Research of interrelation between polyolefine/clay nanocomposites structure and their mechanical properties

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Abstract

The object of this study are polyolefin polymers and nanocomposites with a group of silicate filler on them. These materials have a complex hierarchical structure. First, the polyolefins are themselves part of crystallizing materials. That is, they are structurally heterogeneous at the nano and micro levels: lamellae (thickness of about 5-10 nm) and spherulitic formation (from 0.1 to 1000 microns)[1, 2]. The second type of structural heterogeneity introduces a filler. In the investigated materials as used in this layered clay minerals (smectite). Filler particles have the form of ultra-thin flakes of thickness of several nanometers and a typical diameter of tens of nanometers to 1 micron. Were carried out experimental investigations of the elastic, viscous and plastic properties of nanocomposites with a polyethylene matrix and the filler of layered silicate nanoparticles. For samples with varying degrees of filling of the dependencies between the stresses and deformations under cyclic loading with increasing amplitude and relaxation after a stop at the loading and unloading, as well as the corresponding relaxation curves. Tests were conducted on the waste before the procedure, allowing for an experiment to obtain all necessary for further theoretical modeling of the data on the elasto-visco-plastic behavior Using the experimental data has been built structurally phenomenological elasto-visco-plastic finite-deformable model of a heterogeneous environment. At the same time used the differential approach to the construction of constitutive equations based on the interpretation of the mechanical behavior of materials with the help of symbolic schemes.

Tested materials and experiments

In Fig. 1 shows the results of the cyclic deformation of polyethylene mark "PE-107-02K" with increasing amplitude in the mode: stretching → stress relaxation for 10 minutes → decrease in strain to zero tensile force → stress relaxation for 10 minutes → next cycle of deformation. This mode allows you to separate viscoelastic and elastoplastic behavior of the sample in one experiment and learn them yourself. The rate of deformation of in tension and compression of the sample was 1 min^{-1}. Extension was carried out before such time as the sample does not begin to take shape "plastic collar".

Model of the mechanical behavior of nanocomposites

The mechanical behavior of nanocomposites is described by the model schematically represented in Fig. 2, where each point corresponds to a particular set of constitutive equations. The first branch (the elastic-plastic) models the behavior of the agglomerates of crystallites are more stringent (and nanofiller particles), their displacement and destruction during the deformation. The second (visco-elastic) describes the flow of the amorphous polymer

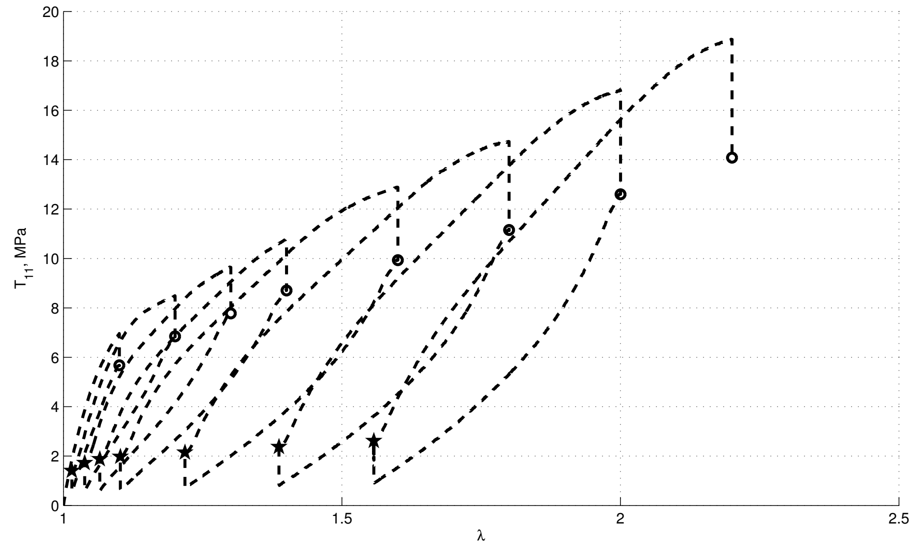

Figure 1: The scheme of cyclic loading of the sample. Circles - the end of stress relaxation at the maximum strain in this cycle, stars - the end of the relaxation after removal of the load on a given cycle.

between the lamellae inside the crystallites and in the space around the crystallites and particles. As shown by certain experiments, these processes are practically independent, that was the rationale for the choice of the scheme. The scheme shows how the tensor nonlinear equations are combined into the system of equations used to calculate the complex viscoelastic behavior of the medium deformed in an arbitrary way. The algorithm for constructing constitutive equations consisting of separate groups of equations (elastic, viscous, plastic) is described in detail in work [3]. The model uses the approach that is based on additive decomposition of the deformation-rate tensor of the medium into the deformation-rate tensors of the scheme elements [4]. The internal scheme points are required to meet the condition of correlation of the Cauchy stress tensors [3]. The scheme for the mechanical behavior of the material involves elastic, viscous and plastic elements that correspond to the folowing equations.

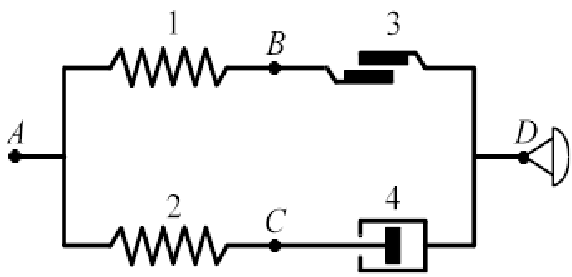

Figure 2: Schematic of the model of the mechanical behavior of nanocomposites.

The material is assumed to be incompressible. The deviator of the Cauchy stress tensor of the elastic element is calculated from the equations of the theory of elasticity

$$\operatorname{dev}\mathbf{T}_i = \operatorname{dev}\Big(\rho\sum_{k=1}^{3}\lambda_k^{(i)}\frac{\partial f}{\partial\lambda_k^{(i)}}\,\mathbf{n}_k^{(i)}\otimes\mathbf{n}_k^{(i)}\Big),$$

in which the mass density of the medium free energy f depends on the extension ratios of elastic elements.

$$f = w_n = C_i(\lambda_1^N + \lambda_2^N + \lambda_3^N - 3) = C_i(tr(\mathbf{V}^N) - 3)$$

where $\lambda_1^{(i)}$, $\lambda_2^{(i)}$, $\lambda_3^{(i)}$ and $\mathbf{n}_1^{(i)}$, $\mathbf{n}_2^{(i)}$, $\mathbf{n}_3^{(i)}$ — are the extension ratios and eigenvectors of the stretch tensor $\mathbf{V}_i$ of the i-th elastic element . Time variations in the tensor $\mathbf{V}_i$ are calculated by the evolution equation.

$$\frac{2}{\nu_i}\,\mathbf{Y}_i^{0.5}\,\mathbf{D}_i\mathbf{Y}_i^{0.5} = \dot{\mathbf{Y}}_i - \mathbf{Y}_i\,\mathbf{W}_{\mathbf{R}}^{\mathrm{T}} - \mathbf{W}_{\mathbf{R}}\,\mathbf{Y}_i, \qquad \mathbf{W}_{\mathbf{R}} = \dot{\mathbf{R}}\,\mathbf{R}^{\mathrm{T}}.$$

The formula uses the following notations:

$$\mathbf{Y}_i = \mathbf{V}_i^{\frac{2}{\nu_m}}, \qquad \nu_m > 0,$$

where $\mathbf{R}$ — is the rotation tensor in the polar decomposition $\mathbf{F} = \mathbf{VR}$ of the strain gradient of the medium $\mathbf{F}$ into the left stretch tensor $\mathbf{V}$ and the rotation $\mathbf{R}$; ν_m is the ratio of the m-th transmission element, which is connected on the left to the elastic element under consideration. The rate of work done in the i-th elastic element is determined by the formula

$$\mathbf{T}_i\cdot\mathbf{D}_i = \rho\sum_{k=1}^{3}\frac{\partial f}{\partial\lambda_k^{(i)}}\,\dot{\lambda}_k^{(i)} - \frac{\rho\,\dot{\nu}_m}{\nu_m}\sum_{k=1}^{3}\frac{\partial f}{\partial\lambda_k^{(i)}}\,\lambda_k^{(i)}\ln(\lambda_k^{(i)}).$$

The deviator of the Cauchy stress tensor $\mathbf{T}_j$ of the viscous element is calculated from the equations of the theory of nonlinear viscous fluid using the appropriate strain rate tensor $\mathbf{D}_j$:

$$\operatorname{dev}\mathbf{T}_j = 2\,\eta_j\,\mathbf{D}_j,$$

For the n-th plastic element, the Cauchy stress tensor deviator is determined by the equations of the theory of plastic flow

$$\mathbf{D}_n = \sqrt{\frac{\mathbf{D}_n\cdot\mathbf{D}_n}{\operatorname{dev}\mathbf{T}_n\cdot\operatorname{dev}\mathbf{T}_n}}\,\operatorname{dev}\mathbf{T}_n,$$

To complete the system of equations, the proportional relation between the strain rate tensors of the plastic element $\mathbf{D}_n$ and that of the material is used $\mathbf{D}$.

$$\sqrt{\mathbf{D}_n\cdot\mathbf{D}_n} = \kappa_n\sqrt{\mathbf{D}\cdot\mathbf{D}},$$

where the term κ_n is the non-negative function obtained from the relation

$$\kappa_n = \begin{cases} 0, & \text{when } \Phi_n(\mathbf{T},...) < g_n, \\ \zeta_n(g_n), & \text{when } \Phi_n(\mathbf{T},...) = g_n. \end{cases}$$

The flow function Φ_n that is used to formulate the criterion for the development of plastic deformations in the medium is the function of the Cauchy stress tensor $\mathbf{T}$ of the medium. The plastic deformation of the medium takes place only in the case when the flow function Φ_n reaches its maximum value over the entire history of the medium development.

$$g_n = \max \Phi_n.$$

To describe the nonlinear visco-elastic-plastic behavior of the environment with the help of this model, you need to know four of dependence, which can be obtained from the experimental data for uniaxial cyclic loading with increasing sample at each cycle, the maximum strain (Fig. 1). This $C_1(g)$, $C_2(g)$, $\kappa(g)$ and $\eta(g)$, where $g = g_3 = \max \Phi_3(\text{V})$.

Results

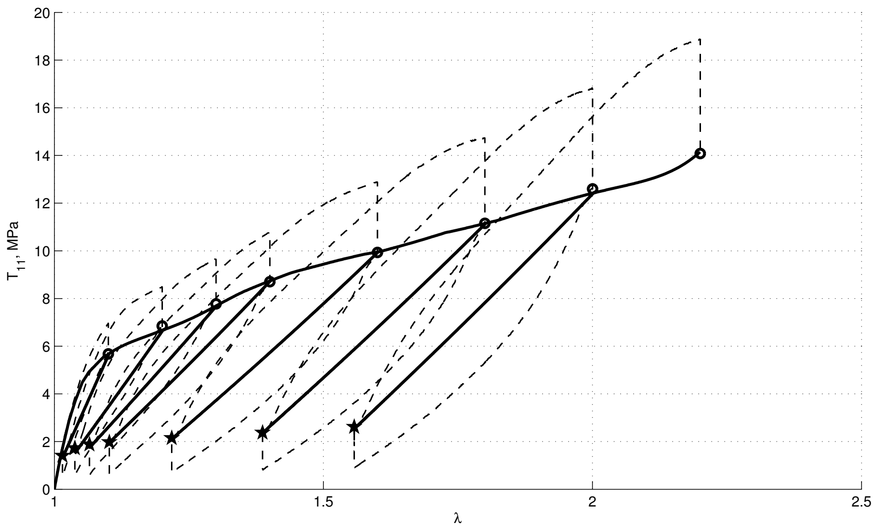

Figure 3: Scheme of the equilibrium cycle loading (excluding the viscous properties of the medium).

Calculating dependencies carried out in two stages. In the first phase were determined $C_1(g)$ and $\kappa(g)$. At the same time believed that the medium is elastic-plastic, ie, considered the equilibrium loading of the material (so slow that the relaxation processes associated with the viscous flow of the medium can be ignored) (Fig. 3). In this case the elastic stiffness of the elastic element number 1 for the maximum in a given cycle of deformation can be determined from the unloading curve through the points marked with $\circ$ (the end of the relaxation after the load) and * (end of relaxation after unloading), as this process was considered a purely elastic. Doing it this way: There are two points $\circ$ and *. Through them it is necessary to carry out the purely elastic curve of uniaxial tension (compression):

$$\sigma(C_1, \lambda_e) = \sigma^0 \lambda_e$$

where λ_e - the multiplicity of elastic elongation of the sample, λ - complete (ie, taking into account the multiplicity of plastic elongation λ_p). You must solve a system of two nonlinear equations with two unknowns: C_1 and λ_p.

Contact the plastic and elastic deformation viewed as relations between λ_e λ_p, and because of the multiplicative decomposition of the Lie:

$$\lambda = \lambda_e \times \lambda_p$$

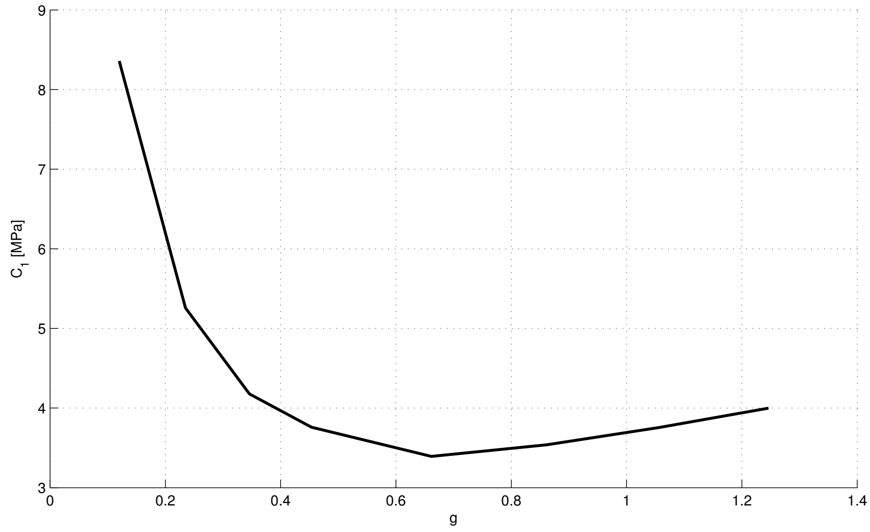

Figure 4: The dependence of the elastic stiffness of the element number 1 on the parameter g.

Substituting in the desired elastic equation (uniaxial loading) will have the form:

$$\begin{cases} \sigma \mid_0 = NC_1[(\lambda_o/\lambda_p)^N - (\lambda_o/\lambda_p)^{-N/2}] \\ \sigma \mid_* = NC_1[(\lambda_*/\lambda_p)^N - (\lambda_*/\lambda_p)^{-N/2}] \end{cases}$$

write the functional $\Psi(C_1,\, \lambda_p)$ and minimize it:

$$\Psi(C_1, \lambda_p) = \\ = \{\sigma \mid_0 - NC_1[(\lambda_o/\lambda_p)^N - (\lambda_o/\lambda_p)^{-N/2}]\}^2 + \{\sigma \mid_* - NC_1[(\lambda_*/\lambda_p)^N - (\lambda_*/\lambda_p)^{-N/2}]\}^2.$$

The values C_1, λ_p, the corresponding $\Psi(C_1,\, \lambda_p) = 0$, are the required quantities.

The dependence of the plastic parameter κ on q were selected from the incremental elastic-plastic solutions of the model problem (excluding at this stage, the viscous component of the model) so as to maximize overlap with the experiment. In this case it means that the calculated curve corresponding to an increase in the load must pass through the "circles" and the handling of dependence - through the "circles" and "stars" (see Fig. 3, 4). Seeking κ dependence on g is shown in Fig. 5.

It was believed that the parameter C_2 is responsible for the elastic properties of the amorphous phase of the polymer, which does not undergo structural changes during deformation of the medium.

Therefore, the model C_2 was considered constant.

By setting different values for the constants C_2 and choosing the appropriate form of the curve $\eta(g)$ was found optimal in terms of coincidence of calculation and the experimental value of C_2 is approximately 10 MPa. For the Neo-Hooke, this corresponds to the initial Young's modulus $E_0 = 60$ MPa, which agrees well with known data on polyethylene.

In Fig. 6 shows the final calculated curves and the experiment.

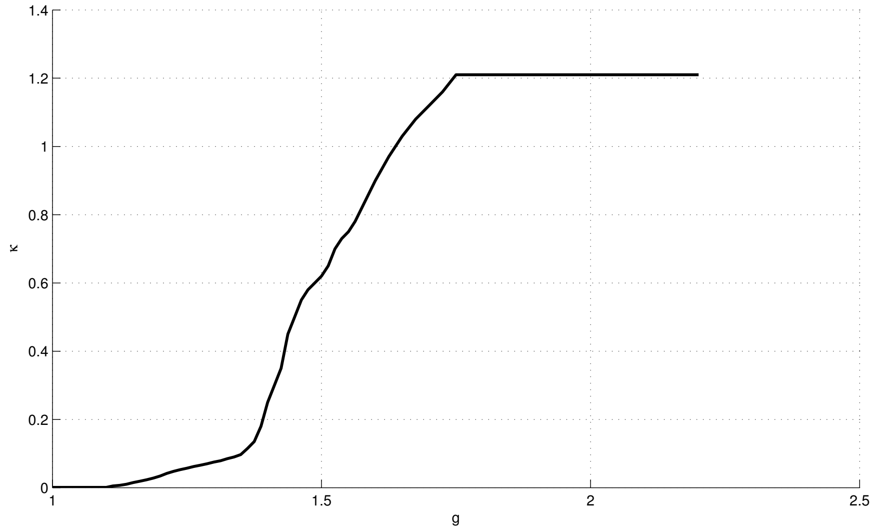

Figure 5: The dependence of the plastic parameter κ on g.

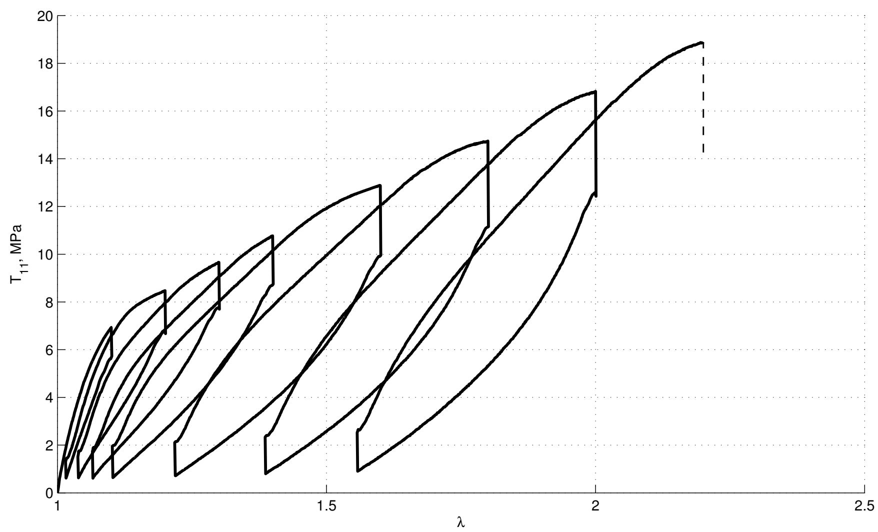

Figure 6: Curves of cyclic elasto-visco-plastic loading of polyethylene. Dashed line - experiment, solid - the calculation.

Conclusion

As can be seen from the last graph, the model allowed to describe accurately the actual cyclic loading of polyethylene with an increasing strain on each cycle.

Acknowledgements

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References

[1] Fengge G. Clay/polymer composites: the story. Materials Today. - 2004. - N 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] Svistkov A. L., Lauke B., Heinrich G. Modeling of viscoelastic properties and softening of rubber materials // Proceedings of 5th European conference "Constitutive models for rubbers" Paris, 2007. P. 113-118.

[4] Palmov V. A. Comparison of different approaches in viscoelastoplasticity for large strain // ZAMM. 2000. V. 80. P. 801-806.

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