Thermodynamics of the microfracture process in polymers

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A POLYMER body subjected to statically applied mechanical and thermal actions, in which microfracture process proceeds is considered. The microfracture is examined as first stage of the fracture process. The microfracture process is described with the nonlinear thermodynamics of the irreversible processes. The irreversible changes are described by aid of the internal state variables, and a special tensor of the microdamages is introduced. The microfracture is considered as a complex process comprising different interconnected processes — mechanical, thermal, diffusion, chemical.

Rozważono ciało polimerowe, w którym zachodzi proces mikrozniszczenia, poddane statycznie przyłożonym działaniom mechanicznym i termicznym. Zbadano mikrozniszczenie jako pierwszy etap procesu zniszczenia. Proces mikrozniszczenia opisano za pomocą nieliniowej termodynamiki procesów nieodwracalnych. Zmiany nieodwracalne są opisane za pomocą wewnętrznych zmiennych stanu. Wprowadzono specjalny tensor mikrozniszczenia. Mikrozniszczenie rozważa się jako złożony proces mechaniczny, termiczny i chemiczno dyfuzyjny.

Рассматривается полимерный материал в процессе микроразрушения, вызванного статически прилагаемыми механическими и тепловыми воздействиями. Микроразрушение рассматривается как первая стадия процесса разрушения и описывается в рамках нелинейной термодинамики необратимых процессов. Необратимые изменения описаны при помощи внутренних параметров состояния. Вводится специальный тензор микроповреждённости. Микроразрушение рассматривается как сложный процесс, состоящий из различных взаимно связанных явлений механического, теплового, диффузионного и химического характеров.

1. Statement of the problem

IN THIS PAPER is investigated the process of microfracture of high polymers under mechanical and thermal actions. In this process, polymers undergo structural changes as well as plastic and viscous deformations. Microfracture can be considered as a micromechanism of these deformations.

The following assumptions concerning the process of microfracture of polymers can be made on the basis of investigations of such processes, together with the results of one-dimensional experiments of fracture of specimens under constant tension:

A. The fracture process begins with rupture of the chemical bonds in the polymer molecule chains, when the energy of the thermal fluctuations of the atoms reaches a specific for each material activation bound of the chemical reaction of degradation. In general, a lower polymer is obtained in the chemical reaction and volatile gases are exuded. Atmospheric oxygen may also take part in the reaction [1, 2].

B. When the stress increases at a certain point of the polymer body, the activation energy of the fracture process decreases [1, 3].

C. When the temperature increases, the thermal motion energy increases and the beginning of the fracture process is facilitated [1, 2, 3]).

D. The fracture process under mechanical actions, the thermal degradation and the fracture under simultaneous mechanical and thermal actions have one and the same physical-chemical basis ([2, 4]).

E. Formation of a multitude of sub-microcracks, located in the volume of the polymer body in the microfracture zone, is initiated together with the beginning of the fracture process in the polymer under consideration. As soon as the external mechanical and thermal actions become sufficiently intense and a sufficient time has passed, the microcracks orientate themselves, join, and grow into magistral cracks, which comprise the total fracture of the polymer [1, 2]. This makes it possible to consider the fracture process as consisting of two stages: The first stage is the microfracture process. This begins as soon as the bound activation energy of the fracture process is reached. It is connected with the formation of sub-microcracks located in the volume, with structural changes in the polymer, with a chemical reaction of degradation, with plastic and viscous deformations, etc. As soon as the microcracks become sufficiently large, the process passes into its second stage, which is the process of growing and propagation of microcracks and their accumulation into magistral cracks. This stage leads to the total fracture of the polymer body.

The two stages of the fracture process are characterized by different mechanisms. This makes necessary their separate investigation.

F. The following temperature-time relationship is often used for describing experimental results [1, 3]:

$$(1.1) \qquad\qquad \tau = \tau_0 \exp\left\{\frac{U_0 - \gamma\sigma}{k\theta}\right\},$$

where τ is time-to-break of the specimen under constant stress σ and absolute temperature θ; τ_0 is a multiplier in front of the exponential, depending on the structure of the material; U_0 is the bound activation barrier of rupture of the chemical bonds; k is Boltzman's constant; γ is a coefficient depending on the structure defects and taking into account the influence of the intermolecular forces on the fracture process. Some authors propose the following expression for the chemical reaction rate of degradation:

$$(1.2) \qquad\qquad \frac{dC}{dt} = -A \cdot C^m \cdot \exp\left\{\frac{-Ea}{k\theta}\right\},$$

where C is the concentration of the substance degraded; A is a multiplier in front of the exponential; m is the degree of the order of the reaction. These relations show that the process of fracture of polymers proceeds in time, and that it is accompanied by irreversible structural changes in the material. The quantities describing this process are connected with nonlinear relations.

The aim of the present investigation is to describe the microfracture process in a three-dimensional case of compound stress and strain state by means of nonlinear thermodynamics of irreversible processes and the model of continuous media. Use of this model enables the application of the proposed investigation to description of the microfracture and the inelastic deformation of polymer elements of machines and structures to which the model of continuous media can be applied.

This investigation can also be used for describing chemorheological phenomena (chemical creep, chemical relaxation etc.) observed with certain kinds of spatial cross-linked polymers [1, 6]. These phenomena can be considered as fracture processes under specific conditions.

2. Macroscopic characteristics of the process

A polymer body is considered as subjected to static external mechanical and thermal actions in the time-interval (t_0, t). It is assumed that the body behaves elastically until a certain magnitude of these actions. When the magnitude of the external actions increases, at some points of the body at time t^* (which is in general different for the different points), the energetic state will reach a certain bound, corresponding to the activation energy. At these points the microfracture process will begin. Zones of microfracture, variable in time, will occur in the body.

Microfracture is a complex process comprised of different interconnected processes: kinematic process, deformation process, process of change of structure, thermal process, thermal-diffusion process, diffusion, diffusion-chemical and chemical processes.

The kinematics of the polymer body motion will be described by means of two rectangular coordinate systems: material coordinate system $\{X_K\}$, $(K = 1, 2, 3)$ for the reference configuration and spatial coordinate system $\{x_i\}$, $(i = 1, 2, 3)$ for the actual configuration of the body. At the point under consideration, during the interval $t_0 \leqslant t \leqslant t^*$, there will be one kind of particles X^I of the initial polymer (I). These particles have material coordinates $X_K^I = X_K$ and spatial coordinates $x_i^I = x_i$. At time t^* a chemical degradation reaction will begin there. In general, it can be assumed for this reaction that the initial polymer (I) reacts with the air oxygen (II) and a new polymer (III), lower in general is obtained and volatile gases (IV) are exuded. Four kinds of particles X^α, $(\alpha = I, II, III, IV)$ are obtained. They have material coordinates X_K^α and spatial coordinates x_i^α. According to the theory of reacting mixtures [7], it is assumed that these four kinds of particles occupy simultaneously one and the same place in space. Hence the law of the motion has the form:

$$(2.1) \qquad x_i = x^\alpha(X_K^\alpha, t), \quad \alpha = I, II, III, IV$$

as

$$(2.2) \qquad x_i^\beta = \begin{cases} 0, & \text{at } t_0 \leqslant t \leqslant t^*, \\ x_i, & \text{at } t > t^*, \end{cases} \quad \beta = II, III, IV.$$

It is accepted that the solid phase particles have identical law of motion at each $t > t^*$, i.e. $x_i^I = x_i^{III} = x_i(X_K, t)$ as $X_K^I = X_K^{III} = X_K$ and the inverse relation $X_K = X_K(x_i, t)$ exists.

The velocity of the particles X^α at time t is:

$$(2.3) \qquad v_i^\alpha = \left. \frac{\partial x_i^\alpha}{\partial t} \right|_{X_K^\alpha = \text{const}} = v_i^\alpha(x_i, t),$$

as

$$(2.4) \qquad v_i^I = v_i^{III} = v_i = \left. \frac{\partial x_i}{\partial t} \right|_{X_K = \text{const}}$$

The relative velocity of the particle X^α with respect to the solid phase particles is:

$$(2.5) \qquad\qquad w_i^\alpha = v_i^\alpha - v_i$$

as $w_i^I = w_i^{III} = 0$.

It is assumed that the mechanical actions are totally taken from the solid phase. The macroscopic characteristics of the deformation process are:

spatial deformation tensor $e_{ij} = \dfrac{1}{2}(\delta_{ij} - X_{K,i} X_{K,j})$,

spatial strain-rate tensor $d_{ij} = \dfrac{1}{2}(v_{i,j} + v_{j,i})$,

material deformation tensor $E_{KL} = \dfrac{1}{2}(x_{i,K} x_{i,L} - \delta_{KL})$,

material strain-rate tensor $\dot{E}_{KL}$,

Chauchy stress tensor $t_{ij} = t_{ji}$,

second Piola-Kirchhoff stress tensor $\tilde{T}_{KL} = \tilde{T}_{LK}$.

A dot above a symbol denotes material derivative with respect to time, according to the solid phase motion.

A quasi-statical mechanical process is considered for which inertial and body forces are disregarded. The equilibrium equation is:

$$(2.6) \qquad\qquad t_{ij,j} = 0.$$

The chemical process is characterized by the extent of the reaction ξ, the chemical reaction rate $\dot{\xi}$, the molecular mass M^α of the α-constituent and the stoichiometric coefficient ν^α of the α-constituent [8]. The law of definite proportions is valid. The stoichiometric equation of the chemical reaction has the form:

$$(2.7) \qquad\qquad \sum_{\alpha=I}^{IV} M^\alpha \nu^\alpha = 0.$$

The diffusion and diffusion-chemical processes are characterized by the mass-density of the αth-constituent $\varrho^\alpha = \hat{\varrho}^\alpha(x_i, t)$ as $\hat{\varrho}^\beta = 0$ for $t_0 \leqslant t \leqslant t^*$, $\hat{\varrho}^\beta \neq 0$ for $t > t^*$, ($\beta = $ = II, III, IV) and $\varrho_0^I = \varrho_0(X_K)$ at $t = t_0$.

The total mass density of the system is defined as $\varrho = \sum\limits_{\alpha=I}^{IV} \varrho^\alpha$. The solid phase density is $\varrho^* = \varrho^I + \varrho^{III}$.

Also characterizing these processes are: the chemical potential μ^α of the α-constituent, its spatial gradient $\mu_{,i}^\alpha$ and its material gradient $\mu_{,K}^\alpha = X_{K,i}\mu_{,i}^\alpha$, the diffusion flux vector $J_i^\alpha = \varrho^\alpha w_i^\alpha$ and the corresponding material vector $J_K^\alpha = \varrho_0/\varrho^* X_{K,i} J_i^\alpha$.

We consider a body exchanging mass (gaseous phase) with the surroundings and the presence of growth of mass of the αth constituent $M^\alpha \nu^\alpha \dot{\xi}$ per unit time and per unit volume as a result of the chemical reaction. The equation of the balance of mass in this case has the form:

$$(2.8) \qquad\qquad \int\limits_S \varrho^\alpha w_i^\alpha n_i \, dS + \int\limits_V \varrho^* \dot{c}^\alpha dV = 0,$$

as

$$(2.9) \qquad \int\limits_V \dot{\bar{c}}^\alpha \varrho^* dV = \left(\int\limits_V \varrho^\alpha dV\right)^{\cdot} - \int\limits_V M^\alpha v^\alpha \dot{\xi}\, dV,$$

where V is the volume of the body; S is its enclosing surface; n_i is the unit normal vector to S; $\dot{\bar{c}}^\alpha$ is the relative mass change rate of the α-constituent per unit mass solid phase. If sufficient smoothness of the integrands in (2.8) and (2.9) is assumed, and taking into account that the equations are valid for an arbitrary volume, the following local expression is obtained:

$$(2.10) \qquad \varrho^* \dot{\bar{c}}^\alpha = \dot{\varrho}^\alpha + \varrho^\alpha v_{i,i} - M^\alpha v^\alpha \dot{\xi}, \quad \dot{\bar{c}}^\alpha = -\frac{1}{\varrho^*}(\varrho^\alpha_{\_} w^\alpha_i)_{,i}.$$

The equation of the change of the mass of the system as a whole has the form:

$$(2.11) \qquad \dot{\varrho} + \varrho v_{i,i} = \varrho^* \sum_\alpha \dot{\bar{c}}^\alpha$$

and the equation of the change of the mass of the solid phase is:

$$(2.12) \qquad \dot{\varrho}^* + \varrho^* v_{i,i} = \overset{+}{\varrho}{}^*, \quad \overset{+}{\varrho}{}^* = (M^{\mathrm{I}} v^{\mathrm{I}} + M^{\mathrm{III}} v^{\mathrm{III}}) \dot{\xi}.$$

The thermal and the thermal-diffusional processes are characterized by the heat flux vector q_i, the absolute temperature θ, its spatial gradient $\theta_{,i}$ and material gradient $\theta_{,K} = X_{K,i}\theta_{,i}$, the entropy per unit mass solid phase $\bar{\eta}$, the entropy η^α of the αth constituent per unit mass α-constituent, the reduced heat flux vector $q_i^* = q_i + \theta \sum_\alpha \eta^\alpha I_i^\alpha$ and its corresponding material vector $Q_k^* = \varrho_0/\varrho^* X_{K,i} q_i^*$ [9].

The equation of the balance of entropy is:

$$(2.13) \qquad \frac{d}{dt}\left(\int\limits_V \bar{\eta}\varrho^* dV\right)\Big|_{X_K = \text{const}} = -\int\limits_S q_i^* \theta^{-1} n_i \, dS + \int\limits_V \theta^{-1}(\bar{q} + \bar{\sigma})\varrho^* dV,$$

where $\bar{q}$ is the heat supply and $\frac{1}{\theta}\bar{\sigma}$ is the dissipation energy per unit time and per unit mass solid phase. The local form of Eq. (2.13) is:

$$(2.14) \qquad \dot{\bar{\eta}}\varrho^* + \bar{\eta}\overset{+}{\varrho}{}^* = -(q_i^* \theta^{-1})_{,i} + \theta^{-1}(\bar{q} + \bar{\sigma})\varrho^*.$$

Irreversible structural changes and microdamages occur in the microfracture zone of the body. The symmetric spatial second order tensor e_{ij}^a, called microdamage tensor, is introduced as the macroscopic characteristic, by analogy with the damage tensor proposed by Ilyushin [5] for description of the fracture process. The microdamage tensor characterizes the residual strains also, and can be determined by them. Also used can be the corresponding material microdamage tensor $E_{KL}^a = x_{i,K} x_{j,L} e_{ij}^a$, together with its rate $\dot{E}_{KL}^a$.

The energy changes of the body are described by means of the following macroscopic characteristics: the internal energy $\bar{U}$ per unit mass solid phase or the functions of the free energy $\bar{\psi}$, the enthalpy $\bar{H}$ and the free enthalpy $\bar{Z}$ per unit mass solid phase uniquely related with it [7].

3. Basic equations of the problem

The thermodynamic theory with internal state variables [10] will be used for describing the behaviour of the polymer body when a microfracture process proceeds in it. The following quantities are accepted as state variables: the deformation tensor E_{KL}; the enthropy $\bar{\eta}$ per unit mass solid phase; the mass characteristics of the αth constituent $\bar{c}^\alpha$ per unit mass solid phase. The internal state variables are the microdamage tensor E_{KL}^a and the extent of the chemical reaction ξ. The internal energy $\bar{U}$ per unit mass solid phase is a function of these variables — i.e., $\bar{U} = \hat{\bar{U}}(E_{KL}, \bar{\eta}, \bar{c}^\alpha, E_{KL}^a, \xi)$. It is also convenient to use the free enthalpy $\bar{Z}$ per unit mass solid phase, connected with $\bar{U}$ by the relation:

$$(3.1) \qquad \bar{Z} = \bar{U} - 1/\varrho_0 \tilde{T}_{KL} E_{KL} - \bar{\eta}\theta - \sum_\alpha \mu^\alpha \bar{c}^\alpha$$

as

$$\bar{Z} = \hat{\bar{Z}}(\tilde{T}_{KL}, \theta, \mu^\alpha, E_{KL}^a, \xi).$$

A thermoelastic process, which is characterized by the state variables E_{KL} and $\bar{\eta}$, the internal energy $\bar{U}(E_{KL}, \bar{\eta})$ and the free enthalpy $\bar{Z}(\tilde{T}_{KL}, \theta)$, proceeds in the body outside the microfracture zones.

As indicated in Sec. 1 the microfracture process begins when the energetic state at the point considered reaches a certain bound, depending on the stress state and the absolute temperature. This gives a possibility of accepting the function $\bar{Z}(\tilde{T}_{KL}, \theta)$ as a measure of the state of energy. The condition for beginning the process is now $\bar{Z} = \bar{Z}_0$, where $\bar{Z}_0$ is a limit value, experimentally determined. This condition divides the body into two types of zones: zone for which $\bar{Z} < \bar{Z}_0$, where a thermoelastic process proceeds, and a zone for which $\bar{Z} > \bar{Z}_0$, where a microfracture process proceeds. The microfracture process passes into the second stage of fractures, when the microcracks grow sufficiently large. This transition condition has the form:

$$\max\{E_A^a\} = E_0,$$

where E_A^a, $(A = 1, 2, 3)$ are the principle values of the tensor E_{KL}^a, and E_0 is a limit value, experimentally determined.

The equations of evolution for the internal state variables are necessary for description of the microfracture process. These equations must be determined by means of experiments in conditions of complex stress and strain state. The one-dimensional experiments, mentioned in Sec. 1, may yield certain information concerning their character. We can accept the following general form of these equations:

$$(3.2) \qquad \dot{E}_{KL}^a = \langle \Phi(\mathscr{F}) \rangle H_{KL}(\tilde{T}_{KL}, \theta, \mu^\alpha, E_{KL}^a, \xi),$$

$$\dot{\xi} = \langle \Phi(\mathscr{F}) \rangle \varphi(\tilde{T}_{KL}, \theta, \mu^\alpha, E_{KL}^a, \xi),$$

as

$$\langle \Phi(\mathscr{F}) \rangle = \begin{cases} \Phi(\mathscr{F}) & \text{at} \quad \mathscr{F} = \bar{Z} - \bar{Z}_0 > 0, \\ 0 & \text{at} \quad \mathscr{F} \leqq 0, \end{cases}$$

where the functions Φ, φ and the tensor $H_{KL} = H_{LK}$ are experimentally determined. The methods described in [11] could be used for this purpose. For the most part, the function Φ is an exponential one (see Sec. 1). Equations $(3.2)_1$ are similar to the equations of the visco-plastic strain rates of metals [10, 12]. This is due to the nature of E^a_{KL} when polymers are considered; it is a visco-plastic deformation by its nature. The reason for the resemblance is the similar manner in which the micromechanisms of visco-plastic flow of metals and of polymers are connected with the activation energy of the corresponding process [10].

It is seen from (3.2) that both velocities are interrelated by the relation $E^a_{KL} = \dfrac{1}{\varphi} H_{KL}\dot{\xi}$; this is due to the interconnection of the plastic deformation process and the chemical degradation reaction. The equations of the reduced heat flux and flux of diffusion should be determined on the basis of a special investigation of the thermal-diffusional and the diffusion-chemical processes. According to the principle of objectivity [7], they can in general be written as follows:

(3.3)
$$Q^*_M = \psi_M(\tilde{T}_{KL}, \theta, \theta_{,K}, \mu^\alpha, \mu^\alpha_{,K}, E^a_{KL}, \xi),$$
$$J^\alpha_M = F^\alpha_M(\tilde{T}_{KL}, \theta, \theta_{,K}, \mu^\alpha, \mu^\alpha_{,K}, E^\alpha_{KL}, \xi).$$

When both the kinetic energy due to the quasi-static character of the process and the body forces are disregarded, the balance of the energy changes is:

(3.4) $$\frac{d}{dt}\left(\int_V \bar{U}\varrho^* dV\right)\bigg|_{X_K=\text{const}} = -\int_S q^*_i n_i dS + \int_V \bar{q}\varrho^* dV + \int_S t_{ij} n_j v_i dS - \sum_\alpha \int_S \mu^\alpha I^\alpha_i n_i dS$$

or in local form

(3.5) $$\dot{\bar{U}}\varrho^* + \bar{U}\dot{\varrho}^* = -\theta(q^*_i\theta^{-1})_{,i} + \bar{q}\varrho^* + t_{ij}d_{ij} + \sum_\alpha \mu^\alpha \varrho^* \dot{\bar{c}}^\alpha - \theta_{,i}q^*_i\theta^{-1} - \sum_\alpha \mu^\alpha_{,i} I^\alpha_i.$$

By using the Eqs. (2.10). (2.14), (3.1) and (3.5), after some rearrangement, we obtain:

(3.6) $$\varrho^*\bar{\sigma} = -\varrho^*\left(\frac{1}{\varrho_0}E_{KL} + \partial_{\tilde{T}_{KL}}\bar{Z}\right)\dot{\tilde{T}}_{KL} - \varrho^*(\bar{\eta} + \partial_\theta\bar{Z})\dot{\theta} - \sum_\alpha (\varrho^*\partial_{\mu^\alpha}\bar{Z} + \bar{c}^\alpha)\dot{\mu}^\alpha$$
$$-\bar{\psi}\dot{\varrho}^* - \theta_{,i}q^*_i\theta^{-1} - \sum_\alpha \mu^\alpha_{,i} I^\alpha_i - \varrho^*\partial_{E^a_{KL}}\bar{Z}\dot{E}^a_{KL} - \varrho^*\partial_\xi\bar{Z}\dot{\xi}.$$

The following relations are used in (3.6):

(3.7) $$\frac{1}{\varrho^*}t_{ij}d_{ij} = \frac{1}{\varrho_0}\tilde{T}_{KL}\dot{E}_{KL}, \quad \bar{\psi} = \bar{U} - \theta\bar{\eta}.$$

According to the second principle of thermodynamics, we can assume that $\varrho^*\bar{\sigma} \geqq 0$. If we take into account that $\dot{\tilde{T}}_{KL}$, $\dot{\theta}$ and $\dot{\mu}^\alpha$ can be varied independently, the following system of constitutive equations is obtained:

(3.8)
at $\bar{Z} > \bar{Z}_0$
$$\begin{cases} E_{KL} = -\varrho_0\partial_{\tilde{T}_{KL}}\bar{Z}(\tilde{T}_{KL}, \theta, \mu^\alpha, E^a_{KL}, \xi), \\ \bar{\eta} = -\partial_\theta\bar{Z}(...), \qquad\qquad\qquad (a) \\ \bar{c}^\alpha = -\varrho^*\partial_{\mu^\alpha}\bar{Z}(...), \end{cases}$$

at $\overline{Z} \leqq \overline{Z}_0$ $E_{KL} = -\varrho_0 \partial_{\tilde{T}_{KL}} \overline{Z}(\dot{T}_{KL}, \theta),$

$$\overline{\eta} = -\partial_\theta \overline{Z}(\ldots),$$ (b)

when

(3.9) $\varrho^* \partial_\xi \overline{Z}\dot{\xi} + \varrho^* \partial_{E_{KL}^a} \overline{Z}\dot{E}_{KL}^a + \theta_{,i} q_i^* \theta^{-1} + \sum_\alpha \mu_{,i}^\alpha I_i^\alpha + \overline{\psi}\dot{\varrho}^* \leqq 0$ (a),

or $\theta_{,i} q_i \theta^{-1} \leqq 0$ (b).

The system of constitutive equations takes into account the thermodynamical principles. It is seen from (3.9a) that the dissipative effects are due to: the internal chemical reaction (the first term), the internal structural changes and damages (the second term), the heat transfer and the thermodiffusion (the third term), the diffusion (the fourth term), and the open thermodynamic system (the fifth term).

Equations (2.6), (2.10), (2.12), (2.14), (3.2), (3.3) and (3.8a) form the complete system of equations describing the microfracture process, considered as an irreversible thermodynamic process. The substitution of (3.2), (3.3) and (3.8) into (2.14) leads to the equation for determination of temperature. The substitution of the same three equations into (2.10) leads to the equation for determination of the chemical potential.

When one-dimensional experiments with thin specimens are considered, the diffusion effects of which can be neglected, the microfracture process can be described by means of the following constitutive equations, obtained from (3.8) after some rearrangements:

(3.10) $$\dot{\varepsilon} = H\dot{\sigma} + N\dot{\theta} + G\dot{\xi} + M\dot{\varepsilon}^a$$

as

$$H = -\varrho_0 \partial_\sigma(\partial_\sigma \overline{Z}), \quad N = -\varrho_0 \partial_\theta(\partial_\sigma \overline{Z}), \quad G = -\varrho_0 \partial_\xi(\partial_\sigma \overline{Z}), \quad M = -\varrho_0 \partial_{\varepsilon a}(\partial_\sigma \overline{Z}).$$

It is seen from (3.10) that the strain rate consists of an instantaneous elastic part $H\dot{\sigma}$, an instantaneous thermal part $N\dot{\theta}$, an instantaneous mechanical part $G\dot{\xi}$ and an inelastic part $M\dot{\varepsilon}^a$. In the case of creep $\dot{\sigma} = 0$ and constant temperature $\dot{\theta} = 0$ Eqs. (3.2) and (3.10) lead to:

(3.11) $$\dot{\varepsilon} = \hat{\dot{\varepsilon}}\langle \Phi(\mathscr{F})\rangle.$$

Equation (3.11) describes the creep of the deformation as a result of the chemical reaction of degradation and the structural changes in the polymer. It is seen that the system of equations obtained in the present paper can describe also chemorheological phenomena in polymers.

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