Constructing a transformation curve of the age resistance coefficient

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Abstract. One of the possible approaches to the analysis of the materials’ age resistance coefficient dependence physical mechanism is proposed. The material’s durability at constant voltage is described using the Zhurkov equation and at alternating voltage it is described using the Bailey criterion. Under the action of small deformations on the material, its structure is ordered, which is expressed in a decrease the structurally sensitive coefficient value in the Zhurkov equation. This leads to an increase in durability by 20%. The resistance coefficient dependence is of an extreme character and can be maximum observed at the time to failure \( \lg t_p \approx 2 \) (sec).

Introduction

The materials resistance coefficient is defined as the strength current value ratio to its initial value. The resistance coefficient is often used to assess the durability of the material and to predict the duration of its operation under given conditions. The physical meaning analysis of the factors determining the rate of the material’s aging is of great importance, as well as the rate of the structure restoration over time, which can occur simultaneously with aging. Let us consider one of the possible reasons for the peculiar course of the transformation kinetic curve in the age resistance coefficient, which is associated with the strength of polymers. In turn, the strength of the polymer is associated with its durability \( \tau \), which, in accordance with the thermo-fluctuation concept of the fracture mechanism, justified by S.N. Zhurkov, can be determined by the ratio

\[
\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{RT}}
\]  

(1)

where \( \tau_0 \) is the pre-exponential factor; \( U_0 \) is the initial activation energy of the destruction process; \( \gamma \) defines the material parameter called a structurally sensitive parameter; \( \sigma \) is constant pressure; \( T \) denotes the absolute temperature; \( R \) is a universal gas constant.

The Zhurkov equation is described in detail in monographs [1-6].

Main part

To describe durability let us apply \( t_p \) Bailey criterion, which is valid in case voltage \( \sigma \) is not permanent:

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Main part

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where \( t_b \) denotes the time elapsed from the moment the load is applied to the sample until it breaks; \( \tau[\sigma(t)] \) is the durability described by the equation (1) at a constant voltage equal to the instantaneous value \( \sigma(t) \).

In this case, the voltage \( \sigma(t) \) may vary in time according to any law. Using the criterion (2), it is possible to calculate the lifetime of a sample when the function is known \( \sigma(t) \), and also, if the equation parameters (1) are known. When calculating \( t_b \) using the equation (2), it is necessary that these parameters do not change during the sample’s loading. The temperature should also be constant. Actually, during the loading process, the structure and temperature of the sample can change (which causes a change in the structurally sensitive parameter \( \gamma \)). Even if the ambient temperature is kept strictly constant under cyclic influences on the sample, its heating can occur. Then, using the Bailey criterion, we get the inflated values of durability \( t_b \), since we will substitute the temperature lower than that which is actually present in the sample.

In the general case, the Bailey criterion for alternating voltages, temperature, and a structurally sensitive parameter should be written as follows:

\[
\int_0^{t_b} \frac{dt}{\tau[\sigma(t); T(t); \gamma(t)]} = 1, \tag{3}
\]

where \( \tau[\sigma(t); T(t); \gamma(t)] \) define the durability described by the equation (1) at a constant voltage equal to the instantaneous value \( \sigma(t) \); constant temperature equal to instantaneous value \( T(t) \); unchanged material structure, which corresponds to the instantaneous value of the structurally sensitive parameter, equal to \( \gamma(t) \).

If the voltage \( \sigma \) and temperature \( T \) in time are constant, and only the structurally sensitive parameter changes \( \gamma \), then the Bailey criterion is written as

\[
\int_0^{t_b} \frac{dt}{\tau[\sigma(t); T(t); \gamma(t)]} = 1. \tag{4}
\]

We assume that the structurally sensitive parameter as a result of the constant voltage action on the sample and the deformation arising from this, decreases linearly within time

\[
\gamma = \gamma_0 - at, \tag{5}
\]

where \( \gamma_0 \) is the initial structurally sensitive parameter, \( a \) is the decrease rate in the structurally sensitive parameter over time as a result of improving the material structure.

Then the equation (1) can be written as:

\[
\tau = \tau_0 e^{-\frac{U_0-(\gamma_0-at)\sigma}{RT}}. \tag{6}
\]

The Bailey criterion has the form:

\[
\int_0^{t_b} \frac{dt}{\tau_0 e^{-\frac{U_0-(\gamma_0-at)\sigma}{RT}}} = 1. \tag{7}
\]

The solution of this integral equation leads to the following relation:
\[
\frac{1}{\tau_0} \cdot \frac{1}{e^{\frac{U_0 - \gamma \sigma}{RT}}} \cdot \left(\frac{-at \sigma}{e^{\frac{-at \sigma}{RT}}} - 1\right) = 1.
\] (8)

It follows from the relation (8) that the time to failure \( t_b \) at constant voltage \( \sigma \) is equal to:

\[
t_b = -\frac{RT}{a \sigma} \ln \left(1 - \frac{\tau_0 \cdot e^{\frac{U_0 - \gamma \sigma}{RT}}}{a \sigma}\right).
\] (9)

We choose the following typical values of the equation parameters (9), the characteristic of many polymers: \( \sigma = 30 \text{ MPa}, U_0 = 150 \text{ kJ/mol}, T = 293 \text{ K}, a = 1.7 \cdot 10^{-8} \text{ sec}^{-1}, \gamma_0 = 1.6 \text{ kJ/mol \cdot MPa}. \) Constant \( R = 8.314 \text{ J/mol \cdot K}, \) constant \( \tau_0 = 10^{-12} \text{ sec}. \)

With these parameters, the expression (9) has the form:

\[
t_b \text{ (sec)} = -4776471 \ln \left(1 - 20.9 \cdot 10^{-20} \cdot 1.57 \cdot 10^{18}\right).
\] (10)

If we want to express \( t_b \) after a number of years then

\[
t_b \text{ (years)} = -0.151 \ln \left(1 - 20.9 \cdot 10^{-20} \cdot 1.57 \cdot 10^{18}\right).
\] (11)

We calculate how the dependency will look \( \sigma \) from \( t_b. \)

**Table 1.** Durability \( t_b \) at a decline rate in the structural sensitive parameter \( a = 1.7 \cdot 10^{-8} \text{ sec}^{-1}.\)

| \( \sigma, \text{MPa} \) | \( t_b, \text{sec} \) | \( \lg t_b \) | \( \sigma / \sigma_0 \) | \( \sigma / \sigma_0 \) | \( \sigma / \sigma_0 \) | \( \sigma / \sigma_0 \) |
|-----------------|-----------------|-------------|-----------------|-----------------|-----------------|-----------------|
| 29              | 4605176         | 6.663       | 0.879           | 0.805           | 0.744           | 0.690           |
| 30              | 1903576         | 6.279       | 0.909           | 0.833           | 0.769           | 0.714           |
| 31              | 895390          | 5.952       | 0.939           | 0.861           | 0.795           | 0.738           |
| 32              | 442132          | 5.645       | 0.967           | 0.889           | 0.820           | 0.762           |
| 33              | 224715          | 5.352       | 1               | 0.917           | 0.846           | 0.786           |
| \textbf{36}     | \textbf{30516}  | \textbf{4.484} | 1               | 0.923           | 0.857           |                 |
| \textbf{39}     | \textbf{4212}   | \textbf{3.624} | 1               | 0.929           |                 |                 |
| \textbf{42}     | \textbf{590}    | \textbf{2.771} |                 |                 |                 |                 |

The data in Table 1 describe the descending branch of the dependence curve \( \sigma / \sigma_0 \) from \( \log t_b. \) To describe the ascending branch of such a curve, we use the original equation (1). According to this equation, the voltage dependence \( \sigma \) from durability \( \tau \) can be described by the relation:

\[
\sigma = \frac{U_0 - 2.3RT (\lg \tau - \lg \tau_0)}{\gamma}.
\] (12)

**Table 2.** The stress values \( \sigma \), leading to different values of durability \( \tau = t_b.\)

| \( \sigma, \text{MPa} \) | \( t_b, \text{sec} \) | \( \lg t_b \) | \( \sigma / \sigma_0 \) |
|-----------------|-----------------|-------------|-----------------|
| 38              | 363659949       | 8.561       | 0.848           |
| 39              | 3039574         | 6.483       | 0.879           |
| 40              | 1745901         | 6.242       | 0.909           |
| 41              | 859319          | 5.934       | 0.939           |
| 42              | 433079          | 5.637       | 0.970           |
| 43              | 222301          | 5.347       | 1               |
Figure 1 shows the dependencies $\sigma_t/\sigma_0$ from $\log t_b$, obtained at different initial voltages $\sigma_0$ from 33 till 42 MPa.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Dependencies $\sigma_t/\sigma_0$ from $\log t_b$ at different initial voltages: 33 MPa (1), 36 (2), 39 (3) and 42 MPa (4). Time $t_b$ is expressed in sec

It is seen that the larger the initial voltage $\sigma_0$, the smaller $\sigma_t/\sigma_0$ is the transition from increasing to falling branches of the curve. Thus, the proposed mechanism for the peculiar course of the kinetic transformation curve in the age resistance coefficient, associated with a decrease in the structurally sensitive coefficient in the durability equation, allows us to adequately describe the analyzed curve, which is similar to the Weller curve.

Now we will change the speed $a$ decrease in the structurally sensitive parameter in time. We take the value $a = 1.0 \cdot 10^{-8} \text{sec}^{-1}$. The time to failure at different constant voltages is shown in Table 3.

**Table 3.** Durability $t_b$ at descent rate structurally sensitive parameter $a = 1.0 \cdot 10^{-8} \text{sec}^{-1}$.

| $\sigma$, MPa | $t_b$, sec | $\lg t_b$ | $\sigma_t/\sigma_0$ |
|---------------|------------|-----------|-------------------|
| 28            | 9708842    | 6.987     | 0.848             |
| 29            | 3039574    | 6.483     | 0.879             |
| 30            | 1745901    | 6.242     | 0.909             |
| 31            | 859319     | 5.934     | 0.939             |
| 32            | 433079     | 5.637     | 0.970             |
| **33**        | **222301** | **5.347** | **1**             |

Now let us take an even smaller value $a = 0.5 \cdot 10^{-8} \text{sec}^{-1}$. Then we obtain the following values of quantities $t_b$, sec, $\lg t_b$ and $\sigma_t/\sigma_0$ (Table 4).

**Table 4.** Durability $t_b$ at descent rate structurally sensitive parameter $a = 0.5 \cdot 10^{-8} \text{sec}^{-1}$.

| $\sigma$, MPa | $t_b$, sec | $\lg t_b$ | $\sigma_t/\sigma_0$ |
|---------------|------------|-----------|-------------------|
| 27            | 17705141   | 7.248     | 0.844             |
From Tables 3 and 4 it follows that the dependencies $\ln t_b$ from $\sigma_t/\sigma_0$ at equal values $\sigma$ do not differ greatly.

Finally, we analyze the dependence $\sigma_t/\sigma_0$ from $\ln t_b$ at different values of the initial activation energy $U_0$.

The results of the calculations carried out by the formula (9) are presented in Table 5.

**Table 5. Durability $t_b$ at various values of the initial activation energy of the destruction process $U_0$.**

| $U_0$, kJ / mole | $\sigma$, MPa | $t_b$, sec | $\ln t_b$ | $\sigma_t/\sigma_0$ |
|------------------|---------------|------------|------------|------------------|
| 150              | 30            | 1903576    | 6.279      | 0.545            |
| 155              | 35            | 485719     | 5.686      | 0.636            |
| 160              | 40            | 135534     | 5.132      | 0.727            |
| 165              | 45            | 39190      | 4.593      | 0.818            |
| 170              | 50            | 1869       | 2.272      | 0.909            |
| 175              | 55            | 6.990      | 0.844      | 1.0              |

It can be seen that an increase in the initial activation energy leads to a rapid increase in the ratio $\sigma_t/\sigma_0$. This is due to the fact that stresses $\sigma$ also increase. Figure 2 shows the relationship $\sigma_t/\sigma_0$ from $\ln t_b$.

**Figure 2.** Dependence $\sigma_t/\sigma_0$ from $\ln t_b$ at different values of the initial activation energy and voltage. Time $t$ is expressed in sec.

This curve characterizes the descending branch of the resistance coefficient dependence on durability.

**Summary**
The proposed procedure for constructing a transformation curve of the age resistance coefficient allows us to evaluate the physical nature of such a change. The resistance coefficient is associated with improving the structure of the material during deformation, which leads to a decrease in the structurally sensitive parameter in the durability equation. Of course, this is not the only reason for the formation of the dependence curve $k$ from $t$ with a maximum that is similar in appearance to the Weller curve. Further work in this direction involves taking into account the relaxation processes [7–10] (creep and stress relaxation) that occur during polymer deformation under load.

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