Experimental studies of polymer-silicate nanocomposites structure

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Abstract

Nanocomposites based on polyolefins and layered clay minerals (smectites) are heterogeneous medium consisting of a polyolefin matrix (polyethylene, polypropylene, etc.), and embedded in it ultra-thin silica flakes. These particles may be randomly distributed over the volume of the material or form a packs of parallel plates. Matrix forming polyolefins are also partially crystallized polymers. Their structure can be divided into two parts with different mechanical properties: amorphous (a chaotic arrangement of the molecules) and crystallites (formations of regularly arranged molecular chains).

Creation of new nanostructured materials is impossible without serious study of their internal structure at the nanoscale. Atomic force microscopy (AFM) is one of the most promising tools for such studies. It allows to obtain information not only on the topology of the internal structure of the material, but also on its local physical properties (which may differ significantly from the macroscopic characteristics).

The original technique of sample surface preparation to the AFM scan was developed. In the first place melting polyethylene crystallites, and then restore them (recrystallization) occurred in polyethylene by special heat treatment. Thus, the crystallite formations on the surface became more visible, and the micro damages caused in the sample manufacture disappeared.

Experiments were performed in semicontact mode of nanomechanical mapping. As a result AFM scans of topography, hardness and adhesion to surface areas measuring were built. It was found that the highest hardness and practically zero adhesion is characteristic of nanofiller particles. Amorphous phase was the least hard, but had the greatest adhesion. Stiffness and adhesion characteristics of the crystallites were somewhere in the middle.

Polymer-silicate nanocomposites based on polyethylene matrix and a layered clay filler (Na^+ montmorillonite) are the main object of experimental studies presented in this paper. Currently, these composites are widely used in industry, both as a constructional material and for other purposes. Adding even small amounts of polymer (typically 3–5% by weight) of nano silicate platelets can significantly improve the barrier properties of the diffusing material, thermal stability, resistance to thermal warping [1–5]. Unlike conventional composites extremely high area of interfaces typical for nanomaterials, resulting in their role in the physical properties of a material is defined [6].

First use of ultrafine clay filler was proposed as early as 1974 [7], but only in the early years of the two thousandth such materials really began to enjoy great demand. Filler particles are in the form of ultra-thin flakes of thickness of a few nanometers and a typical diameter of tens of nanometers to 1 micron, depending on the mineral deposits and the conditions of its formation. These plates can form crystallites (tactoids) of the parallel arrangement of the particles (usually within one — two dozen) [5] .

Such widespread as polyethylene polymer used as a template. This is partially crystallized material, and even pure has a complicated multi-level hierarchical structure. That is, one can see a well-defined structural heterogeneity at the nano-, meso-and micro-level [8].

It is clear that the problem of improving the physical and mechanical characteristics of such complex structurally composites requires serious fundamental studies of their internal structure. Today, one of the most promising tools for such studies is the atomic force microscopy (AFM). Its main advantage over traditional electron microscopy is that the atomic force microscope allows to obtain information not only on the topology of the internal structure of the material, but also on its local physical properties (which may differ significantly from the macroscopic characteristics) [9–15] .

Experimental studies of the polyethylene nanostructure

An experimental study of the structure of polyolefin polymers (thermoplastics) and composites with silica nanofillers based on them was. The goal caaied out of this work was to study the topology and local mechanical properties of the materials at the nanoscale. Experience has shown that nano-and macroproperties of heterogeneous polymers can be very significantly.

The main object of study was chosen polyethylene PE 107-02K filled ultra-thin layered silicate particles modified clay brand Cloisite 20A. In chemical composition it is Na^+ montmorillonite modified surface-active substances (surfactants). The degree of filling of nanocomposites studied ranged from 0 to 15% by weight. PE 107-02K — is a widespread industrial low-density polyethylene (0.91 g/cm^3. The degree of crystallinity of about 50%, which is in it, there are well-defined supramolecular structures — crystallites. Macro mechanical tests carried out showed that the initial modulus of elasticity as a function of particle concentration varied from 70 MPa (pure polymer) to 180 MPa (filling 15% wt.).

There is one major problem in the study of nanostructures such materials. In contrast to the soft elastomers, which are easy to handle standard cutting tool, plastic surface of the sample is much more difficult to prepare for AFM scanning. In addition, well expressed plasticity inherent thermoplastics promotes occurrence of residual deformations on the cut surface of the sample (and changes in mechanical properties of the surface compared to the inner regions). Therefore, the original technique of preparation of the polymer surface preparation was developed and tested.

The polymer was subjected to special heat treatment before testing. The sample in the form of a tablet with the diameter of 5 mm and the height of 2.3 mm was placed in an oven heated to a temperature near the melting point (120–140 °C) and held for some time (30 minutes). Next, the temperature was lowered to 90–95 degrees, and the material was kept for two hours. As a result of the heat treatment of the polyethylene crystallites melting occurs first, and then their restoration (recrystallization). Thus, there is a “annealing of” material. Possible damages in the manufacture of the sample on the surface were removed and crystallite structures became more “relief”.

Experiments were carried out on atomic force microscopes Nano-DST and Bruker Icon. AFM scanning performed in semicontact mode nanomechanical mapping (PeakForce QNM). In this case, the probe moves with the harmonic frequency of about 2 Hz in the normal to the sample plane, “tapping his” on the surface. Information about the local physical properties is determined from the analysis of the oscillations amplitude rebound and phase shift. Simultaneously with relief map mechanical properties such as adhesion F_{adh} and hardness E_s were built. F_{adh} — this is the maximum force to the return AFM probe when

an interruption of its contact with the surface. $E_s = 3/4(1 - {\nu_s}^2)(F - F_{adh})/(Ru^3)^{0.5}$ — measured module on the model of Derjaguin-Muller-Toropov (based on the elastic Hertz solution plus the account of adhesion between the tip and the sample surface). Here u — indentation depth of the probe, F — the force at the end of the cantilever, ν_s — Poisson's ratio of the specimen.

Samples of PE 107-02K with nanoparticles filling 0 and 15% by weight were selected for study. Square areas with sides of 1.5, 5 and 15 microns were scanned during the experiment. The large 15-micron scans were used to obtain a general overview of the material structure — inclusions and crystallite aggregates are badly visible on them. On small scans these structures reveals a lot better — especially on 1.5 micron. As a result of an assessment of sizes and shapes of crystallites and silicate inclusions was done. Their mechanical properties were also evaluated.

The AFM scan images providing information about the surface relief, stiffness and adhesion of the sample made from filled polyethylene PE 107-02K (15% wt.) are presented in Figures 1, 2 and 3, respectively. These images are obtained for the same surface area of size 1.5×1.5 microns.

Established that the highest hardness and lowest adhesion possessed nanofiller particles. Their hardness reached 1000 MPa. In fact, it could be higher, since these values were at the upper limit of the sensitivity cantilever (feature of device: values exceeding the limit are shown as equal to the limit). Force of adhesion to the silicate inclusions was approximately 0.1–2 nN, that is almost nonexistent. Amorphous phase was the least hard — 15–30 MPa, but had the greatest adhesion — about 15–20 nN. Stiffness and adhesion characteristics of the crystallites were somewhere in the middle: about 300 MPa and 7 nN, respectively.

Filler particles on the scans are in the form of flat, "coins" with a typical diameter of about 80–100 nm.

Crystallites, emerging on the surface of the sample, represents formation of a few

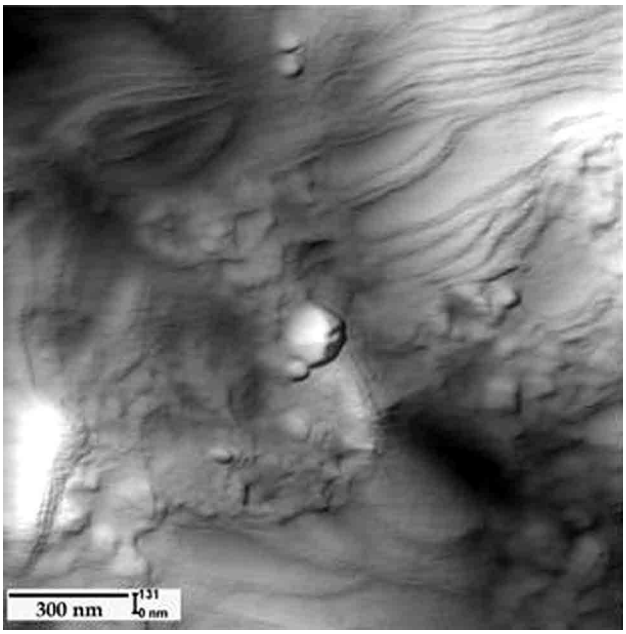

Figure 1: AFM topography scan of the filled polyethylene (15% wt.). Dimples appear darker, upland bright. The bright spot in the center — silicate inclusion. Light strips — crystallite formations with amorphous phase between the plates.

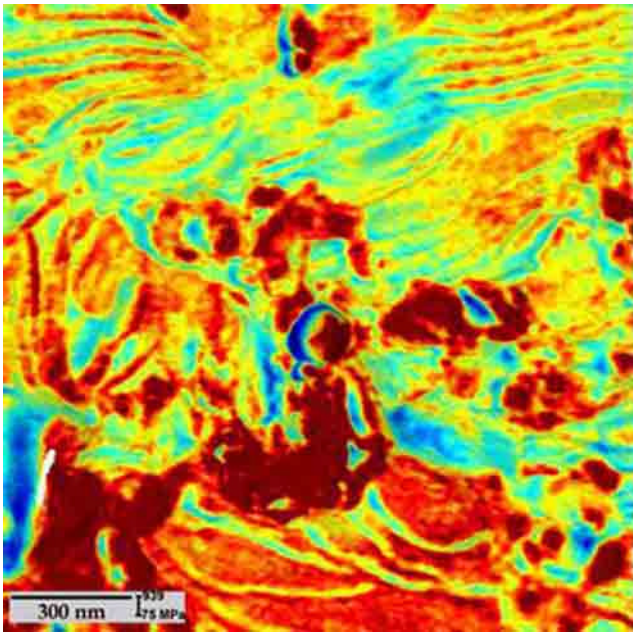

Figure 2: AFM scan of the stiffness (E_s) of the filled polyethylene (15% wt.). Maximum values are shown in dark red, minimum values in dark blue, and intermediate values in ascending order in blue, green and yellow.

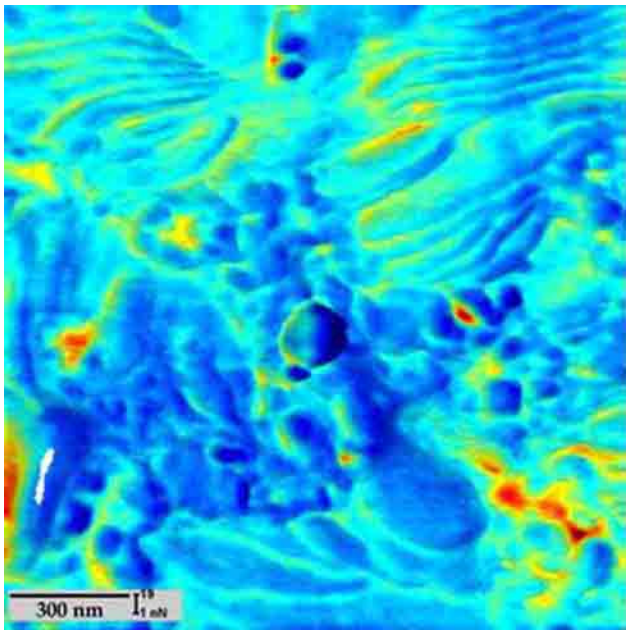

Figure 3: AFM scan of adhesion (E_{adh}) of the filled polyethylene (15% wt.). Maximum values are shown in dark red, minimum values in dark blue, and intermediate values in increasing order in blue, green and yellow.

slightly curved packs of parallel plates with thickness of 30–60 nm. The number of these layers varies from 10 to 20 pieces.

At first sight (judging by the pictures), when compared topology filled and unfilled PE, it can be concluded that the presence of filler particles has little effect on the crystallization process. But it is uneasy question and to answer it should require more detailed and thorough research.

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