New approaches for evaluating rheological models in composites

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Abstract. The classic rheological models constructed of elastic and viscous elements are briefly analyzed. A model of relaxation mechanism in composites is proposed.

1. Introduction

Kinetic processes are of great importance in materials science since they determine the stages and duration of structure formation influencing the final state of the materials and products based on them. In operating practice they appear in the form of creep, relaxation, shrinkage, swelling and etc. However both technological and operating parameters are determined by the state of the material structure under study. In this paper the classic rheological models constructed of elastic and viscous elements are analyzed to evaluate kinetic processes in composites [1-4].

It is well known that when developing the new composite materials the stress relaxation is of great importance because it is directly related to the response of the material structure to the prolonged mechanical impact in the mode of constant strain [3, 4]. Kinetic regulations of the relaxation in classical consideration have trivial exponential solution which of the does not correspond to the experimental values. More complicated empirical regularities which are however based on the exponential function are used for adequate interpretation of the experimental data.

In this situation quite an urgent task is to search for the new kinetic models that provide noncontradictory evaluation of these phenomena and reveal their nature [4].

2. Governing equations

We will briefly analyze the classical rheological models which provide more consistent and reasoned transition to the developed model of relaxation mechanism. Composite materials show tendency to viscous flow under long exposure on them of applied load. When the load is removed due to the display of elastic properties part of the strain is instantly restored. Afterwards the remaining rubbery deformation gradually decreases. Therefore under load composite materials exhibit viscoelastic properties which are considered from the perspective of rheology.

In rheology behavior of materials is most often described by the mechanical models constructed of elastic and viscous elements. Elastic structural elements are simulated by a spring in which the relationship between stress and strain is linear according to Hooke’s law:
\[ \sigma_y = E \varepsilon_y, \]  
\(1\)

where \( E \) – modulus of elasticity, \( \varepsilon_y \) – elastic strain.

Viscous element is represented as a fluid damping device its behavior is described by the Newtonian flow law.

\[ \sigma_b = \eta \dot{\varepsilon}_b / \dot{t}, \]  
\(2\)

where \( \eta \) – viscosity coefficient, \( \varepsilon_b \) – viscous strain. Various combinations of elastic and viscous elements allow making efficient modeling of rheological processes.

Stress relaxation process in the elementary representation is described by the Maxwell model with the simplest (consecutive) combination of elastic and viscous elements. A distinctive feature of this model is in the fact that with increasing strain viscous properties of Maxwell’s model element become exhausted and disappear while elastic properties are fully kept.

Deforming the model on a certain finite value \( \varepsilon \) leads to the instantaneous elastic strain \( \varepsilon_y \) and gradual development of viscous strain \( \varepsilon_b \) in time. Consequently the total strain is determined according to the principle of additivity taking into account the model structure

\[ \varepsilon = \varepsilon_y + \varepsilon_b. \]  
\(3\)

The rate of change of the strain is given by the expression

\[ \frac{d\varepsilon}{dt} = \frac{d\varepsilon_y}{dt} + \frac{d\varepsilon_b}{dt}. \]  
\(4\)

Using (1) and (2) we get \( \frac{d\varepsilon_y}{dt} = \frac{1}{E} \frac{d\sigma}{dt} \) and \( \frac{d\varepsilon_b}{dt} = \frac{\sigma}{\eta} \). Taking into account the above equations dependence (4) takes the form

\[ \frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}. \]  
\(5\)

According to the condition at the initial time \( t = 0 \) strain takes the value \( \varepsilon = \varepsilon_0 \) and does not change subsequently \( \frac{d\varepsilon}{dt} = 0 \). This allows you to integrate equation (5)

\[ \sigma = \sigma_0 \exp\left(-\frac{t}{\tau_p}\right), \]  
\(6\)

where \( \sigma_0 = E\varepsilon_0 \) – initial stress, \( \tau_p = \eta / E \) – relaxation time. The obtained widely known relation characterizes the kinetics of the stress relaxation process.

The behavior of real materials is described by a more complex model studied by Kuhn in which the set of Maxwell elements with different values of constants \( E \) and \( \eta \) are connected in parallel. It is obvious that the relaxation properties of the constituent elements are different. Because of the uncertainty of particular values of \( E \) and \( \eta \) for individual Maxwell elements the study of such a model is quite difficult. However Kuhn’s multi-element model allows you to reveal the relaxation mechanism more fully. In this regard we consider the deformation of a heterogeneous composite material. In composite materials the elastic and viscous structural elements are in the different states of deformation. A model of this heterogeneous system can be represented as the set of parallel-connected Maxwell elements with various degrees of deformity (figure 1).

Suppose that elasticity \( E \) and viscosity \( \eta \) coefficients for all the elements are identical. This conditional averaging moves the model away from a real material but allows you to give qualitatively new evaluation of the stress relaxation process.
Most simply the new quality can be seen when considering the following example. Let us analyze the two multi-element models. Each model consists of five Maxwell elements connected in parallel and is stretched by the applied stress to a fixed value of the relative strain (figure 2). Values of $E$ and $\eta$ for all elements of the models are identical. In the first one viscous properties are exhausted in the four elements and only one has a reserve of viscosity (figure 2a). In the second model we can see the opposite situation (figure 2b).

In this regard the difference of stress relaxation time period is of interest. From the intuitive considerations it follows that since the second model has the higher reserve of viscous properties then relaxation will occur over a longer time.

It should be noted that viscous properties of both models can be characterized by a single Newtonian equation [4] since coefficient $E$ and $\eta$ for all elements are identical. Then however the degree of initial deformity of the elements should be taken into account. In this representation we can adapt the Newtonian equation if in the left-hand side we will note the fraction of Maxwell elements $n_b$ with reserve of viscous properties

$$n_b \dot{\sigma} = n b \dot{E}_b / \dot{d}.$$

In heterogeneous materials value $n_b$ is equivalent to the volume fraction with the reserve of viscous properties. Elements of this volume are distributed in the total volume of the material under study in an arbitrary way. Amount of volume with the reserve of viscous properties depend on the production technology of material and its operating conditions.

Topology of the distribution of viscous and hard phases can be represented by the Shklovsky-de Gennes model in which a representative volume is filled with a viscous phase permeated with a spatially connected rigid structural framework [5]. Without describing the structure in detail the framework can be presented in the form of spatial distorted lattice with characteristic cells, their
averaged size is \( l \). With increasing the volume of viscous phase the rigid framework becomes sparser and the size of its cells \( l_c \) increases and vice versa. Thus the following condition \( n_b \propto l \) is satisfied. Taking this into account equation (7) takes the form

\[
l_c(t) = \eta \varepsilon_b / dt .
\]

This implies a very important conclusion that Newtonian equation (2) describes the viscous properties only of the homogeneous systems with identical deformity of the unit elements and is a special case of a more general relation (8). A distinctive feature of equation (8) lies in the fact that via conditional size \( l_c \) of the volume with hard properties it takes into account the degree of heterogeneity that directly affects the kinetics of stress relaxation in the material.

Let us analyze the kinetics of stress relaxation taking into account equation (8). First of all we note that in the relaxation process the volume with a reserve of viscous properties hyperbolically decreases over time

\[
V_b(t) = C_b / t ,
\]

where \( C_b \) – constant. Volume \( V_b \) and characteristic structural size \( l_c \) are interconnected by the dependency

\[
V_b = l_c^{D_t} = C_b / t ,
\]

where \( D_t \) – structural dimension of a heterogeneous system. From the relationship (10) we find

\[
l_c = C_b^{1/D_t} \cdot t^{(-1/D_t)} .
\]

Substituting (11) into equation (8) we get

\[
C_b^{1/D_t} \cdot t^{(-1/D_t)} \sigma = \eta \varepsilon_b / dt .
\]

Taking into account (12) equation (5) takes the form

\[
d\varepsilon / dt = (1/E)(d\sigma / dt) + (\sigma / \eta)C_b^{1/D_t} \cdot t^{(-1/D_t)} .
\]

Taking the initial conditions \( t = 0, \varepsilon = \varepsilon_0, (d\varepsilon / dt) = 0 \) into consideration we get

\[
(1/E)(d\sigma / dt) + (\sigma / \eta)C_b^{1/D_t} \cdot t^{(-1/D_t)} = 0 .
\]

Separating the variables we find

\[
d \ln \sigma = - (E/\eta)C_b^{1/D_t} \cdot [1 - (1/D_t)]^{-1} t^{(-1/D_t)} dt .
\]

Integrating the obtained equality in the limits \( 0 \leq t \leq \sigma \) and \( (\sigma_0 \leq \sigma) \) we obtain

\[
\sigma = \sigma_0 \exp\left[-\alpha_b t^{1/(1/D_t)}\right] ,
\]

where \( \alpha_b = (E/\eta)C_b^{1/D_t} \cdot [1 - (1/D_t)]^{-1} \) – constant. Relationship (13) can be rewritten in a simpler form

\[
\sigma = \sigma_0 \exp\left[-\alpha_b t^n\right] ,
\]

where \( n = 1 - (1/D_t) \) – constant for a given heterogeneous system \( \alpha_b = \tau_p^{-n} \).

We note that analytical equation (14) corresponds to an empirical equation of V.M. Ravinsky for metals [6].

For polymers along with elastic (reversible) and plastic (irreversible) strain the reversible rubbery strain can also be observed it is most evident when removing the strain in elastomers. In this case the Maxwell model becomes inapplicable. The Zener model in which Maxwell element is connected in parallel with the elastic element is most common and well known to adequately describe the rheological behavior of such materials. It should be noted that Zener model can be easily converted either in the Maxwell model (at \( E_1 = 0 \)) or the Kelvin-Voigt model (at \( E_2 = \infty \)). Let us rewrite the equation (5) for the Maxwell model in the following form

\[
\eta (d\varepsilon / dt) = (\eta / E)(d\sigma / dt) + \sigma .
\]
Then differential equation corresponding to the Zener model will have the form

\[ E_1 \varepsilon_0 + \eta (d\varepsilon_0/dt) = (\eta/E_2) (d\sigma/dt) + \sigma \]  \hspace{1cm} (15)

where \( E_1 \) – equilibrium modulus of elasticity (figure 3). In the stress relaxation process the initial strain is kept constant during the whole time \( \varepsilon = \varepsilon_0 = \text{const} \), \( d\varepsilon/dt = 0 \). Taking the initial conditions into consideration we transform (15)

\[ E_1 \varepsilon_0 - \sigma = (\eta/E_2) (d\sigma/dt) + \sigma \]  \hspace{1cm} (16)

We introduce a new variable \( z = \sigma - E_1 \varepsilon_0 \), \( dz = d\sigma \), taking it into account we obtain the solution of equation (16)

\[ z = z_0 \exp[-(E_2/\eta)t], \]  \hspace{1cm} (17)

where \( z_0 = (\sigma_0 - E_1 \varepsilon_0) \) – constant, \( \sigma_0 \) – stress at the initial time (at \( t = 0 \)). Let us represent relationship (17) in the final form

\[ \sigma = E_1 \varepsilon_0 + (\sigma_0 - E_1 \varepsilon_0) \exp[-(E_2/\eta)t], \]  \hspace{1cm} (18)

We express the value of \( \sigma_0 \) according to Hooke’s law

\[ \sigma_0 = E_0 \varepsilon_0, \]  \hspace{1cm} (19)

where \( E_0 \) – modulus of instantaneous elasticity for most of the polymers it is \( \sim 10^3 \) MPa.

Taking into account the latter equality we simplify expression (18)

\[ \sigma = E_1 \varepsilon_0 + E_2 \varepsilon_0 \exp[-(E_2/\eta)t], \]  \hspace{1cm} (20)

where \( E_2 = (E_0 - E_1) \) – modulus of elasticity of Maxwell element in the Zener model.

Introduced variable \( z = \sigma - E_1 \varepsilon_0 = \sigma_z (dz = d\sigma_z) \) in equation (16) is substantially the part \( (\sigma_z) \) of the total stress \( \sigma \) which undergoes relaxation (figure 3). Therefore taking into account the topology of the distribution of viscous and hard phases equation (16) can be written in another form

\[ l, \sigma_z = -(\eta/E_2) (d\sigma_z/dt). \]  \hspace{1cm} (21)

Solving equation (21) using dependency (11) we finally find

\[ \sigma = E_1 \varepsilon_0 + E_2 \varepsilon_0 \exp(-\alpha_b t^n), \]  \hspace{1cm} (22)

where \( \alpha_b = (E_2/\eta) C_b^{1/D} [1-(1/D)]^{-1} \), \( E_1 \varepsilon_0 = \sigma_0 \) – equilibrium stress. It is noteworthy that the resulting equation (22) completely coincides with the empirical Kohlrausch formula studied by the G.L. Slonimsky with colleagues with regard to polymers [7].

Value of empirical measure \( n \) is estimated by the interval \( n = 0 \div 1 \) which corresponds to the equality \( n = 1 - (1/D) \) where dimension of \( D \), taking into account the occurrence of fractality in the structure of heterogeneous material theoretically can be in the range 1 < \( D < \infty \). Thus change in the measure \( n \) is determined by the fractal variability of the structure of heterogeneous material this allows you to reveal the physical nature of the stress relaxation process more deeply. Defining experimentally
the measure \( n \) and determining values of structural dimensions \( D_i \) and \( D_e \), you can make the topological evaluation of state of distribution of the effective relaxation zones in the material structure.

**Figure 4.** Stress relaxation in an epoxy-filled composite (1 – \( \sigma_0 = 6 \text{ MPa}, \sigma_x = 2.9 \text{ MPa} \); 2 – \( \sigma_0 = 9 \text{ MPa}, \sigma_x = 4 \text{ MPa} \)).

Experimental data on stress relaxation in epoxy-filled composite (see figure 4) show that the depth \((\sigma_0 - \sigma_\infty)\) of relaxation increases with the growth of initial \( \sigma_0 \) stress \( (t = 0) \). In this case according to dependency (22) coefficient \( \alpha_0 \) does not change \( (\alpha_0 = 7.4 \text{ hour}^{-n}) \) and measure \( n \) increases. Here the change in the value of measure \( n \) is of interest.

When initial stress \( \sigma_0 = 6 \text{ MPa} \), measure \( n \) is equal to 0.47 and external dimension of relaxation areas is determined by the value \( D_e = 1.94 \). In turn when \( \sigma_0 = 9 \text{ MPa} \), measure \( n \) is equal to 0.51 and this corresponds to the dimension \( D_e = 2.02 \). Consequently, dimension of relaxation areas increases with the growth of initial stress. If dimension \( D_e = 1.94 \) determines the fractal between line and surface then dimension \( D_e = 2.02 \) is related to the relaxation zones having the surface topology. It is obvious that areas with higher dimension provide deeper relaxation (see figure 4).

Depth of the relaxation depends significantly on the external environment. Figure 5 illustrates the relaxation dependences of polymethylmethacrylate (PMMA) in various environments. From these experiments we can see that environmental activity with respect to the material increases the completeness of stress relaxation like the increase of the initial stress \( \sigma_0 \) (figure 4). For PMMA environmental activity increases in the series water – kerosene – acetone – benzene. Environments – solvents (acetone and benzene) provide the most efficient relaxation related to both crack formation and release of molecular mobility.

**Figure 5.** Stress relaxation in PMMA depending on the environment: 1 – water, 2 – kerosene, 3 – acetone, 4 – benzene.

In this case coefficient \( \alpha_0 \) in equation (22) also remains constant \( (\alpha_0 = 1.8 \text{ min}^{-n}) \) and external dimension \( D_e \) of relaxation areas increases with the growth of environmental activity: water \( – D_e = 2 \); kerosene \( – D_e = 2.1 \); acetone \( – D_e = 2.46 \); benzene \( – D_e = 2.56 \). Thus for water the relaxation occurs...
along structural surfaces whereas for benzene it is provided by the fractal objects that are close to the volumetric ones.

3. Conclusions
Thus the presented theoretical and experimental studies confirm the urgency of the task – the search for new kinetic models which give a noncontradictory evaluation of the physical phenomena and reveal their nature. In order to solve this task the kinetic model developed using the concepts of the theory of topological dynamics was used which allowed giving a qualitatively new understanding of the relaxation processes.

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