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MODELING MICROSTRUCTURAL STRESSES IN POLYMER-SILICATE NANOCOMPOSITE WITH THE INFLUENCE OF SPHERULITIC STRUCTURES

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Polymer nanocomposites based on polyolefins and layered clay minerals (smectites) are multi-layered structure. Even unfilled polyolefins (polyethylene, polypropylene, etc.) are structurally heterogeneous environment consisting of amorphous and crystalline phases. Adding filler further complicates the structure of the material. The results of computer simulation of interaction of silicate inclusions, crystalline supermolecular formations in the matrix (spherulites) and its amorphous part. Composite is modeled as a square periodicity cell with inclusion and spherulites. Inclusion was a pack of silica plates separated by thin layers of polymer. Spherulite modeled as "snowflakes" of crystallized lamellae (band areas with an ordered arrangement of polymer molecules). Problem was solved by finite element method in nonlinear-elastic formulation (plane strain).

Keywords: microstructural stresses, polymer-silicate nanocomposite, spherulitic structure.

1. Introduction

Currently, nanocomposites based on polyolefins and layered clay minerals (smectites) are becoming more common in various industries. In the past decade [1, 2] around the world has seen rapid growth in the number of publications and patents relating to the process of their construction and study of the mechanical properties of a huge increase in the funding of basic and applied research on this issue. For such systems, managed to achieve a substantial increase in elastic modulus, strength, fire resistance, resistance to thermal warpage, improved barrier properties with respect to the diffusing substance. However, despite the obvious achievements, analysis of the known publications shows that this branch of materials science from the standpoint of understanding and explanation of accumulated factual material developed more clearly not enough. Therefore, the task of theoretical study of the formation of the mechanical properties of nanocomposite systems based on the features of their internal structure, is important and relevant.

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2. Structure of nanocomposites

The structure of these systems is a mixture of many thin silicate plates with thickness of about 1 nm and lateral dimension of 30 nm to several microns, placed in a polyolefin matrix [3]. Filler particles can form individual crystallites (taktoid) from several (several tens) of

parallel plates or placed on the volume of material randomly. In the first case, called intercalated nanocomposites, in the second - exfoliated (Fig. 1).
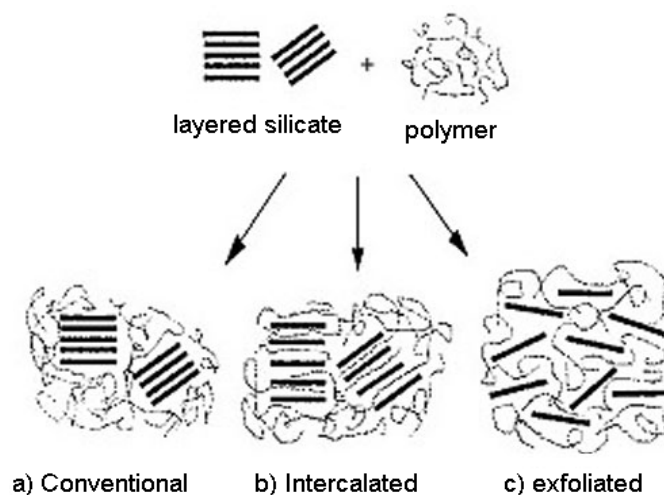

Fig. 1. Schematic representation of the dispersion models layered silicate in polymer matrix: (a) conventional, (b) intercalated nanocomposite, (c) exfoliated nanocomposite

Structural heterogeneity of these systems is not limited to the presence of nanofillers. Matrix itself may also contain a variety of supramolecular structures, in particular the spherulites.

Spherulites - the most common type of morphological formations for crystallize out of melt semi-crystalline polymers.

Spherulite size depends on the supercooling during crystallization. Spherulites have a scale of 0.1 - 1000 microns. For polyethylene in the usual conditions of crystallization of the diameter of the spherulite reaches approximately 100 microns. Spherulites - polycrystalline formations consisting of lamels arranged in a "snowflake". Lamella in the spherulites - a relatively large thin plates (polietilen) separated by amorphous layers. Lamella growing from a common core in the center of the spherulite and embedded in a matrix of amorphous material [4].

3.   Model of the mechanical behavior of nanocomposites

Problem was solved for plane-strain state of the finite element method [5–7]. Taktoid consisted of ten elastic parallel plates of thickness 1 nm and a length of 80 nm. The distance between the plates in the unloaded state was 1 nm. Spherulite was modeled as a structure in the form of "snowflakes" of crystallized lamellae with the stiffness is much higher than the material in the surrounding matrix. Believed that the matrix material in the gaps tactoid, spherulite and around as incompressible and can be described by Treloar elastic potential:

$$W = C_m(tr\,\mathbf{B} - 3) \tag{1}$$

where $\mathbf{B}$ - the Cauchy-Green left tensor in the polar decomposition of deformation gradient medium, C_m - elastic constant equal to half the initial shear modulus. For polyethylene, it corresponds to 80 MPa. It is known that the modulus of the individual plates of silicate (Na^+-montmorillonite) close to the module glass (49000-78000 MPa), which is about two orders of magnitude higher than the module polyethylene. It was therefore decided that the stiffness of the

filler particles is 150 times greater than that of the matrix (72,000 MPa). Stiffness of the filler particles is 150 times greater than that of the matrix. Stiffness of the material "branches" of the spherulite is 10 times higher than the filler (matrix).

Seen several cases of the location of the spherulite with respect to taktoid:
- Composite without spherulitic structures;
- Spherulite in the center of the periodicity cell without silicate plates;
- Spherulite in the center of the periodicity cell with silicate plates;
- Spherulite formed on the surface of silicate plates;

On the basis of the solutions were evaluated effective modulus of the nanocomposite depending on the location of the spherulite in the composite. We used a standard method of regularization, widely used in mechanics of composite materials. Composite is regarded as a system with a regular ordered structure, which greatly simplifies the calculations, since all the necessary information can be obtained from the analysis of the periodicity cell. This method has worked well for small and medium filling (10-20 by volume), ie while irregular mutual arrangement of particles and their interactions did not become the determining factor in shaping macroproperties heterogeneous environment (as occurs in highly filled systems) [8].

4. Results

The results of the calculations showed that the presence of spherulites in the composite is not substantially affect the macro-module as the input composite silicate particles. The greatest increase in modulus was observed when the spherulite is located on the plates taktoid (Fig. 2). In this case, the module compared to the option when the matrix contained only taktoid increased by 12%.
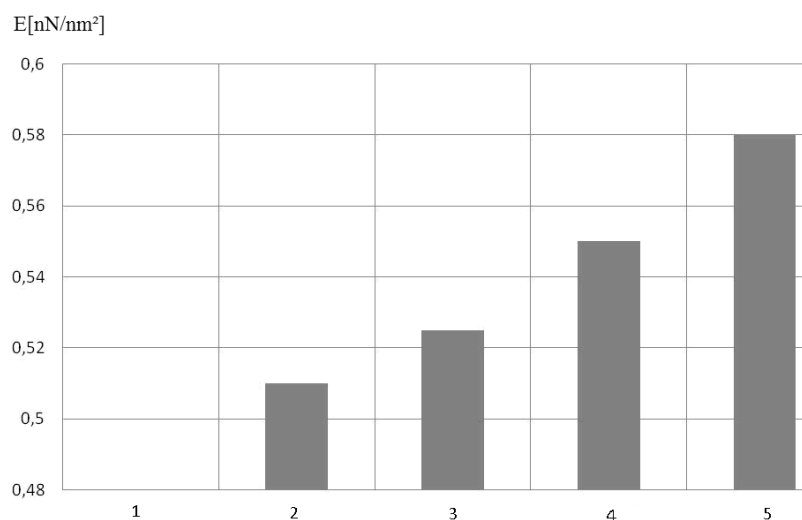

Fig. 2. Dependence of the modulus of the nanocomposite depending on the location of the spherulite. 1 - pure polyethylene, 2 - composite without spherulitic structures, 3 - spherulite in the center of the periodicity cell without silicate plates, 4 - spherulite in the center of the periodicity cell with silicate plates, 5 - spherulite formed on the surface of silicate plates.
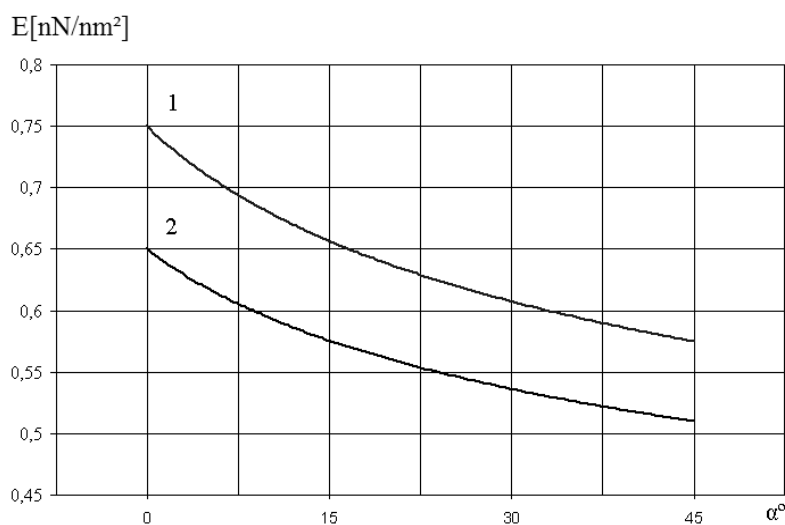
E[nN/nm²]

Fig. 3. Dependence of the modulus of the nanocomposite depending on the orientation of the plates relative to axis stretching. 1 - spherulite formed on the surface of silicate plates, 2 - composite without spherulitic structures.

Figure 3 shows the results of the calculation module, depending on the orientation of the plates relative to the axis stretching for two options: a spherulite is formed on the surface taktoida and without spherulites. The appearance of the spherulite leads to some increase in the rigidity of the cell.

5. Conclusion

Calculations showed that for this case the location and form of spherulites, their presence in the composite is not substantially affect the macro module of the composite as the introduction of silicate particles. The greatest increase in modulus was observed when the spherulite is located on the plates taktoid. In this case, the module compared to the option when the cell had only inclusion, increased by 12%.

6. Acknowledgements

References

[1] Fengge G. Clay/polymer composites: the story // Materials Today. — 2004. — No. 11. — P. 50–55.
[2] Sheng N., Boyce M. C., Parks D. M., Rutledge G. C., Abes J. I., Cohen R. E. Multiscale micromechanical modeling of polymer/clay nano-composites and the effective clay particle // Polymer. — 2004. — V. 45. — P. 487–506.
[3] Guseva M. A. Struktura i fiziko-mehanicheskie svojstva nanokompozitov na osnove nepoljarnogo polimera i sloevogo silikata [in Russian] // Dis. kand. fiz.-mat. nauk. — M., 2005. — 155 p.
[4] Oleinik Je. F. Plastichnost' chastichno-kristallicheskih gibkocepnyh polimerov na mikro- i mezo-urovnjah [in Russian] // Vysokomolek. Soed. S. — 2003. — V. 45, No. 10. — P. 1–129.

[5] Garishin O. C., Lebedev S. N., Svistkov A. L. Shape distortion of silicate nanoinclusions in dispersly filled polyolefines [in Russian] // XXXV Summer school "Advanced problems in mechanics": Proceedings. — St. Petersburg (Repino), 2007. — P. 118–122.

[6] Garishin O. K., Lebedev S. N., Korlyakov A. S. Issledovanie mikronaprjazhennogo sostojanija v polimernyh nanokompozitah na osnove glinistogo napolnitelja i poliolefinovoj matricy [in Russian] // Vestnik PGTU: Matematicheskoe modelirovanie sistem i processov. — Perm: PGTU, 2007. — No. 15. — P. 9–14.

[7] Garishin O. K., Korlyakov A. S. Modelirovanie mehanicheskogo vzaimodejstvija mezhdu chasticami napolnitelja i svjazujuwim v polimer-silikatnyh nanokompozitah pri konechnyh makrodeformacijah [in Russian] // Vychislitel'naja mehanika sploshnyh sred. — 2009. — V. 2, No. 3. — P. 25—33.

[8] Bahvalov N.S., Panasenko G.P. Osrednenie processov v periodicheskih sredah. Matematicheskie zadachi mehaniki kompozicionnyh materialov [in Russian]. — M.: Nauka, 1984. — 352 p.