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MECHANICAL PROPERTIES OF POLYMER NANOCOMPOSITES BASED ON STYRENE BUTADIENE RUBBER WITH DIFFERENT TYPES OF FILLERS

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This article examines the theoretical description of the mechanical behavior of elastomeric nanocomposites based on butadiene styrene polymer, and several species with different filler volume fraction in 30phr and 50phr. To construct the determining equations we use the scheme, whose points are connected by elastic, viscous, plastic and transmission elements. To describe the properties of each element used well-known equations of nonlinear elasticity theory, the theory of nonlinear viscous fluids, the theory of plastic flow of material in the finite deformation of the medium. To obtain the constants of the model used stepwise algorithm. Used in the experiments (cyclic loading, relaxation and creep) can get more information about the viscoelastic properties of rubber.

Keywords: polymer nanocomposites, styrene butadiene rubber, filler.

This article examines the theoretical description of the mechanical behavior of elastomeric nanocomposites based on butadiene styrene polymer, and several species with different filler volume fraction in 30phr and 50phr. To construct the determining equations we use the scheme (Fig. 1), whose points are connected by elastic, viscous, plastic and transmission elements [1]. To describe the properties of each element used well-known equations of nonlinear elasticity theory, the theory of nonlinear viscous fluids, the theory of plastic flow of material in the finite deformation of the medium. To obtain the constants of the model used stepwise algorithm [3]. Used in the experiments (cyclic loading, relaxation and creep) can get more information about the viscoelastic properties of rubber.

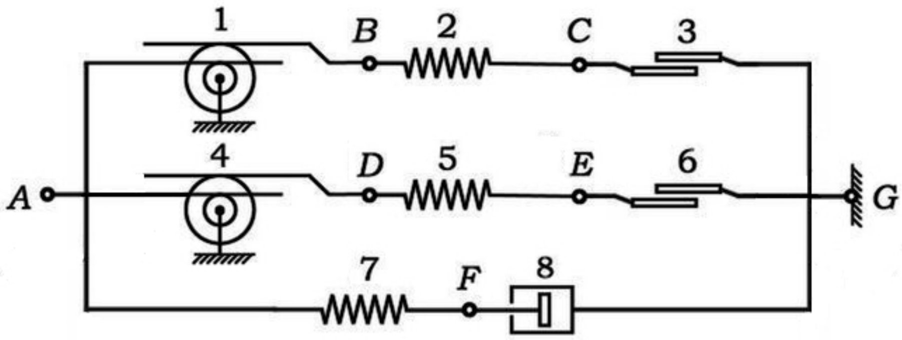

Fig. 1. Schematic of the model of the mechanical behavior of rubber

1. Tested materials and experiments

Experiments were conducted on eight of elastomeric nanocomposites based on butadiene styrene polymer, and three kinds of filler including a carbon black, with surface modification for two fillers (Tab. 1). Volume fraction of filler 30 and 50 phr. The materials provided by Lanxess (Leverkusen, Germany).

Table 1. Nanocomposite formulation

Nano-composite code name	Polymer S-SBR Buna VSL 5025	filers			
		precip. Silica		Carbon Black N330	Silane TESPT SI69
		Aerosil R974	Aerosil 200		
1	100	30			
2	100	50			
3	100		30		
4	100		50		
5	100		30		2.4
6	100		50		4
7	100			30	
8	100			50	

In previous studies, we used the special experiments with a complex cyclic loading condition [3]. Each cycle contained a stretch at a constant rate, stress relaxation under constant tension, unloading at a constant rate and creep. Experiments proposed type give a large amount of information about the mechanical properties of the material. On one sample in one experiment, the data on the softening of the medium on the first cycle of deformation (Mullins effect), the viscoelastic properties of the relaxation and creep. Determination of constants of the model can be implemented step by step, using a constant discovery of new information obtained in the previous steps.

In this paper, our experiment consisted of seven cycles. Each cycle consisted of a load at a constant rate to the multiplicity of extensions in this series, stress relaxation under constant tension, unloading of material at a constant rate to zero strain and the rest of the material. Data for each cycle are shown in Tab. 2, and the experiment in Fig. 2. As a result of this experiment, we observed the effect of softening Mullins on the first cycle of deformation of the material. The next two cycles, the strain rate was changed so as to assess the influence of speed on the viscoelastic properties of the materials. In the experiment can be clearly seen (Fig. 2) that there is no difference in mechanical behavior of material at a deformation rate of 20% per minute, and 50% per minute and 100% per minute (see 1,2 and the third cycle in the Tab. 2). The next cycles of deformation had the multiplicity of elongation less than the maximum that we could to construct an equilibrium curve of the material using the bottom points of relaxation. Under the equilibrium curve we mean the limit for experimental stress relaxation with time equal infinite at a given multiplicity of extensions. In this paper, we interpolate the equilibrium curve of the median line between the curve of loading and unloading for the multiplicity of extensions $\lambda < 2$ and the lower points of relaxation for 4,5,6 and 7 cycles. For the equilibrium curve viscoelastic processes in the material already completed and we can use the model to determine the elastic properties of the material.

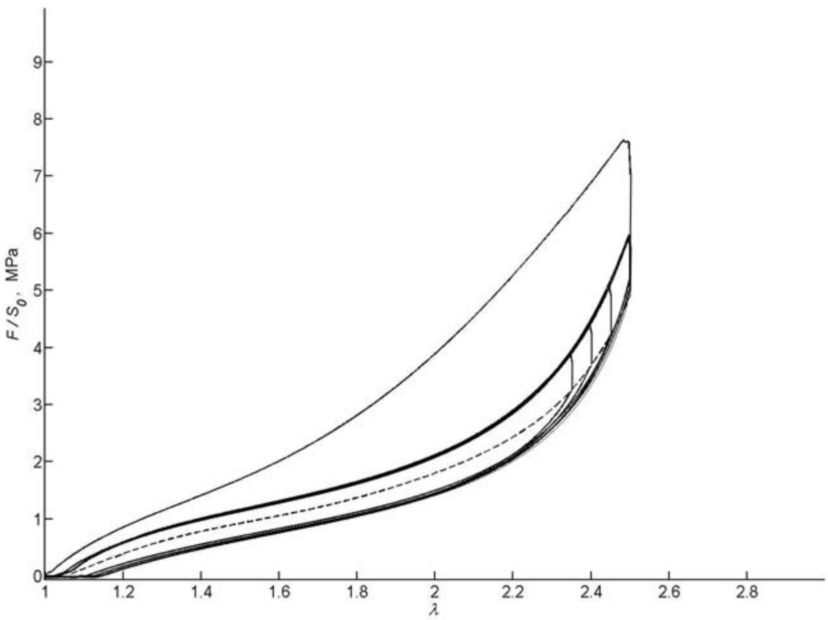

Fig. 2. The experimental data - solid line, the equilibrium curve - dotted line

Table 2. Algorithm of the experiment

number	loading		relaxation	unloading	rest
of	to			to zero stress	of material
cicle	extensions	deformation rate	time	deformation rate	time
1	2.5	100% per min	30 min	100% per min	30min
2	2.5	20% per min	30 min	20% per min	10 min
3	2.5	50% per min	10 min	50% per min	10 min
4	2.35	100% per min	10 min	100% per min	10 min
5	2.4	100% per min	10 min	100% per min	10 min
6	2.45	100% per min	10 min	100% per min	10 min
7	2.5	100% per min	10 min	100% per min	10 min

2. Model of the mechanical behavior of rubber

The mechanical behavior of rubber is described by the model schematically represented in Fig. 1, where each point corresponds to a particular set of constitutive equations. 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, transmission) is described in detail in work [1]. 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 [2]. The internal scheme points are required to meet the condition of correlation of the Cauchy stress tensors [1]. The scheme for the mechanical behavior of the material involves transmission, elastic, viscous and plastic elements that correspond to the folowing equations. 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

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

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

$$f = f(\lambda_1^{(2)},\lambda_2^{(2)},\lambda_3^{(2)},\lambda_1^{(5)},\lambda_2^{(5)},\lambda_3^{(5)},\lambda_1^{(7)},\lambda_2^{(7)},\lambda_3^{(7)}),$$

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 $\mathbf{F} = \mathbf{V}\mathbf{R}$ 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 structural deformation of the elastomeric binder fraction and the macroscopic deformation of the rubber differ significantly. This difference is taken into account by the transmission elements. Application of these elements increases the strain rate tensor at the right point of the transmission element by a factor of ν_m in comparison with the corresponding tensor at the left point and simultaneously decreases the Cauchy stress tensor.

$$\mathbf{D}_m^{\mathrm{left}} = \frac{1}{\nu_m}\,\mathbf{D}_m^{\mathrm{right}}, \qquad \mathbf{T}_m^{\mathrm{left}} = \nu_k\,\mathbf{T}_m^{\mathrm{right}}.$$

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.

$$g_n = \max \Phi_n.$$

3. Results

In this article we have simulated the behavior of the elastic properties of the material, which are described by 1, 2, 3, 4, 5 and 6 elements of scheme. Elastic properties of the material describes the equilibrium curve, since at these points viscoelastic processes in the material over. Therefore, the constants in the desired elements were chosen from the best convergence of theoretical calculations and the equilibrium curve

First, we searched for the constants for 1, 2 and 3 of the circuit elements. Constants for the third plastic element found with the residual strain after the first cycle of loading. Further modeled the elastic properties described by the first and second elements of the scheme. Potential of the medium takes the form:

$$w = w_2 = c_1^{(2)} \left(\sum_{i=1}^{3} (\lambda_i^{(2)})^2 - 3 \right) + c_2^{(2)} \left(\sum_{i=1}^{3} (\frac{1}{\lambda_i^{(2)}})^2 - 3 \right).$$

Simulation results for 1, 2 and 3 elements are shown in Fig. 3 for sample 8 (carbon black with a mass fraction 50phr). Next, we model the elastic properties of fibers, which are described using 4, 5 and 6 of the first elements of the scheme.

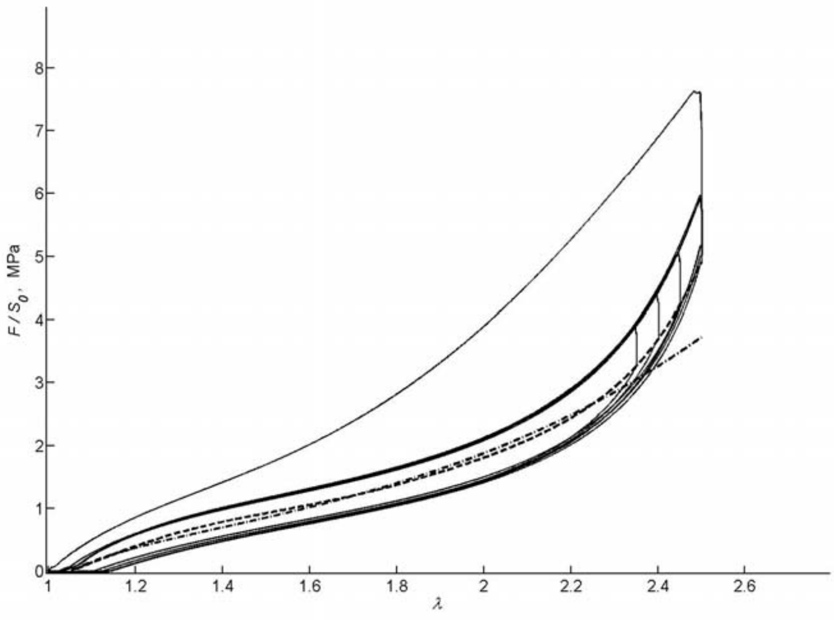

Fig. 3. Solid line - experimental data for the sample 8; bar dotted line - theoretical calculation for the 1, 2, 3 elements; dotted line - the equilibrium curve

The potential of the fifth elastic element is expressed as:

$$w_5 \;=\; \begin{cases} 0, & \text{where } \xi_5 < 0, \\ c_1^{(5)}\xi_5, & \text{where } \xi_5 \geq 0. \end{cases}$$

and

$$\xi_5 = (\lambda_1^{(5)} - 1)(\lambda_2^{(5)} - 1)(\lambda_3^{(5)} - 1).$$

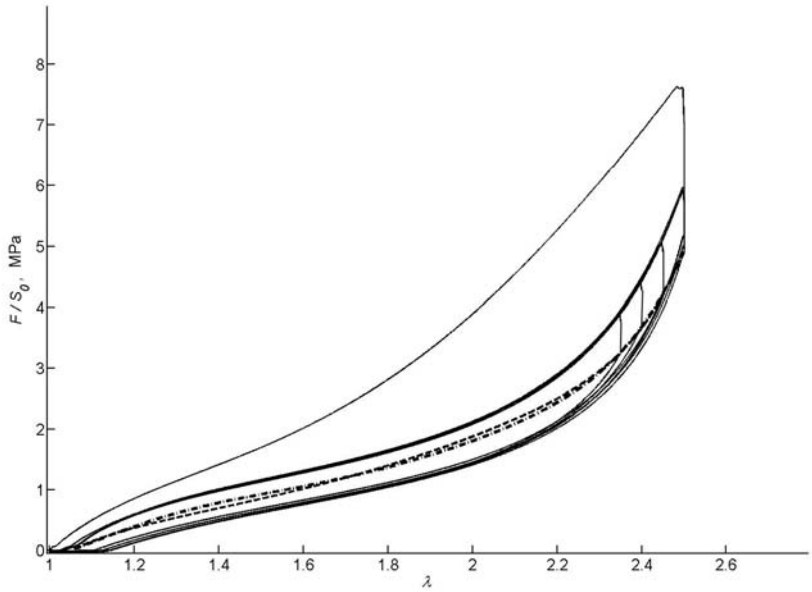

Fig. 4. Solid line - experimental data for the sample 8; bar dotted line - theoretical calculation for the 1, 2, 3, 4, 5 and 6 elements; dotted line - the equilibrium curve

Then the potential free-energy environment in the form sum. In Fig. 4, resulted in the simulation results for sample 8 (carbon black with a mass fraction 50phr).

4. Conclusion

Proposed in the experiments provide information on the mechanical behavior of materials with which to determine the equilibrium curve of the material under loading. With the help of the model we have described (Fig. 3, 4) the elastic properties of the materials. Using the experimental data and simulation results for the materials, we found a correlation between the amount of energy spent on the softening of the material and the constants for 5, 6, 7 element model. The experiments revealed that virtually no difference in mechanical behavior of material at a deformation rate of 20% per minute, and 50% per minute and 100% per minute.

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