Mechanical model of damage and fracture of aging polymer materials

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Abstract

Polymers and polymer-based materials are used in many applications in medicine and industry. These applications frequently have a very high performance demand, which makes their long-term aging characteristics of paramount importance. At the same time they are subjected to degradation due to environmental factors, including light, temperature, stress, and others. During the aging the degradation of polymers lead to changes in the physical and mechanical properties. As a result of degradation the material may become less deformable and brittle. These effects are studied in long-term tests of specimens made of polyurethane in tension, compression, cyclic loading, climatic and strain aging, as well as in experiments carried out on the rubber samples in tension and climatic aging at room temperature. In all experiments a significant effect of hardening and embrittlement of materials during long-term aging is observed. The obtained results allow us to formulate the interconnected kinetic equations for the creep rate and damage parameter. These equations are written in the scale of real and effective time. The analytical relations for creep, damage parameter and the criteria of long-term strength are obtained. Corresponding theoretical curves are constructed and their qualitative agreement with the experimental curves is shown.

1 Introduction.

Polymers were introduced in many fields of modern industry as structural materials because they were relatively cheap and easy to manufacture compared with commonly known materials such as metals and wood. Today polymers and polymer-based materials are used in many applications in medicine and industry, including electronic and optical production. These applications frequently have a very high performance demand, which makes their long-term aging characteristics of paramount importance. At the same time they are subjected to degradation due to environmental factors, including light, temperature, stress, pollutants and others. During the aging the degradation of polymers lead to changes of their physical and mechanical properties. As a result of degradation the material may become less deformable and brittle. To predict these behaviors and useful lifetimes the aging of polymers to weathering is usually studied. However, the problem of deformation

aging is not considered sufficiently in literature. In this paper an effective time is introduced and a mechanical model (modified Maxwell model) for description of deformation aging behavior of polymer materials is presented. The relaxation time is considered as a measure of the aging process and the parameters of the model are defined to describe the experimental creep curves for aged and unaged polymer materials.

The most important results of polymer aging are obtained for the case of outdoor exposition [1-4], which often called weathering or UV-degradation. UV radiation can initiate chemical reactions, which may lead to breaking of the chemical bonds in the polymer chains. UV-radiation together with oxygen can lead to photo oxidation reactions. For example, in polyethylene products used outdoors, photo oxidation is a principal degradation process. Chain breaking and cross-linking will change the structure of polymers and finally may cause embrittlement (the strain decrease at failure). The increase in Young's modulus with exposure time is attributed to the uptake of oxygen, the change in the number of tie-molecules, the increase in crystallinity and the increase in density. The free volume concept can be applied to explain the aging phenomena. It states that the transport mobility of particles in a closely packed system primarily depends on the degree of packing, in other terms, on the free volume. With increasing degree of packing, this mobility decreases, at first slowly, but later on at an ever increasing rate. Since the relaxation time of polymers is directly related to the mobility and free volume, the mechanical parameters (elastic modulus and viscosity coefficient) also will be influenced by way of changing in the relaxation time. The other conclusion is that the viscosity coefficient changes essential relative to the elastic modulus. It happens because of the strong structural dependence of viscosity coefficient. In contrast the value of elastic modulus is in a very week dependence of the material structure.

As it was mentioned above, the deformation aging of polymers is not studied well. However it is known that, the processing methods (like injection molding or extrusion) can have an effect on the degradation and aging behavior. Some aspects of deformation aging were considered in [5]. It was determined that the deformation may promote the acceleration of aging process and, the additional increase in elastic modulus.

2 Modified Maxwell model for description of deformation aging of polymer materials.

To describe the process of deformation the aging parameter α is introduced [6]

$$d\alpha = f_1(\alpha, \varepsilon, T, t)dt + f_2(\alpha, \varepsilon, T, t)d\varepsilon, \tag{1}$$

where ε is the value of deformation, t is the real time, T is temperature.

Parameter α will be considered as an effective time, which is capable to describe the aging (deformation and quench). According to relation (1) in the instantaneous active loading this parameter can be considered as 'deformation time' ε. In unloading state $d\varepsilon = 0$ and α reduces to the real time t. We may call it as the 'chemical time'. For the Maxwell equation we will receive the following modified relation

$$\frac{d\varepsilon}{d\alpha} = \frac{d}{d\alpha}\left[\frac{\sigma}{E(\alpha)}\right] + \frac{\sigma}{\eta(\alpha)}. \tag{2}$$

Further we will consider the simple version of elastic viscous model (2) expressed in scale of effective time (1)

$$\frac{d\varepsilon}{d\alpha} = \frac{1}{E}\frac{d\sigma}{d\alpha} + \frac{\sigma}{\eta}, \tag{3}$$

$$d\alpha = k(\alpha_\infty - \alpha)t^m dt, \tag{4}$$

where E, η, k, α_∞, n are constants, α is a parameter of material degradation ($\alpha = N/N_0$, N_0 are the initial numbers of chemical bonds, N are the current numbers of fractured chemical bonds). So the equation (4) can be considered as an equation of chemical reaction and parameter α has a meaning of chemical time. With the initial conditions $t = 0$, $\alpha = \alpha_0$, $\varepsilon = \sigma_0/E_0$, the solution of the system (3)-(4) can be written in the form

$$\varepsilon = \frac{\sigma_0}{E_0}\left[1 + \frac{\alpha_\infty - \alpha_0}{\tau}\left(1 - \exp\left(-\frac{k}{m+1}t^{m+1}\right)\right)\right]. \tag{5}$$

The theoretical creep (compliance) curves (5) for the following coefficients: $\alpha_0 = 0$, $\alpha_\infty = 1$, $n = 0$, $k = 0,021\ s^{-1}$, relaxation times and modulus of elasticity $\tau_1 = 1\ s$, $E_0 = 25\ MPa$ (curve 1) and $\tau_2 = 1\ s$, $E_0 = 30\ MPa$ (curve 2) are shown on Fig. 1. The experimental results are marked by cross and circle points. The theoretical curves in this figure are in good agreement with the results of creep aging experiments [7] for the polyethylene films. Upper curve was received in experiments with unaged specimens; lower curve was received in experiments with aged specimens. The specimens were aged seven days at temperature $373°K$.

3 The long-term strength criterion of polymer materials based on damage parameter.

For the formulation of long-term strength criterion in addition to the equations (3)-(4) we will consider the damage (continuity) parameter ψ [6, 8] which is determined by the following kinetic equation

$$\psi^a \frac{d\psi}{dt} = -A\sigma^n. \tag{6}$$

Taking into account the mass conservation law $\rho_0 l_0 F_0 = \rho l F$, from which follows the relation $\sigma = \sigma_0 \psi e^\varepsilon$, equation (6) can be written in the form

$$\psi^\alpha \frac{d\psi}{dt} = -A\sigma_0^n \psi^n e^{n\varepsilon}. \tag{7}$$

where a, A, n are constants, $\psi = \rho/\rho_0$ ($1 \geq \psi \geq 0$, ρ_0 is initial, ρ is current density). We have considered several variants of the approximate solution of equation (7). The simplest solution, describing qualitatively the experimental curves of damage, can be obtained by taking the following approximations

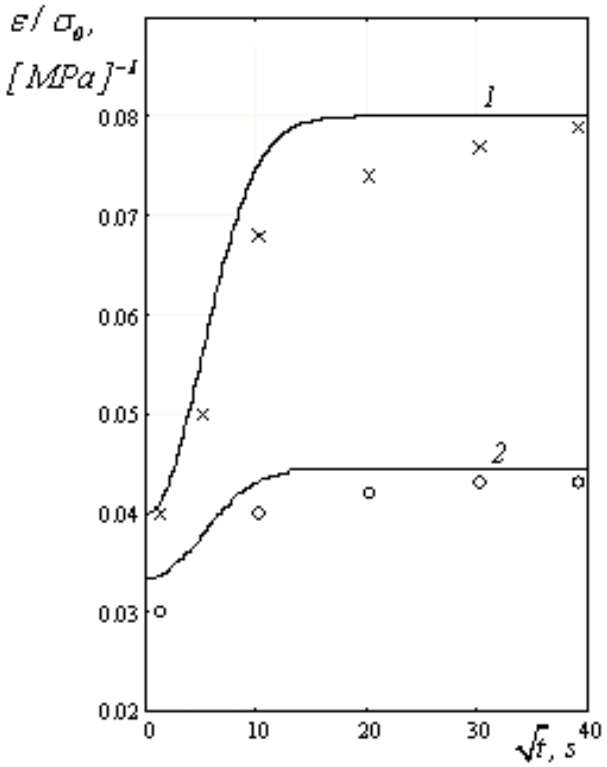

Figure 1: The theoretical creep curves according relation (5): $\tau_1 = 1\ s$, $E_0 = 25\ MPa$ (curve 1) and $\tau_2 = 1\ s$, $E_0 = 30\ MPa$ (curve 2).

$$\varepsilon = \frac{\sigma_0}{E_0}\left[1 + \frac{(\alpha_\infty - \alpha_0)k}{\tau(m+1)}t^{m+1}\right], \tag{8}$$

$$\psi^\alpha \frac{d\psi}{dt} = -A\sigma_0^n \psi^n (1 + n\varepsilon). \tag{9}$$

Introducing the relation (8) into equation (9) and solving it with the initial conditions $t = 0$, $\psi = 1$, we will receive the following relation

$$\psi = \left[1 - (a - n + 1)A\sigma_0^n \left(\frac{n\sigma_0(\alpha_\infty - \alpha_0)k}{E_0\tau(m+1)(m+2)}t^{m+2} + \left(\frac{n\sigma_0}{E_0} + 1\right)t\right)\right]^{\frac{1}{a-n+1}}. \tag{10}$$

In Fig. 2 are shown the curves for the continuity parameter according to equation (10) for different values of constants ($\alpha = 6$ - curve 1, $\alpha = 4$ - curve 2 and $\alpha = 2$ - curve 3), which are in agreement with the corresponding experimental curves. In the calculations the following values of coefficients were used: $n = 0$, $A = 10^{-7}\ [MPa]^{-2}$, $\sigma_0 = 60\ MPa$, $\alpha_0 = 0$, $\alpha_\infty = 1$, $m = 0$, $k = 0,021\ s^{-1}$, $\tau = 1\ s$, $E_0 = 2000\ MPa$. Taking the fracture condition $t = t_f$, $\psi = 0$ and for $m = 0$ from (10) we obtain the creep fracture criterion

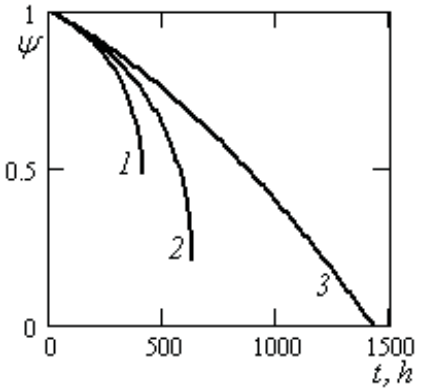

Figure 2: The curves for the parameter of continuity ψ according to the formula (10) for different values of constants: $\alpha = 6$ - curve 1, $\alpha = 4$ - curve 2 and $\alpha = 2$ - curve 3.

$$t_f = \frac{E_0\tau}{n\sigma_0(\alpha_\infty - \alpha_0)k}\left[-\left(\frac{n\sigma_0}{E_0}+1\right)+\left(\left(\frac{n\sigma_0}{E_0}+1\right)^2+\frac{n(\alpha_\infty-\alpha_0)k}{E_0\tau(a-n+1)A\sigma_0^{n-1}}\right)^{\frac{1}{2}}\right]. \tag{11}$$

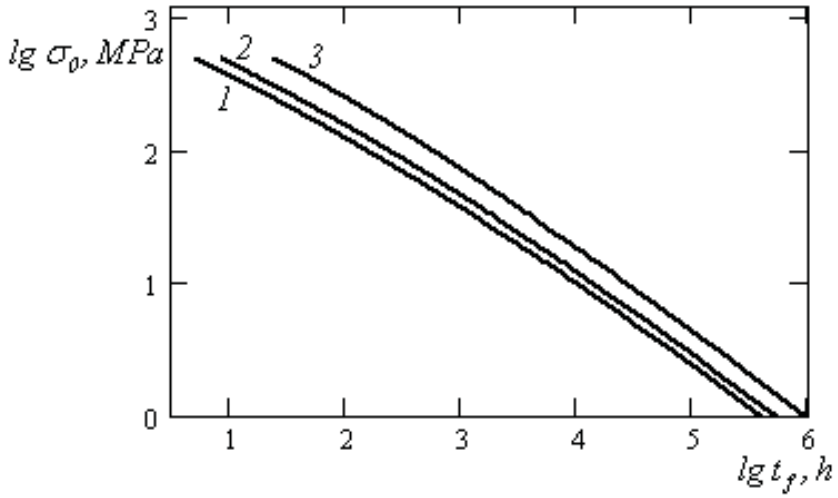

Figure 3: The long-term strength curves under criterion (11) for different values of constants: $\alpha = 6$ - curve 1, $\alpha = 4$ - curve 2 and $\alpha = 2$ - curve 3.

In Fig. 3 in the double logarithmic coordinates are shown the creep fracture curves according to the formula (11) for different values of the coefficients ($\alpha = 6$ - curve 1, $\alpha = 4$ - curve 2 and $\alpha = 2$ - curve 3). In the calculations the following values of coefficients were used: $n = 0$, $A = 10^{-7}$ $[MPa]^{-2}$, $\alpha_0 = 0$, $\alpha_\infty = 1$, $m = 0$, $k = 0,021$ s^{-1}, $\tau = 1$ s, $E_0 = 2000$ MPa.

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