamic methods is the Force modulation method (FMM) [19]. Development since the 90s has led to the fact that with its help it is possible to obtain maps of mechanical properties of a material on nanoscale with high resolution [20].

In this paper, we propose a new method for processing experimental data obtained in the semicontact AFM mode. The method is based on the use of a phase portrait to clarify experimental information in order to determine in more detail the geometry of the filler particles and their location in the material.
2. Materials and methods

Oil-filled butadiene-methylstyrene rubber (SKMS-30ARKM-15) with carbon fillers was used as a material for testing the proposed technique. It is a nanocomposite, the main filler of which is carbon black with a mass fraction of 47 phr. Detonation nanodiamonds in the amount of 7 phr were used as additional filler.

The surface for scanning was prepared by rupture of a stretched and then notched specimen. The advantage of this method is its promptness, i.e. the ability to start scanning rather quickly until the liquid low-molecular components of the binder emerge on the surface and the deposition of molecules and charged particles from the air has not occurred. In addition, the method allows the formation of areas that are sufficiently flat for scanning.

Scanning was carried out on an NTEGRA Prima atomic force microscope in a semi-contact mode. The cantilever model FMG01_SS (manufacturer: Tipsnano) was used with the following parameters: resonant frequency \( w_0 = 68 \text{ kHz} \), spring constant \( k = 3.5 \text{ N/m} \), cantilever tip radius \( R = 2 \text{ nm} \). The scanning of the 1x1 \( \mu \text{m} \) areas was carried out with a frequency of 1 Hz and a resolution of 500x500 pixels.

3. Theoretical basis of the method

The method we propose is based on the fact that when the probe touches the surface, one section of the interface arises in the «material-probe-air» system instead of two. This is illustrated in Figure 1. Instead of part of the «probe-air» contact surface (red curve \( A_1B_1 \) in the figure) and part of the «material-air» surface (curve \( A_2B_2 \)), there is a single «probe-material» interface (red curve \( AB \)). This is key to understanding how the AFM probe interacts with the material. Let's consider this in detail.

![Figure 1. An illustration of the formation of one new «probe-material» interface after the probe is indented into the specimen (b) instead of two interfaces («probe-air» and «material-air»)) before the probe touched the material (a)](image)

The existence of the interface is always associated with the presence of surface energy. Therefore, the change in the size of the interface must be taken into account in the law of conservation of energy of the «material-probe-air» system in the mathematical model. When studying macroscopic effects, such changes are negligible in comparison with the energy consumption for deformation of the material. But in nanomechanics, it is necessary to take into account the role of surface phenomena. The appearance of one new surface instead of two surfaces is energetically favorable. Therefore, when the probe touches the surface of the material, the probe tends to move inside the specimen. This is observed in experiments on nanoindentation as jumps of the probe into the material. The jump continues to such a depth at which the elastic forces of the material create sufficient resistance to the movement of the probe. In elastomeric materials, such jumps can reach 20 nm. This is the first point to which you need to pay attention. Taking into account the elastic resistance of the medium and changes in the surface energy in the system upon penetration of the probe into the material underlies the mathematical models of nanoindentation (in the models DMT [21], JKR [22], Izyumov-Svistkov [23, 24] and so on).

The second point is the influence of this effect when the probe is removed from the material. For the formation of two new surfaces («probe-air» and «material-air») instead of one surface «probe-material»,
the work is required to be done. This causes the material to stick to the probe and pulls behind the probe as it is removed (figure 2). The contact of the probe with the material remains for a long time. A phase shift appears in the AFM semicontact mode. In this case, the force of adhesion of the probe with the material depends on the area of their contact. If the probe could not penetrate to a greater depth due to collision with the agglomerate of filler particles, then the contact area of the probe with the material will be smaller (figure 2) and the force of adhesion of the probe to the specimen will be less. This will immediately affect the value of the phase shift.

![Figure 2](image)

Figure 2. Illustration of the dependence of adhesion on the depth of penetration of the probe into an elastomeric material containing aggregates of filler particles

The third factor to consider is the time interval between specimen preparation and AFM experiments. As noted earlier, the phase shift is affected by the depth of immersion of the probe in the material. An illustration of this is shown in figure 3. It shows the relief of the specimen in an area of 1x1 µm. For greater clarity, lines of a constant level of relief are plotted on the surface and a source of illumination located close to the horizon is used. The surface is painted in accordance with the value of the phase shift $\Delta \phi$ which is measured in degrees. The phase shift is taken as zero when the probe vibrates in air without touching the specimen surface.

The specimen shown in figure 3 was examined a few days after the surface was created by the rupture of material. The presence of yellow and green areas far from protruding aggregates of filler particles indicates that the surface of the material has different surface energies. This is due to the emergence of oil contained in the elastomer on the surface. The phenomenon of surface energy inhomogeneity must be taken into account when using the proposed method. The surface energy at the surface of the specimen should be the same everywhere. Only in this case, the phase shift depends only on the depth of immersion of the probe into the material. According to our data, it was necessary to carry out a study of this nanocomposite within no more than 5 hours after rupture, while the surface energy is the same everywhere.

An important feature of obtaining a surface by rupture is that the experiment is carried out with a nanocomposite with an active filler. The filler particles have a high degree of interaction with the elastomer. Therefore, the rupture bypasses aggregates of active filler particles at some distance. Therefore, the newly created surface will have the same surface energy everywhere. Experiments confirm this.
4. Results

Taking into account the above features, we propose to use the following formula to clarify the geometry and arrangement of aggregates of filler particles.

\[ z_{\text{new}} = z - c \Delta \varphi \]

Instead of the map of the height distribution obtained in the experiment in the form of a function of \( z \) from the coordinates \( x_1 \) and \( x_2 \), it is proposed to use the refined function \( z_{\text{new}} = z_{\text{new}}(x_1, x_2) \). In this case, fragments of aggregates of filler particles that were previously poorly visible or not visible at all will appear on the surface relief. The choice of the constant \( c \) is not discussed here. It can be obtained from a mathematical model. But in this paper, it is not possible to present the details of this model and the results of calculations. This is a topic for a separate publication.

Figure 4 shows an illustration of the surface relief of 1x1 \( \mu \text{m} \) area. Figure 4a shows the relief \( z = z(x_1, x_2) \) obtained experimentally in the AFM semicontact mode. Some agglomerates on this relief are almost invisible. The most interesting parts of the picture are highlighted with blue boxes. On the refined relief \( z_{\text{new}} = z_{\text{new}}(x_1, x_2) \) more details appear and previously invisible aggregates become clearly visible (figure 4b).
5. Conclusion

A new method for processing the experimental data of atomic force microscopy obtained in the semicontact mode is proposed. An explanation of the underlying features of the interaction of the probe with an elastomeric nanocomposite consisting of a soft matrix and hard inclusions is given. The experiments carried out have confirmed the feasibility of its use.

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