The study of structure and mechanical properties of polyethylene - silicate needle nanofiller at the macro and micro level

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Abstract

The paper presents experimental data obtained by testing composites based on polyethylene and silicate needle filler (palygorskite) of different concentration. At the macro level, stress-strain curves are plotted for materials with different filler concentration, and the mechanical properties of these materials are explored. Research at the micro level examines the microstructure and local mechanical properties of composite materials.

1 Introduction

Nanocomposites based on various types of polyolefins (polyethylene, polypropylene, etc.) and nanodispersed silica ultrafine particles (nanoclay) are currently the subject of intense research. This family of composite materials attracts attention because of their unique physical and chemical properties compared to the conventionally filled polymers. They are known for their high performance, environmental friendliness, relatively low cost and ease of production. Polyolefins are the most popular and accessible group of thermoplastic polymers.

It has been recognized [1, 2] that incorporation of even small quantities of silicate nanoparticles into polymers significantly enhances the diffusion barrier properties of the material, its thermal stability and resistance to thermal buckling. Most likely this is due to the fact that nanostructured materials have some specific features. Firstly, unlike conventional composites, whose individual components are of micron and submicron sizes, nanomaterials have an extremely high interface area enabling the volume concentration of surface layers formed on dispersed particles to very significant. Modifying their physical properties, one can effectively change the macro properties of the material. Secondly, the size and shape anisotropy of filler inclusions contribute much to filler texturing in a polymer. Thirdly, the very small particle sizes inhibit the processes of matrix delamination due to enormous surface tension, which certainly favors the increase in the strength of the composite. Taken together, all these factors provide a considerable improvement of various physical characteristics of nanomaterials at low filler concentration [3].

This paper presents the results of experimental studies of composites based on polyethylene and silicate needle-like nanofiller at the macro and micro levels. At the

macroscopic scale, the experimental stress-strain curves obtained for materials with different filler fraction were analyzed. The microstructural and local mechanical properties were studied by the AFM techniques.

2 Fabrication of materials and preparation of samples

Low density polyethylene grade PE 107-02K ($\rho = 0.91$ g/cm^3) was taken as a polymer matrix. The initial modulus was 85 MPa, and the degree of crystallinity determined by differential scanning calorimetry was equal to approximately 35-40 %.

As a filler (the filling degree varies from 0 to 15 wt. parts), the modified nanoclay based on palygorskite (produced by "Keramzit" Serpukhov) was used. This mineral is water magnesium aluminum silicate. The crystalline structure of palygorskite is intermediate between the so-called belt and layered silicates. Palygorskite crystals are composed of double chains of Si-H tetrahedra interconnected by octahedrally coordinated magnesium and aluminum cations. During the grinding, the mineral breaks into particles having the form of elongated bars fibers. Under mechanical treatment, needle particles form tangled fibrous aggregates. Palygorskite clay generally has a light gray color, sometimes with a yellowish tinge. Its density is 2000-2300 kg/m^3, and its hardness is 2-2.5 in mineralogical scale and increases significantly after calcination. This mineral in its pure form is widely used in construction as an eco-friendly thermal insulator.

The surface of palygorskite crystals, as well as other clay minerals, is hydrophilic, making it difficult to wetting with hydrophobic organic substances. Before combining with polymers, it must be treated with special surface active substances (surfactants) to create organophilic layers with the necessary level of interaction with a polymer matrix.

For the production of polymer-silicate nanocomposites, a one-step mixing procedure developed at the Institute of Petrochemical Synthesis, Russian Academy of Sciences was applied [4, 5]. This method assumes that a polymer, a silicate and a surfactant are loaded into the extruder simultaneously. Surfactant molecules diffuse to silicate particles directly in a polymer melt.

3 The experiments

Mechanical testing. The mechanical properties of the materials under study were investigated at the macro level on a testing machine Testometric FS-100CT at room temperature. The strain rate was 100%/min. The loading of the samples was carried out until their rupture. For each filler concentration, five experiments were performed.

Atomic force microscopy. The properties of composites at the nano scale were studied by an atomic force microscope (AFM) Dimension Icon in the nanomechanical mapping regime (PeakForce QNM). In this mode an AFM tip performs nanoindentation in each point of the surface with a frequency of 2 kHz. Hence, the following

structural-mechanical properties of the surface can be mapped: (a) relief; (b) adhesion force between the tip and the sample; (c) indentation u - the depth of penetration of the tip into the material; (d) Young modulus, i.e. the material stiffness E calculated by the DMT-model. In our experiments, the NSG10 probes (NT-MDT) with a nominal radius of 10 nm and a calibrated stiffness 9 N/m were used. For each material, ten AFM images of 10x10 μm with a resolution of 1024x1024 points in the xy-plane were captured and analyzed (Fig. 1). Hereinafter, in the lower left-hand corner of the image (Fig. 1) the horizontal line shows the length of the examined segment. To the right of the vertical scale, the range of the measured value and units are given. Apart from needle-shaped palygorskite, the flat and round-shaped

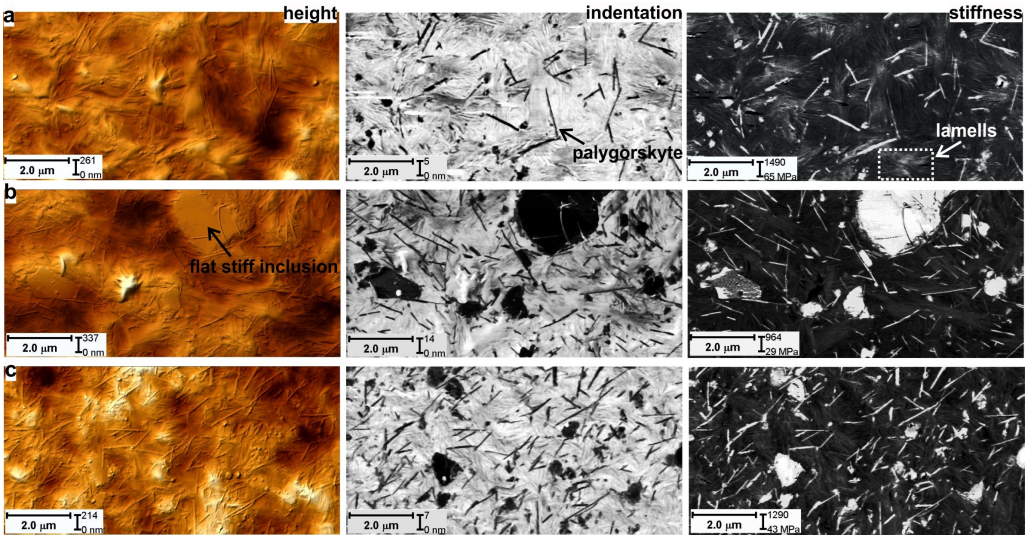

Figure 1: AFM images of the surface (left column) of the appropriate indentation depth (middle column) and stiffness (right column) of materials with filler wt. fractions: (a) 5, (b) 10, (c) 15.

inclusions of different sizes are clearly visible in the images (see. Fig. 1b); this is probably the clay. Note that the fraction of large inclusions is comparable with the palygorskite fraction.

The microstructure of materials was studied in both the undeformed and stretched states. In the latter case, the samples were fixed and stretched in a special device. The experiments were performed without removing the load from the samples.

4 Results and discussion

Mechanical properties. The averaged engineering stress-strain (σ-ϵ) curves obtained for samples subjected to uniaxial load at constant rates are presented in Fig. 2. At the stage of the plastic flow corresponding to different concentrations, the curves $\sigma^0(\epsilon)$ are very close. Therefore, the evolution of the plastic flow causes actual stresses to become aligned for the systems with different filler concentration. There is a two-fold difference in Youngs modulus (85 MPa for unfilled polyethylene versus 170 MPa for 15% filler polyethylene). It has been found that incorporation of

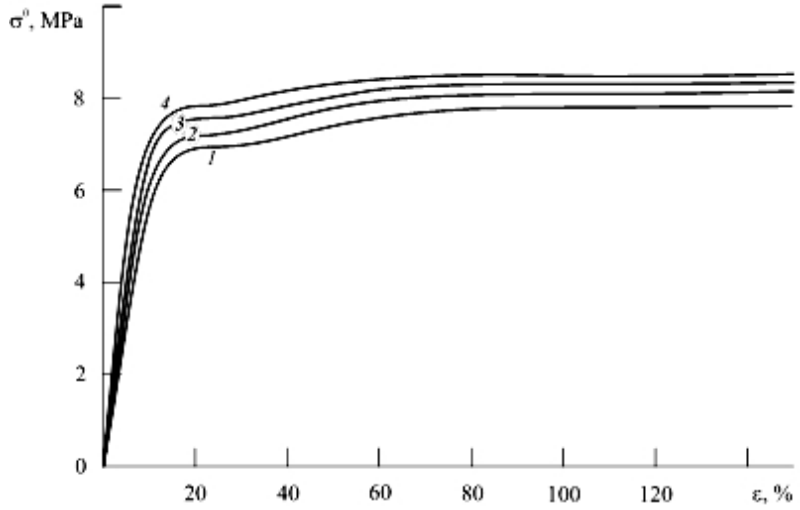

Figure 2: Stress-strain curves obtained for samples tested under uniaxial stretching for filler weight fractions: 1 – 0, 2 – 5, 3 – 10, and 4 – 15.

needle-like filler into the polymer reinforces the material much more strongly than in the case of conventional micro-sized filler. For instance, considering the appropriate concentration obtained by Farris [6] and supposing that the filler density is approximately twice as much as that of the matrix (15% by weight corresponds to the 7.6% by volume), an 1.5 fold increase in the modulus of the polymer filled with conventional micro-particles could be expected.

Microstructural analysis. Despite the fact that the filler is well seen in the maps of mechanical properties (Fig. 1), the polymer-filler interface has never been contrast, yet it has a certain slope up to several tens of nanometers wide. This can be attributed to the fact that some portion of the filler lies hidden under the polymer surface, as well as to the fact that the probe slips over the edge of the filler inclusion. For a quantitative analysis of the filler structure, especially the thickness of palygorskite needles, the criteria for belonging of a certain point in the AFM image to polymer or filler need to be defined. Figure 3 presents the histograms of indentation depth corresponding to the maps given in Fig. 1. For 2.3 nm depth indentation,

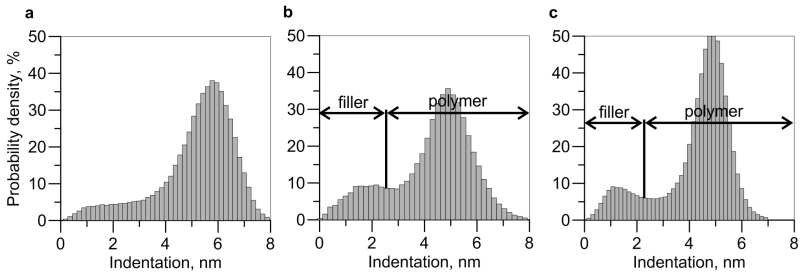

Figure 3: Distribution histograms of indentation depth for the surfaces depicted in Fig. 1. Filler fraction: (a): – 5%, (b) - 10%, (c) – 15 % wt.

the distribution histograms for materials with 10 and 15% filler content exhibit a local maximum (Fig. 3b, c). A similar pattern was observed for the rest of the

images obtained for these materials. Such a pronounced local maximum was not observed for the material with 5% of filler content because of the low filler fraction. Let us assume that in all the images the indentation depth ≤ 2.3 nm corresponds to the filler. Figure 4 shows filler silhouettes isolated in Fig. 1. Further the structural

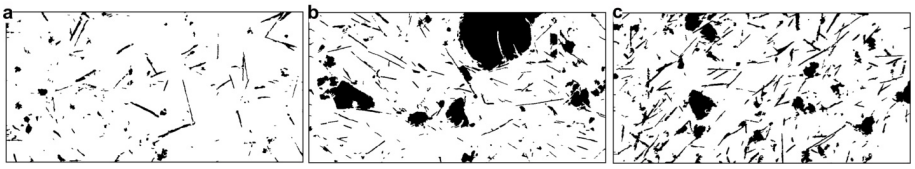

Figure 4: Fig. 4. Filler silhouettes (Fig. 1).

analysis of black-and-white images was carried out. For each material, several hundreds of needles were explored. The average thickness of filler inclusions 27 nm was the same for all materials, and the average length was equal to 0.63, 0.50 and 0.56 microns for different filler concentration. Long needles up to 1.8 microns long were also observed. Palygorskite is able to form in the material secondary structures in the form of multiple stacks of needles arranged in parallel and in close proximity to one another (Fig. 5). It is not always possible to unambiguously identify the bound-

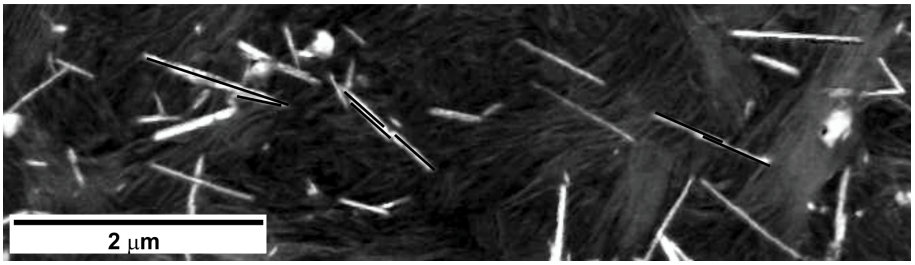

Figure 5: Stiffness map for the material with 10 % of filler. The formation of secondary structures having the form of parallel needles (black lines) is shown. The lamellar structure of polyethylene (gray filaments) is visible.

aries of individual needles in agglomerates. This may cause an overestimation of the length and thickness of the objects to be measured. The study of the microstructure of the stretched materials reveals that some needles become wavy shaped (see. Fig. 6a, the axis of elongation is vertical). Apparently, this is due to the non-uniform local deformation of polyethylene and/or the compression of the material in the direction orthogonal to its elongation. Figure 6a shows dense inclusions with round surfaces (shown in boxes) that have good adhesion with a polymer. Inclusions that look like flat tablets are also encountered in the material; the delamination of the polymer, i.e. microcrack nucleation, can be observed near such inclusions (Fig. 6b). An increase in elongation causes the surfaces of the material to become sufficiently inhomogeneous - the oriented structure of polymer heterogeneities appears on the surface of polyethylene, and the effects observed (palygorskite waving, delaminations) are strengthened.

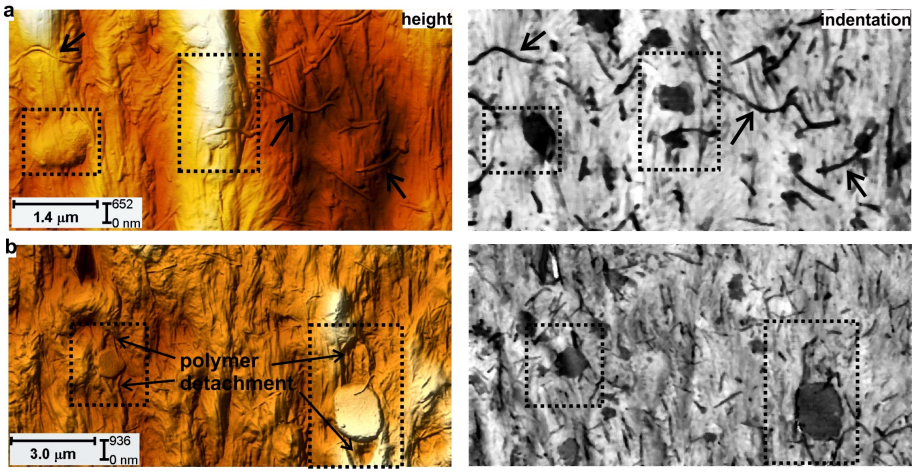

Figure 6: AFM-height images and the corresponding indentation maps of the 10% filled material at 100% tension; the arrows (a) point to the wavy structure of palygorskite; the frames (b) indicate the detachment of the polymer near the large and flat inclusions.

5 Conclusions

The structure and mechanical properties of polyethylene filled with silicate needle filler (palygorskite) have been studied. Compared to the unfilled polymer, such composites have improved resistance to combustion, i.e. they are less inflammable and toxic.It has been found that the addition of the filler results in a roughly two-fold increase in the initial elastic modulus. At the stage of the plastic flow the mechanical properties of the material differed only slightly. Therefore, it has to be emphasized that the mechanical properties of the material did not worsen. The analysis of the polymer microstructure indicates that some filler needles form in the material secondary structures in the form of stacks. The average thickness of a palygorskite needle is 27 nm, and its length is 0.6 microns. As the stretch of the composite increases, the shape of inclusions becomes wavy.

Acknowledgements

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