# Experimental research and computer modeling of the mechanical behavior of polymer/clay nanocomposites under large deformations

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**Abstract**

The results of experimental and theoretical studies of the mechanical properties of nanocomposites based on polyethylene filled with ultrathin flakes of modified clay (montmorillonite) are presented. Experimental studies were carried out using a special technique, based on the cyclic deformation of the sample in the mode: stretching — stress relaxation — reducing the strain to some predetermined constant value of tensile strength — again relaxation — the next cycle of deformation. Each subsequent cycle is made with increasing amplitude in the deformations. The calculations were executed using structural-phenomenological model describing elastic- viscous-plastic behavior of finite-deformable medium. The model is based on a differential approach to the construction of constitutive equations of material mechanical behavior with the help of symbolic schemes. The model symbolic schema consists of two parallel branches containing two serially connected elements: a) the elastic and plastic, b) the elastic and viscous. As a result, theoretical deformation and relaxation dependences of model parameters that characterize the change in the elastic, viscous and plastic properties of the composite during deformation were obtained. Comparison of calculated and experimental dependences showed that they are practically identical.

Polymer clay nanocomposites is a promising class of industrial materials. At present time they are the subject of intense basic and applied research [1, 2]. The main advantages of filled polyolefins compared to metal products are light weight (low mass density), high corrosion resistance, good heat and electrical insulation properties. These materials are easy to various kinds of mechanical machining and well molded. They are thermoplastic, that is, they are easy to recycle, and then re-used to make new products, which is important from an environmental point of view. Disadvantages include a lower strength, so the plastic parts are usually used as elements of designs, and mechanisms where the load is relatively small.
The object of these studies were nanocomposites based on polyethylene (semicrystalline polymer) filled with nanoparticles of a modified clay (montmorillonite). The filler particles have a shape of ultrathin flakes: thickness about 1 nm, characteristic

transverse size — from 30 nm to several microns. These materials are characterized by a complex mechanical behavior, showing well-defined elastic-plastic and visco-elastic properties during deformation. The experimental and theoretical study of these properties is the subject of this work.
Experimental studies were carried out using a special technique based on cyclic uniaxial loading of the sample with increased amplitude of strain at each step. This type of test is used for the study of polymers, when you want to get in one experiment data not only on the elastic, but also the viscous or plastic material properties [3, 4, 5, 6]. Novelty of the proposed test method consists in entering relaxation stops into the loading cycle when the direction of the motion of gripping clamps changes [7]. This mode allowed to clearly separate the visco-elastic and elastic-plastic behavior of the sample and to obtain all necessary input data for further theoretical studies.
The calculations were carried out using structural-phenomenological model describing elastic- viscous-plastic behavior of finite-deformable structural-heterogeneous medium. The model is based on a differential approach to the construction of constitutive equations of material mechanical behavior with the help of symbolic schemes. The mathematical apparatus of mechanics of nonlinear finite deformations involving Runge–Kutta computing method and Nelder–Mead simplex method [8] are used. Additive decomposition of the strain rate tensors (elastic, viscous and plastic) by analogy with the decomposition proposed by Palmov for elastoplastic medium [9] is used at construction of constitutive equations. One major advantage of the additive decomposition is that in this case the dissipation inequality is satisfied automatically [10], so these math expressions are always correct from the point of view of thermodynamics. Algorithm for automated selection of the model parameters from experimental curves of cyclic loading and relaxation dependences is realized in the software suite MatLab.

# 1 Experiment and computer modeling

The widespread industrial polyethylene PE 107-02K filled by clay ultrathin nanoflakes (modified montmorillonite brand Clousite 20A) was taken as a main research object. The filler concentration $\varphi$ was varied from 0 to 15%-mas. Mechanical tests were carried out using a tensile testing machine Testometric FS100kN CT and a mechanical sensor LC100.
Each cycle of the loading program includes the following operations:
1) stretching to some value exceeding the maximum strain obtained in the previous cycle;
2) stop of the gripping clamps for a given time for stress relaxation;
3) unloading up to the given (but not zero) stress;
4) again stop of the gripping clamps for relaxation (the same time period);
5) termination of the cycle and beginning of the next cycle (with increasing strain amplitude).

The speed of motion of the gripping clamps under loading–unloading was set 100% per minute. The relaxation time was equal to 10 minutes. The test program consisted of 8 cycles at maximum strain 10%, 20%, 30%, 40%, 60%, 80%, 100%, and

120%. The tensile force during unloading was reduced to 0.6 MPa at each cycle. The possibility of transverse bending of the sample during the return stroke of grips due to error of the force sensor was excluded by this — sample remained stretched all the test time. As a result, the dependencies of experimental stresses on strain and time (relaxation curves) were obtained for nanocomposites with filler concentration 0, 5, 10 and 15%-mas.

The proposed phenomenological model of the elastic-viscous-plastic medium is a further development of the differential approach to the construction of constitutive equations based on the interpretation of the mechanical behavior of the material with the help of symbolic schemes. Previously, this approach has been used to describe the elastic-plastic behavior of polymers. The results of modeling the elastic-plastic properties of nanocomposites based on the polyolefin matrix and ultrafine filler of layered clay minerals (smectites) are presented in [11]. Further, this model has been modernized, which allows us to take into account the changes in the volume of the polymer due to the accumulation of internal damage (micro debondings) [12].

This approach was extended to the modeling of not only plastic, but viscous polymer properties of the medium in 2014–2015. Detailed description of this variant of the model is given in [7, 13]. The symbolic model scheme (Fig. 1) consists of two parallel branches containing two serially connected elements: a) elastic (1) and plastic (3), b) elastic (2) and viscous (4). Tensor equations that specify the properties of the medium correspond to each element. Stresses in the elements in each branch are the same, and strain rates are summed to such combination of elements. The overall stress in the material is the sum of stresses in the branches, and strain rates in the branches are equal to the total rate of deformation of the material. That is, the additive decomposition of the strain rate tensor (elastic, viscous and plastic) was used in the model.

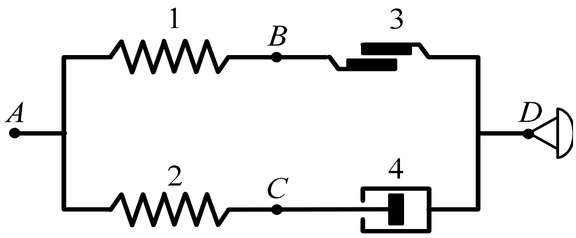



Figure 1: Symbolic scheme of elastic-viscous-plastic model

It was assumed that the elastic-plastic branch simulates displacements, destruction or rearrangement of agglomerates of crystallites (more rigid than the amorphous phase) and filler particles (i.e. irreversible changes in the material structure). The visco-elastic one describes the flow of the amorphous polymer between the lamellae inside crystallites and in the space around the crystallites and particles [14, 15].

The equations of the nonlinear elasticity theory are used to calculate stress tensors in elastic elements 1 and 2. It is assumed that the body volume and temperature in the deformation process do not change, and the elastic properties of the material are described by the neo-Hookean potential. The mechanical properties of the plastic element are determined by analogy with the basic Prandtl-Reuss equations of plastic flow. To close the system of equations defining the plastic features of the material, proportional relation between the deviators of strain rate tensors of the plastic element $\mathbf{D}_3$ and the entire medium $\mathbf{D}$ was used:

$$\sqrt{\mathbf{D}_3 \cdot \mathbf{D}_3} = \kappa\sqrt{\text{dev}\mathbf{D} \cdot \text{dev}\mathbf{D}},$$

where $\kappa$ is the nonnegative parameter (hereinafter the plasticity parameter) indicating the portion of plastic deformation rate in the total deformation rate of the medium. So, if $\kappa = 0$ the material behaves as an elastic, at $0 < \kappa < 1$ — as the elastic-plastic with hardening, the case when $\kappa = 1$ corresponds to perfect plasticity, and finally, when $\kappa > 1$, the load curve becomes a falling, that is the softening of material occurs.
For the yield function $\Phi$, the medium intensity of the medium left stretch tensor $\mathbf{V}$ is used:

$$\Phi = \sqrt{\text{dev}\mathbf{V} \cdot \text{dev}\mathbf{V}}.$$

In the case of the incompressible uniaxially loaded material, $\lambda_1 = \lambda$,
$\lambda_2 = \lambda_3 = \lambda^{-1/2}$, it can be written as

$$\Phi = \sqrt{2/3}\left(\lambda - \sqrt{1/\lambda}\right).$$

For the viscous element, the stress tensor $\mathbf{T}_4$ and its deviator are determined by formula

$$\mathbf{T}_4 = 2\eta\mathbf{D}_4 - \sigma_0\mathbf{I}, \quad \text{dev}\mathbf{T}_4 = 2\eta\text{dev}\mathbf{D}_4 = 2\eta\,\mathbf{D}_4,$$

Where $\eta$ is the shear viscosity, $\sigma_0 = 1/3\text{tr}\mathbf{T}_4$ is the mean normal stress or negative pressure.
Thus, to describe the nonlinear elastic-viscous-plastic behavior of the polymer using this model, we need to know the following four dependencies: $C_1(q)$, $C_2(q)$, $\kappa(q)$ and $\eta(q)$, where $q = \max\Phi\left(\mathbf{V}\right)$ — invariant measure of deformation (the analog of the Odkvist hardening parameter [16] of the classical theory of plasticity that characterizes the accumulated plastic strain). Choosing $q$ as a deformation measure was caused by the fact that in the process of loading its value can only increase or remain constant (in contrast to the elongation ratio $\lambda$). Thus the condition of irreversibility of the changes of the above model parameters is defined in the model. These four dependencies were determined from the analysis of relevant experimental data.
$C_1(q)$ is an elastic parameter (the neo-Hookean stiffness of the first element), which depends on the irreversible structural rearrangements during deformation (processes that lead to the appearance of residual plastic deformations). Stiffness of the second elastic element $C_1(q)$, defining the elastic properties of amorphous polymer phase, that relied unchanged during deformation, was considered constant and taken equal to 10 MPa.

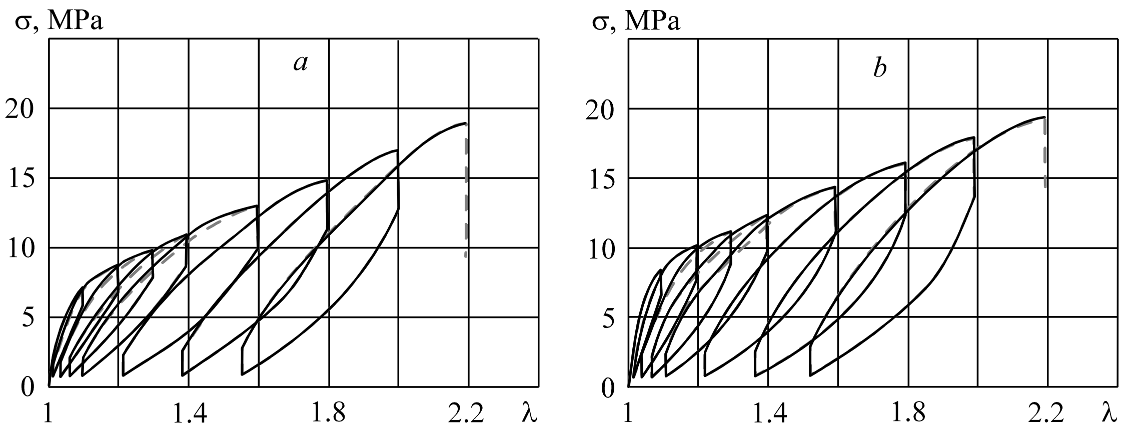
# 2 Results discussion

The experimental data obtained in the above described experiments were theoretically treated using this elastic-viscous-plastic model. This allowed to make quantitative estimates of the processes of development of plastic and viscous flows in these polymeric/clay composites depending on the nanofiller concentration. A comparison of the calculated and experimental results shows that they are practically identical. This is indicative of the fact that the conclusions from the analysis of the findings of model parameters are close to reality. Depending of the true stress $\sigma$ on the sample elongation ratio $\lambda$ for filler concentrations 0, 5, 10 and 15%-mas. are shown in Fig. 2. Calculated dependences of the model parameters $C_1$, $\kappa$ and $\eta$ of $q$ are shown in Figures 3, 4 and 5 relatively.

As for elastic properties, in all cases, the stiffness $C_1$ initially drop sharply, and then again begin to grow (but with much less intensity). The calculations showed that increasing the filler concentration in the polymer increases the natural stiffness of the composite. It is interesting that there is a significant convergence of dependency $C_1(q)$, corresponding to different values of $\varphi$ with the increase of plastic deformation in the sample. Most likely, this is due to the development of the structural orientation processes: translation and rotation of crystallite agglomerates and filler particles.

For unfilled and filled systems the plasticity parameter $\kappa$ at the elastic stage of deformation (elastic zone corresponds to $q < 0.24$ that is similar to $\lambda < 1.2$) are close to zero, then its monotonic increase occurs. For pure polymer the values of $\kappa$ approach 1 for $q$ equal to about 0.85 ($\lambda = 1.8$), i.e. deformation becomes completely plastic. As for the filled systems $\kappa$ values even exceed 1 (in physical sense, this corresponds to the material softening). The greater the value of $\varphi$, the curves $\kappa(q)$ are higher. All curves go up sharply with a further increase in $q$ ($\lambda > 2$) when the plastic neck formation begins. The plastic neck causes the mechanical inhomogeneity along the sample, but the model does not take it into account. This stage is beyond the scope of this model, and this effect, and we did not studied it.

As for dependencies between viscosity and deformation in all cases $\eta$ increases monotonically throughout the load range, and the filler input enhances viscosity of the system (as should be expected).



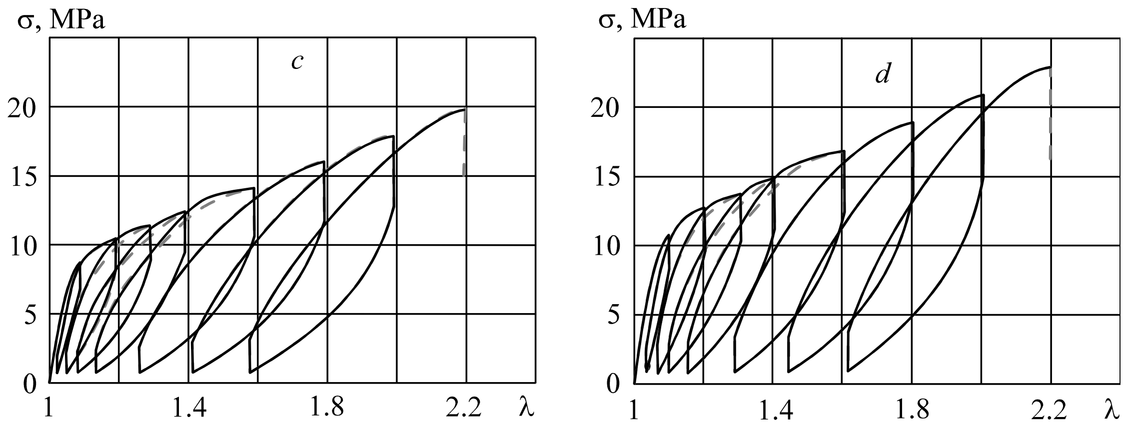



Figure 2: Strain cyclic loading curves for PE 107-02K filled by clay nanoparticles: *a*) $\varphi$=0%-mas.; *b*) 5%-mas.; *c*) 10%-mas.; *d*) 15%-mas. Black lines — calculation, gray lines — experiment.

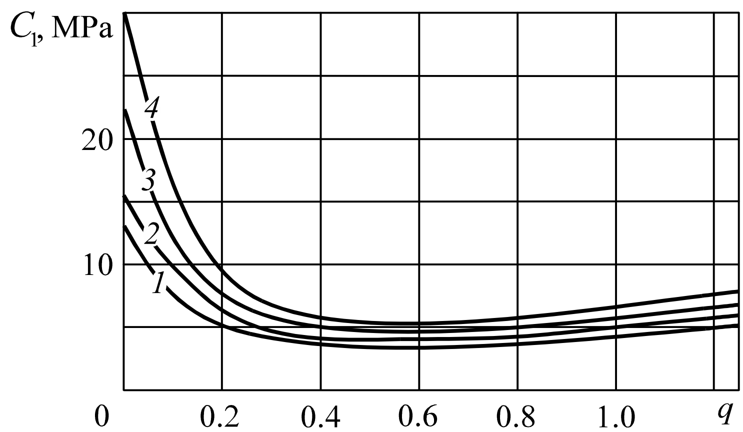



Figure 3: Calculated dependences of elastic parameter $C_1$ on $q$ for PE 107-02K filled by clay nanoparticles: *1*) $\varphi$=0%-mas.; *2*) 5%-mas.; *3*) 10%-mas.; *4*) 15%-mas.

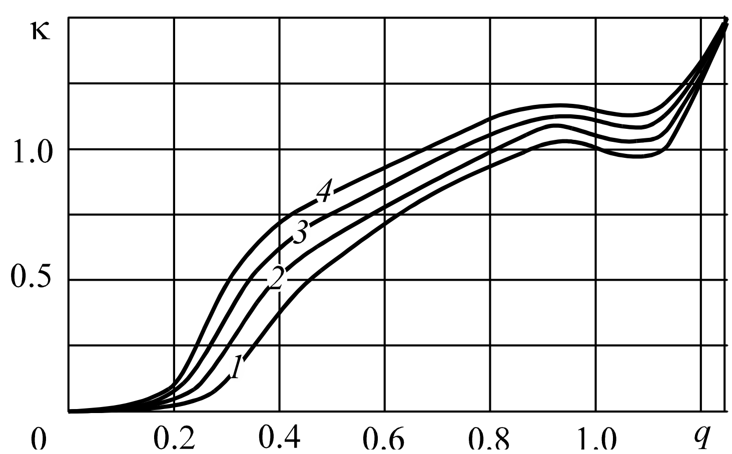



Figure 4: Calculated dependences of plasticity parameter $\kappa$ on $q$ for PE 107-02K filled by clay nanoparticles: *1*) $\varphi$=0%-mas.; *2*) 5%-mas.; *3*) 10%-mas.; *4*) 15%-mas.

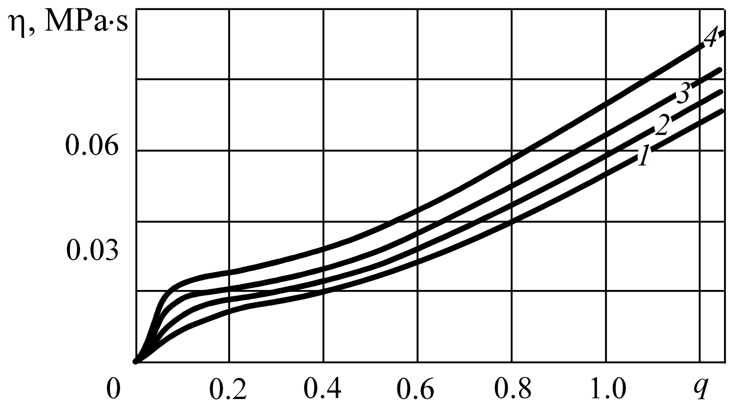



Figure 5: Calculated dependences of viscosity $\eta$ on $q$ for PE 107-02K filled by clay nanoparticles: *1*) $\varphi$=0%-mas.; *2*) 5%-mas.; *3*) 10%-mas.; *4*) 15%-mas.

The studies carried out in this work demonstrated the adequacy and validity of the proposed model for investigation of the elastic-viscous-plastic properties nanoclay filled polymers. Combining experimental and theoretical modeling allowed evaluating the development of plasticity and viscosity during the deformation of these materials not only qualitatively but also quantitatively.

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