NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2011, 2 (2), P. 71–75

UDC 539.3

SIMULATION OF ELASTIC AND PLASTIC PROPERTIES OF POLYMERIC COMPOSITES WITH SILICATE LAMELLAR NANOFILLER

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PACS 46.25.Cc, 68.35.Rh

Polymer/silicate nanocomposites mechanical behaviour under finite deformation is investigated at structural level. Outcomes of computer simulation are presented. Nano-filler particles are modeled represented as sheaves from the several parallel ultrathin silicate plates parted by beds of polymer (tactoids), a matrix - as a nonlinear-elastic or elastoplastic material.

The stress-strain state round separate inclusion in dependence on its orientation to a exterior load direction and properties of a matrix is researched. The problem of the macro-homogeneous elongation of a periodic cell in the form of the rectangular field with a tactoid at centre has been solved for this purpose. Conditions at which a filler particle losses of a bending stability happens in the course of macroelongation of material are defined.

The estimate of nanocomposite macro mechanical behaviour depending on properties of a matrix, filler concentration and orientation of corpuscles is spent on the basis of the gained solutions. Appropriate dependencies between macro and micro-structural parameters associations are built.

Keywords: elastic and plastic properties, polymeric composites, silicate lamellar nanofiller.

The object of this study are polymer / silicate nanocomposites based on a polyolefin binder and filler of layered clay minerals — smectites [1–3]. The idea of creating such materials is not new. Still in 1974 [4], it was proposed to use as a filler layered silicate nanoparticles with a thickness commensurate with the length of the polymer molecule. But only now, these materials began to be widely used in industry. For such systems, managed to achieve a substantial increase of elastic modulus, strength, fire resistance, resistance to thermal warpage, improved barrier properties with respect to the diffusing substance [3–6].

In its structure, the systems are essentially mechanically heterogeneous medium consisting of a polyolefin matrix and implanted in her ultra-thin silicate flakes. Characteristic sizes the inclusions are a few nanometers in thickness and from 30 to 1000 nm in diameter. These particles can be randomly distributed over the volume of a material or to form separate sheaves — tactoids — from several (order of tens) collaterally allocated plates between which are a thin layer of polymer. In the first case of exfoliated nanocomposites are called (Fig. 1*b*), the second — intercalated (Fig. 1*a*).

Experimental studies have shown that the properties of these materials depend strongly on whether any of the particles is filler (intercalated tactoids or separate lamellae [5–7]. This circumstance was the reason for in-depth theoretical study of the formation of the mechanical properties of nanocomposites on the scale of "the matrix — the separate inclusion".

Computational scheme of the problem was as follows. In a rectangular area (cell periodicity), consisting of polymer material (matrix) was placed the inclusion in the bundle of several parallel plates. Uniaxial macro-stretching of the cell with preservation its volume is simulated

Fig. 1. Schematic representation of different types of structure of polymer nanocomposites with a layered silicate filling: a — intercalated nanocomposite; b — exfoliated nanocomposite.

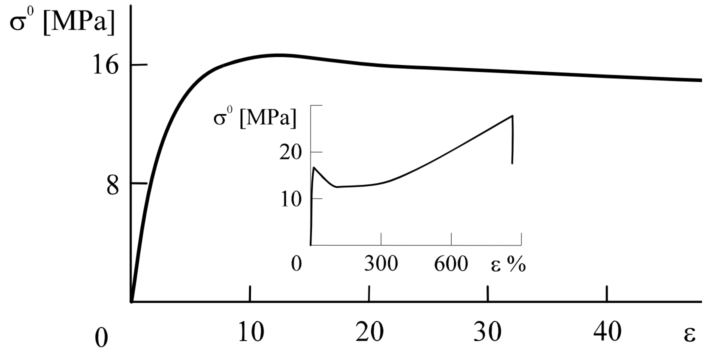

Fig. 2. Experimental basic loading curves for the matrix material (σ^0 — the nominal stress, ε — tensile strain

by expansion of lower and upper boundaries vertically with the simultaneous pulling up the lateral sides horizontally. The problem of cell loading containing such an inclusion is solved in two-dimensional formulation (plane deformation) using the finite element method.

For each specific geometry of the cell boundary value problem was solved several times using grids with different nodes as the number and type of finite elements. The result is considered valid if the difference in the stresses at the control points does not exceed 5%.

Elastoplastic properties of the matrix were determined from the real stress-strain curve of pure polyethylene [8]. The properties of high density polyethylene (HDPE) brand “RA” produced by “Orgsynthes” (Kazan) were taken as the basis. Initial experimental loading curve is shown in Fig. 2. The initial modulus $E_m = 480$ MPa, yield strength is equal to 9 MPa. Associated flow rule used in solving the elastoplastic problem.

The mechanical properties of the matrix in solving the nonlinear elastic problem described by Treloar potential (neo-Hookean) [9]. Initial modulus of elasticity of the polymer matrix $E_m = 480$ MPa (the same as for the elastoplastic case).

In accordance with the experimental data obtained in the Institute of Petrochemical Synthesis (IPS RAS), the length of individual silica plate was assumed to be 80 nm, the thickness — 1 nm. Intercalated tactoid modeled as a stack of 10 parallel plates located (in the unloaded state)

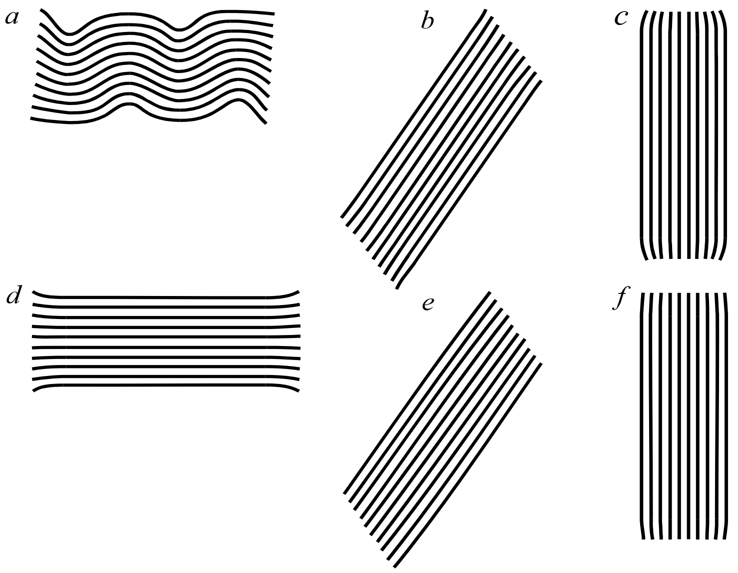

Fig. 3. Tactoid form distortion at 25% of the material macro-deformation, $\varphi = 10\%$

at a distance $\delta = 2$ nm. In the gaps was the polymer with the same properties as the matrix. Young's modulus of single silicate nano flake was $E_p = 72000$ MPa.

Inclusion of this type are essentially thin plates (even in a pack) and the difference by two orders in stiffness between the polymer and the silica they should behave as a rather flexible constructions, that is, we can expect that in the process of deformation nanocomposite will experience a noticeable distortion of the particles – the loss of elastic stability.

Changes the shapes of plates in the intercalated tactoid, when cells are vertically stretched (macro deformation $\varepsilon = 25\%$) is shown in Fig. 3. The filler concentration $\varphi = 10\%$, β — the angle between the normal to the flat surface of silica nanoplate and the direction of the external load.

Variants when tactoid is initially perpendicular to the direction of stretch ($\beta = 0°$), tilted at an angle of 45 degrees and parallel ($\beta = 90°$) are presented. Figures 3a, 3b and 3c correspond to elastic matrix, 3d, 3e and 3f — to elastic-plastic.

The greatest distortion of the inclusions observed in its position perpendicular to the direction of extraction, the lowest in parallel. For the case ($\beta = 45°$ there is a shift of plates with respect to each other.

The maximum local stretching of the matrix was observed near the edges of the outer plates — in areas where the matrix material becomes into gaps between tactoid silicate flakes. In this case, they are more than an order of magnitude higher than the macroscopic. In the elastic-plastic matrix (due to the plastic flow of material), the maximum principal strains were about one and a half to two times more than in purely elastic.

The above numerical solutions have allowed not only to investigate the stress-strain state around the nanofiller particles, but also to evaluate from structural positions the effective mechanical properties of polymer / silicate nanocomposite materials. Composite was regarded as a mechanically inhomogeneous medium with a regular ordered structure. This assumption

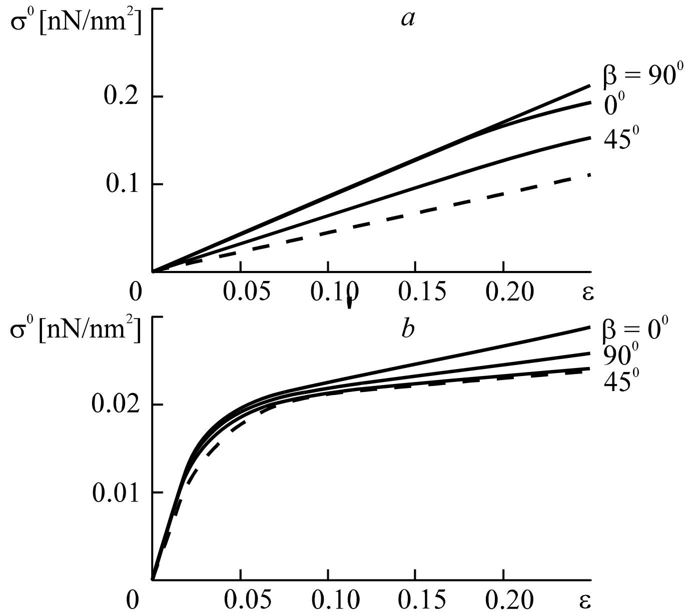

Fig. 4. Strain dependence of nominal macro stresses on the angle of inclusion orientation (β; $\varphi = 10\%$). a — a cell with the elastic matrix, b — with the elastic-plastic one. Dashed line — no particle in the cell

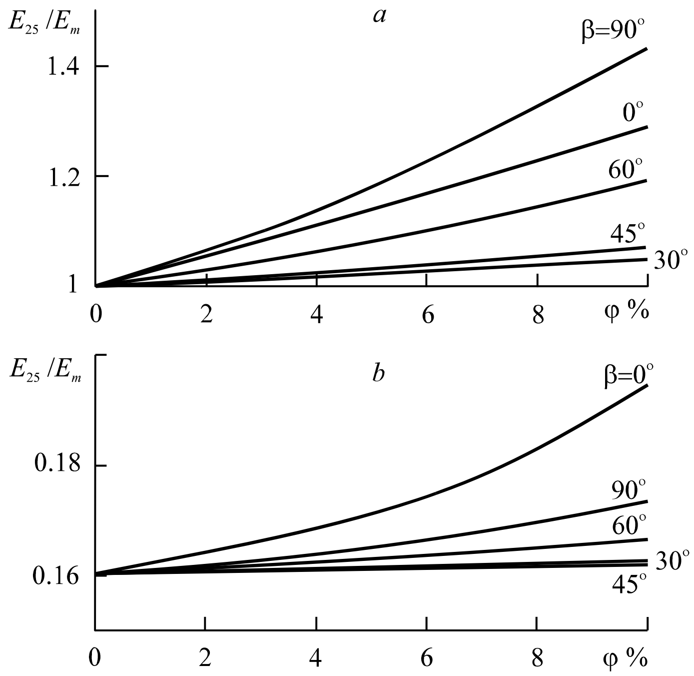

Fig. 5. Concentration dependence of the secant modulus E_{25} on the angle of orientation of the inclusion β: a — in a composite cell with elastic matrix, b — with the elastic-plastic one, E_m — the initial elastic modulus of the matrix, $\varepsilon = 25\%$

allowed applying the classical method of regularization, widely known in the mechanics of composite materials.

Calculated dependencies of nominal stress σ^0 on the strain ε, constructed for the elastic and elastoplastic cells with orientation angle ($\beta = 0^\circ$, 45° and 90°; concentration of $\varphi = 10\%$) are shown in Fig. 4. Dashed lines show the loading curves for cells without inclusion.

Fig. 5 shows concentration dependences of the effective secant modulus calculated for the extended to $\varepsilon = 25\%$ of the periodicity cell, — E_{25}. Evaluation of the mechanical stiffness of elastomeric material on its secant modulus at a given standard strain is commonly used in practice by specialists in polymers [10]. Such an approach allows us to quantify (in first approximation) the difference between the nonlinear loading curves, typical for finite deformable polymeric materials.

Calculations showed that at 25 per cent of nanocomposite macro-elongation secant modules in elastic cells were an order of magnitude higher than in the elastic-plastic (with the same initial geometry and the same initial modulus). As for the influence of orientation of inclusions, in both cases, the most “soft” were composite cells with particles located at $45^\circ \pm 10^\circ$ in the direction of elongation (due to the shear of plates in tactoid — see also Fig. $3b$, and $3d$), and the relative change of secant modulus for the elastic problem was much larger.

Acknowledgements

Work is executed at financial support of Russian fund of basic researches (Grants 09-08-00339, 09-06-00402) and Program of Presidium RAS (Program RAS 09-C-1-1008).

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