



TIME DEPENDENCES OF THE RESISTANCE COEFFICIENTS OF POLYMERIC MATERIALS

A. V. Matseevich and A. A. Askadskii*

Cite this: *INEOS OPEN*,
2020, 3 (4), 146–149
DOI: 10.32931/io2016a

*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia*

Received 11 June 2020,
Accepted 27 July 2020

<http://ineosopen.org>

Abstract

One of the possible approaches to the analysis of a physical mechanism of time dependence for the resistance coefficients of materials is suggested. The material durability at the constant stress is described using the Zhurkov and Gul' equations and the durability at the alternating stress—using the Bailey criterion. The low strains lead to structuring of a material that is reflected in a reduction of the structure-sensitive coefficient in these equations. This affords 20% increase in the durability. The dependence of the resistance coefficient assumes an extremal character; the maximum is observed at the time to rupture $\lg t_r \approx 2$ (s).

Key words: durability of materials, stress, time to rupture, structure-sensitive coefficient.

Introduction

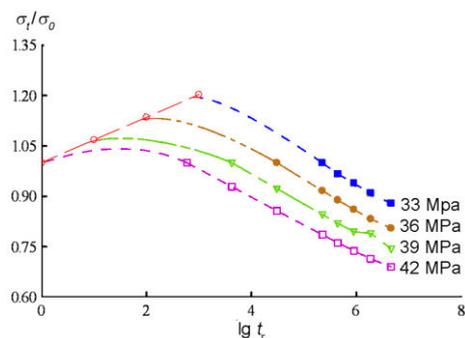
The resistance coefficient of a material is defined as a ratio of the current strength to its initial value. The resistance coefficient is often used to evaluate the material durability and predict the service life under certain conditions. Of particular importance is the analysis of a physical meaning of the factors that define the rate of material aging as well as the rate of structure recovery in time, which can occur simultaneously with aging. Let us consider one of the possible reasons for a peculiar shape of a kinetic curve for the time dependence of the resistance coefficient that is connected with the polymer strength. In turn, the polymer strength is connected with its durability τ , which, according to the thermofluctuation concept of the rupture mechanism rationalized by S. N. Zhurkov, is determined by the following relation:

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{RT}} \quad (1)$$

where τ_0 is the preexponential factor, U_0 is the initial activation energy of rupture, γ is the so-called structure-sensitive parameter of a material, σ is the constant stress, T is the absolute temperature, and R is the universal gas constant.

The Zhurkov equation was discussed in detail in several monographs [1–6].

The time dependence of the resistance coefficients of polymeric materials was studied in a multitude of reports which are summarized in the following monographs [1, 3, 4, 7, 8]. These works analyzed the dependence of durability on stress rather than the resistance coefficient itself. The stress growth always afforded a reduction in the durability. The question about an increase of the durability with strain and stress growth was



not raised and studied in these reports. The investigations were concerned with cellulose, polyamide, and a range of other fibers.

Calculations

Let us describe the durability t_r using the Bailey criterion which is valid in the case when the stress σ is not constant:

$$\int_0^{t_r} \frac{dt}{\tau[\sigma(t)]} = 1 \quad (2)$$

where t_r is the time from loading to sample rupture, $\tau[\sigma(t)]$ is the durability described by equation (1) at the constant stress equal to the instantaneous value $\sigma(t)$.

The stress $\sigma(t)$ can change in time according to any law. Using criterion (2), one can calculate the sample life span when the function $\sigma(t)$ and parameters of equation (1) are known. For the calculation of t_r using equation (2), these parameters must remain unchanged during the sample loading. The temperature must also be constant. Actually, the sample loading can change its structure (which changes the structure-sensitive parameter γ) and temperature. Even if the ambient temperature is maintained strictly constant, the cyclic impacts on the sample can lead to its heating. Then, the application of the Bailey criterion can afford overestimated values of the durability t_r , since we would plug the lower temperature than the real temperature of the sample.

In general, the Bailey criterion at the alternating stress, temperature and structure-sensitive parameter should be written in the following form:

$$\int_0^{t_r} \frac{dt}{\tau[\sigma(t); T(t); \gamma(t)]} = 1 \quad (3)$$

where $\tau[\sigma(t); T(t); \gamma(t)]$ is the durability described by equation (1) at the constant stress equal to the instantaneous value $\sigma(t)$, at the constant temperature equal to the instantaneous value $T(t)$, and corresponding to the unchanged material structure which is defined by the instantaneous value of the structure-sensitive parameter $\gamma(t)$.

If the stress σ and temperature T are constant in time, and only the structure-sensitive parameter γ changes, then the Bailey criterion should be written as follows:

$$\int_0^{t_r} \frac{dt}{\tau[\gamma(t)]} = 1 \quad (4)$$

Let us assume that, due to the constant stress on the sample and arising deformation, the structure-sensitive parameter reduces linearly in time:

$$\gamma = \gamma_0 - at \quad (5)$$

where γ_0 is the initial structure-sensitive parameter and a is the rate of reduction of the structure-sensitive parameter in time due to improvement of the material structure.

The linear reduction of the structure-sensitive parameter is not universal. The structure-sensitive parameter can change according to the exponential, logarithmic, and linear-stepwise dependences, but all this must be analyzed subsequently based on the coincidence of the calculated and experimental data. The linear dependence is fulfilled better for isotropic polymers since, during the action of stresses and arising deformation, they can orient. Note that the structure-sensitive parameter of the oriented polymers always reduces and their durability increases compared to those of the isotropic polymers.

Then, equation (1) can be written in the following form:

$$\tau = \tau_0 e^{\frac{U_0 - (\gamma_0 - at)\sigma}{RT}} \quad (6)$$

The Bailey criterion will be as follows:

$$\int_0^{t_r} \frac{dt}{\tau_0 e^{\frac{U_0 - (\gamma_0 - at)\sigma}{RT}}} = 1 \quad (7)$$

The solution of this integral equation leads to the following relation:

$$\frac{1}{\tau_0} \frac{1}{e^{\frac{U_0 - \gamma_0 \sigma}{RT}}} \frac{-RT}{a\sigma} \left(e^{\frac{-at_r \sigma}{RT}} - 1 \right) = 1 \quad (8)$$

Relation (8) suggests that the time to rupture t_r at the constant stress σ is equal to:

$$t_r = -\frac{RT}{a\sigma} \ln \left(1 - \frac{a\sigma}{RT} \tau_0 e^{\frac{U_0 - \gamma_0 \sigma}{RT}} \right) \quad (9)$$

Let us choose the following typical values of parameters in equation (9) which are characteristic of many polymers: $\sigma = 30$ MPa, $U_0 = 150$ kJ/mol, $T = 293$ K, $a = 1.7 \cdot 10^{-8} \text{ s}^{-1}$, and $\gamma_0 = 1.6$ kJ/mol·MPa. The constant R is equal to 8.314 J/mol·K, and the constant τ_0 is equal to 10^{-12} s.

The polymers used for durability measurement represented fibers and bars based on poly(methyl methacrylate), poly(ethylene terephthalate), polystyrene, polycarbonate, polyethylene, cellulose, polyamide 6, etc. The vulcanizates of different rubbers were also used. The polymers were in the glassy, crystalline and rubbery states.

Relation (9) with these parameters will be as follows:

$$t_r(s) = -4776471 \cdot \ln(1 - 20.9 \cdot 10^{-20} \cdot 1.57 \cdot 10^{18}) \quad (10)$$

If t_r should be expressed in years, then:

$$t_r(\text{years}) = -0.15 \cdot \ln(1 - 20.9 \cdot 10^{-20} \cdot 1.57 \cdot 10^{18}) \quad (11)$$

These parameters afford the material durability $t_r \approx 0.6$ year.

Let us calculate the dependence of σ on t_r .

Table 1. Durability t_r at the rate of reduction of the structure-sensitive parameter $a = 1.7 \cdot 10^{-8} \text{ s}^{-1}$

σ , MPa	t_r , s	$\lg t_r$	σ_r/σ_0	σ_r/σ_0	σ_r/σ_0	σ_r/σ_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
36	30516	4.484		1	0.923	0.857
39	4212	3.624			1	0.929
42	590	2.771				1

The data presented in Table 1 describe a descending branch of the dependence of σ_r/σ_0 on $\lg t_r$. To describe an ascending branch of this curve, let us use equation (1). According to this equation, the dependence of the stress σ on the durability τ is determined by the following relation:

$$\sigma = \frac{U_0 - 2.3RT(\lg \tau - \lg \tau_0)}{\gamma} \quad (12)$$

The results of the calculations are summarized in Table 2.

Table 2. Values of the stress σ leading to different values of the durability $\tau = t_r$

σ , MPa	$\lg t_r$ (s)	σ_r/σ_0
51.73	0	1.0
55.23	1.0	1.068
58.73	2.0	1.135
62.23	3.0	1.203

Figure 1 depicts the dependences of σ_r/σ_0 on $\lg t_r$ obtained at different initial stresses σ_0 ranging from 33 to 42 MPa.

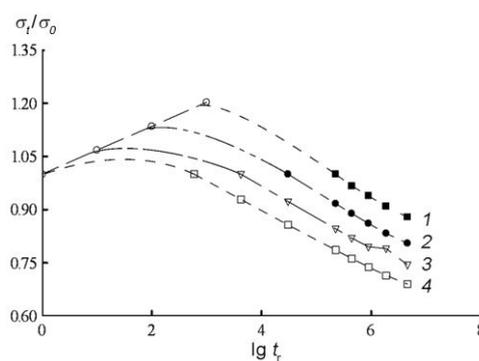


Figure 1. Dependence of σ_r/σ_0 on $\lg t_r$ at different initial stresses: 33 (1), 36 (2), 39 (3), and 42 (4) MPa. The time t_r is expressed in seconds.

It is obvious that the higher the initial stress σ_0 , the lower the value of σ_r/σ_0 that provides a transition from the ascending branch of the curve to the descending one. Hence, the suggested mechanism of a peculiar course of the kinetic curve for the time dependence of the resistance coefficient, which is connected

with a reduction in the structure-sensitive coefficient in the durability equation, allows one to describe adequately the curve under consideration, which resembles the Weller curve.

Now let us change the reduction rate of the structure-sensitive parameter in time a . We assume that $a = 1.0 \cdot 10^{-8} \text{ s}^{-1}$. The values of the time to rupture at different constant stresses are presented in Table 3.

Table 3. Durability t_r at the reduction rate of the structure-sensitive parameter $a = 1.0 \cdot 10^{-8} \text{ s}^{-1}$

σ , MPa	t_r , s	$\lg t_r$	σ_r/σ_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

Let us assume even the lower value of a equal to $0.5 \cdot 10^{-8} \text{ s}^{-1}$. The resulting values of t_r (s), $\lg t_r$, and σ_r/σ_0 are presented in Table 4.

Table 4. Durability t_r at the reduction rate of the structure-sensitivity coefficient $a = 0.5 \cdot 10^{-8} \text{ s}^{-1}$

σ , MPa	t_r , s	$\lg t_r$	σ_r/σ_0
27	17705141	7.248	0.844
28	7124936	6.852	0.875
29	4848072	6.686	0.906
30	1652375	6.218	0.937
31	836063	5.922	0.969
32	427846	5.631	1

The data presented in Tables 3 and 4 suggest that the dependences of $\lg t_r$ on σ_r/σ_0 at the same values of σ differ insignificantly.

Finally, let us analyze the dependence of σ_r/σ_0 on $\lg t_r$ at different values of the initial activation energy U_0 . The results of the calculations performed using formula (9) are presented in Table 5.

Table 5. Durability t_r at different values of the initial activation energy of rupture U_0

U_0 , kJ/mol	σ , MPa	t_r , s	$\lg t_r$	σ_r/σ_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

It is obvious that an increase in the initial activation energy leads to a rapid increase in the ratio σ_r/σ_0 . This is associated with the fact that the stresses σ also increase. Figure 2 demonstrates the dependences of σ_r/σ_0 on $\lg t$.

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

It should be taken into account that the concept of S. N. Zhurkov is not the only one. Many researchers exploring the strength and durability of polymers give special attention not only to chemical but also to intermolecular bonds. The most

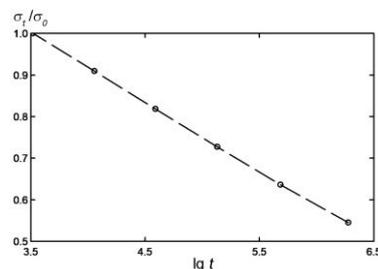


Figure 2. Dependence of σ_r/σ_0 on $\lg t$ at different values of the initial activation energy and stress. The time t is expressed in seconds.

comprehensive studies in this field were performed by V. E. Gul'. According to his concept, in any polymeric body, the loading falls, first of all, on the intermolecular bonds. Because the intermolecular bonds are weak (compared to the chemical ones), they undergo cleavage first, and, as the intermolecular bonds break, the loading on chemical bonds increases. If we deal with an oriented system (for example, fibers), then, the total energy of intermolecular bonds appears to be essentially higher than that of the chemical bonds in a main polymer chain. Therefore, in the oriented systems, the chemical bonds are disrupted first, and the whole rupture mechanism is connected almost only with the cleavage of these bonds. In the nonoriented systems, the intermolecular bonds play a great role. Introducing the possibility of their cleavage, V. E. Gul' deduced the following equation that describes the polymer durability:

$$\tau = \frac{B}{(\sigma - \sigma_x)^\alpha} e^{\frac{U_0 - \gamma\sigma}{RT}\beta} \quad (13)$$

where B , σ_x , α , γ , and β are the material constants, σ is the constant stress.

Let us take a logarithm of equation (13):

$$\ln \tau = \ln B - \alpha \ln(\sigma - \sigma_x) + \frac{U_0 - \gamma\sigma}{RT}\beta \quad (14)$$

We measured the durability of poly(vinyl chloride) under the action of a range of constant stresses σ . The experimental temperature was 293 K. The resulting dependence of the durability on the stress is depicted in Fig. 3.

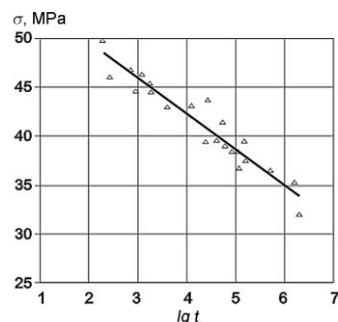


Figure 3. Dependence of the long-term strength of PVC. The time t_r is expressed in seconds.

Let us choose four durability values which correspond to four stresses. These values are listed in Table 6.

Using these data, we obtain the following system of equations (given that $\gamma = \gamma_0 = 1.6 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{MPa}$ and $U_0 = 150 \text{ kJ/mol}$):

$$1) 4.6 = \ln B - \alpha \ln(49.6 - \sigma_x) + 29.0 \cdot \beta$$

- 2) $9.2 = \ln B - \alpha \ln(42.4 - \sigma_x) + 33.73 \cdot \beta$
 3) $11.5 = \ln B - \alpha \ln(38.6 - \sigma_x) + 36.22 \cdot \beta$
 4) $16.1 = \ln B - \alpha \ln(31.05 - \sigma_x) + 41.18 \cdot \beta$

Table 6. Values of $\lg \tau$ and σ for a poly(vinyl chloride) film obtained at different constant stresses σ

$\lg \tau$ (s)	σ , MPa	σ/σ_0
0	57.24	1.0
2.0	49.6	1.154
4.0	42.4	1.350
5.0	38.6	1.483
7.0	31.05	1.843

Let us assume that $\sigma_x = 30$ MPa. The solution of this system of equations leads to the following values of the material parameters: $\sigma_x = 30$ MPa, $\alpha = 2$ s/MPa, $\beta = 0.6$ s, and $\ln B = -6.0$ (s).

The Bailey criterion (4) at the alternating structure-sensitive parameter γ takes the following form:

$$\int_0^{t_r} \frac{dt}{\frac{B}{(\sigma - \sigma_x)^\alpha} e^{\frac{U_0 - (\gamma_0 - at)\sigma\beta}{RT}}} = 1 \quad (15)$$

The solution of definite integral (15) leads to the following relation:

$$-\frac{at_r \sigma \beta}{RT} = \ln \left[1 - \frac{\alpha \sigma \beta B}{RT(\sigma - \sigma_x)^\alpha} e^{\frac{U_0 - \gamma_0 \sigma \beta}{RT}} \right] \quad (16)$$

The latter can be used to define the time to rupture t_r at the constant stress σ :

$$t_r = -\frac{RT}{\alpha \sigma \beta} \ln \left[1 - \frac{\alpha \sigma \beta B}{RT(\sigma - \sigma_x)^\alpha} e^{\frac{U_0 - \gamma_0 \sigma \beta}{RT}} \right] \quad (17)$$

Plugging all the mentioned values of parameters B , σ_x , α , γ , and β into relation (17), we can obtain the values of $\lg t_r$ at different stresses σ as well as the values of the ratio σ_r/σ_0 . These data are listed in Table 7.

Table 7. Values of $\lg \tau$ and σ for a poly(vinyl chloride) film obtained under the action of the alternating stresses σ_r

$\lg \tau$ (s)	σ_r , MPa	σ_r/σ_0
1.567	110	1.0
3.340	100	0.909
5.201	90	0.818
6.256	85	0.773

The total dependence of σ_r/σ_0 on $\lg t_r$ is depicted in Fig. 4.

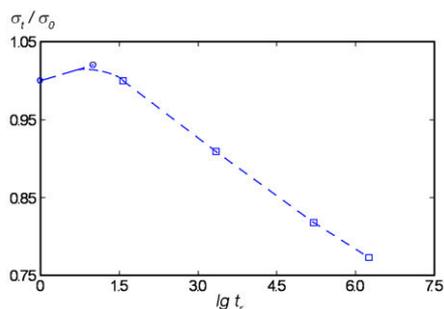


Figure 4. Dependence of σ_r/σ_0 on $\lg t_r$. The time t_r is expressed in seconds.

This dependence looks like the Weller curve since it has a maximum. This maximum is connected with the improvement of the material structure during deformation, which is reflected in a reduction in the structure-sensitive parameter γ with the stress growth. Further investigations in this field will be connected with the analysis of the effect of creep and stress relaxation processes [7–10] at the alternating stresses and strains on the durability of polymeric materials.

Conclusions

The suggested procedure for the construction of the time dependence of the resistance coefficient allows one to establish the physical meaning of its variation. The resistance coefficient is connected with the improvement of the material structure during deformation, which leads to a reduction in the structure-sensitive parameter in the durability equation. Of course, this is not the only one reason for the formation of the curved dependence of $k_r = \sigma_r/\sigma_0$ on t_r featuring a maximum, which resembles the Weller curve. Further investigations in this field will deal with the consideration of relaxation processes (creep and stress relaxation), which occur during polymer deformation upon loading.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

Corresponding author

* E-mail: andrey@ineos.ac.ru. Tel: +7(499)135-9398 (A. A. Askadskii)

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