

STRESS RELAXATION IN POLYCARBONATES

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A procedure is presented for investigation of stress relaxation in various brands of foreign and domestic polycarbonates in different stages of loading. This study is the first to cite results of experimental investigations of stress relaxation in carbonates subject to long-term tests at a constant strain rate. The results are then processed statistically, and stress–relaxation curves are constructed, and the latter analyzed and mathematically described. Model representation of stress relaxation in polycarbonates has made it possible to determine the time required for stress relaxation.

In addition to such basic advantages as high resistance to aggressive media, atmospheric effects, etc., polymeric materials possess a number of disadvantages: low heat stability and thermal resistance, and tendency to creep and stress relaxation. Relaxation is a physical process whereby a system goes over into an equilibrium state, and is sufficient to have altered external energy conditions. As applies to polymeric materials, the rate of relaxation and its intensity will depend on their chemical and physical structure, intermolecular interaction, and parameters of the external energy field (temperature, mechanical stress, amplitude and frequency of loading, etc.). Stress relaxation during constant deformation is described, for example, by the Maxwell equation [1]:

$$\sigma_t = \sigma_0 \exp \{-t/\tau_r\}, \quad (1)$$

where σ_t is the stress acting in the polymeric article during time interval t , σ_0 is the initial stress when $t = 0$ (the relaxing portion of the stress), and τ_r is the relaxation time.

It is considered that the time during which the stress diminishes by a factor e of the total drop-off in stress be adopted as the relaxation time. The Maxwell equation essentially in no way describes the stress relaxation for actual polymeric bodies. It describes only the case when stress relaxation is fully completed, i.e., the stress drops-off to zero. The relaxation of a polymeric material within an article is a complex and multilevel process, which may continue from several minutes to many tens of hours, depending on the chemical and macromolecular structure of the polymer, and the external conditions. It is considered impossible to determine the moment of completion of this process [2]. The model devised by Dogadkin, Bartenev, and Reznikovskii describes the simplest case of stress relaxation for constant strain in which the stress observed over an extended period under relaxation conditions does not fall-off to zero, but remains constant (in equilibrium) [3]. In conformity with the model proposed, the relaxation curve conforms to the equation

$$\sigma(t) = \sigma_0 \exp \{-t/\tau_r\} + \sigma_\infty, \quad (2)$$

where σ_∞ is the equilibrium stress.

In contrast to the Maxwell equation (1), relationship (2) accounts for the fact that relaxation does not occur completely, i.e., the stress does not relax to zero. At the present time, insufficient attention is being turned to experimental inves-

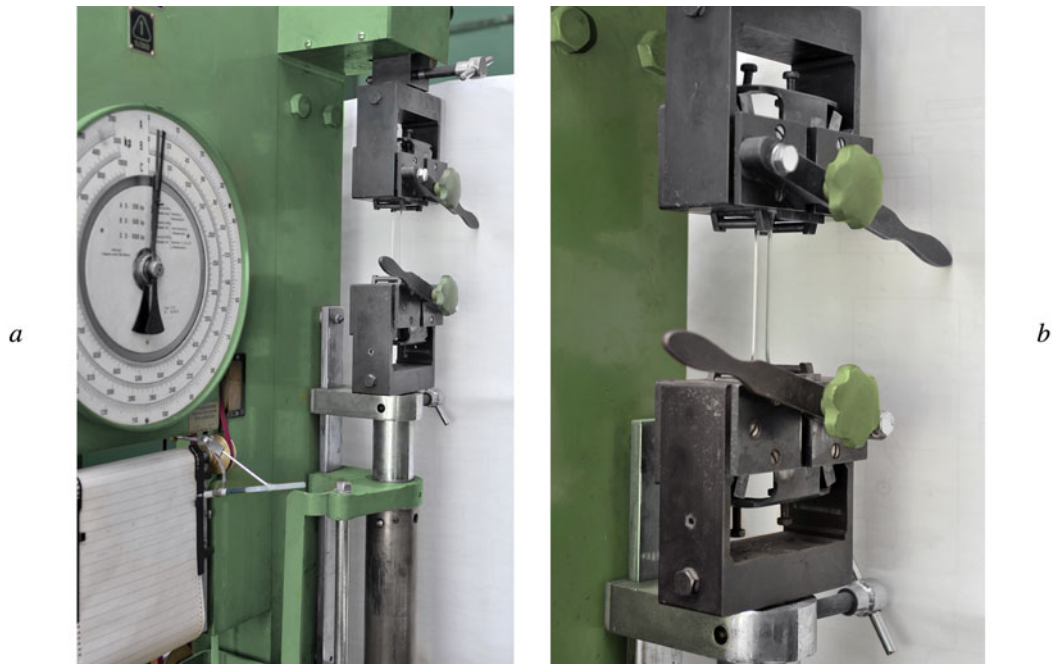


Fig. 1. Tensile-testing machine (a) with polycarbonate blade-specimen for testing of stress relaxation (b).

tigation of stress relaxation in polymeric materials. Data on stress relaxation are required in both cases when during service, polymeric articles experience constant deformation over the long term.

In its first part, this paper cites results of experimental investigations of long-term stress relaxation of polycarbonates in extended tests at constant deformation.* Statistical processing of the results is then cited, and stress relaxation curves are constructed, analyzed, and mathematically described. The model representation of stress relaxation in polycarbonates has made it possible to determine the time required for stress relaxation.

Specimens of general-purpose brands of polycarbonates of the following injection-molded brands were selected as subjects of investigation:

- 143R Thermoplay. Producers – GE Plastics, DuPont (United States);
- Trirex-30251R. Producer – Samyang (South Korea); and
- polycarbonate PC-007. Producer – Kazanorgsintez (Russia).

Specimens in the form of two-sided blades with a length $L = 150$ mm, width $b = 10$ mm, and thickness $h = 4$ mm (GOST 11262–80) were used for the tests. The length of the effective section of the blades $L_0 = 100$ mm. Broadenings at the ends of the blades served to secure them in the clamping devices of an FM1000 tensile-testing machine with a scale range of 0–5 kN (Fig. 1). Prior to the start of testing, the polycarbonate specimens were conditioned to eliminate the effect of moisture content on the experimental results. The tests were conducted at a temperature of 296 ± 2 K, relative moisture content of $50 \pm 5\%$, and constant specimen-strain rate of 10 mm/min in all tests.

Tension diagrams were plotted for the specimens of each consignment in $F-\Delta l$ coordinates, where F is the load, and Δl is the increase in deformation (Fig. 2).

The following were established as a result:

- 1) the elastic deformations where the force applied gives rise to a proportional increase in deformation (0–1);

* Coworkers V. N. Frolov and Yu. M. Sherbakov of the MGUIE participated in tests performed on an FM 1000 tensioning machine.

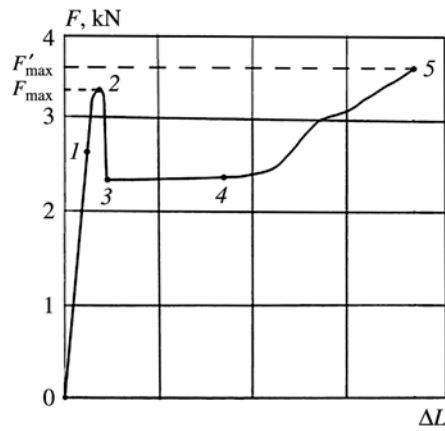


Fig. 2. Tension diagram of 143R Thermoploy polycarbonate.

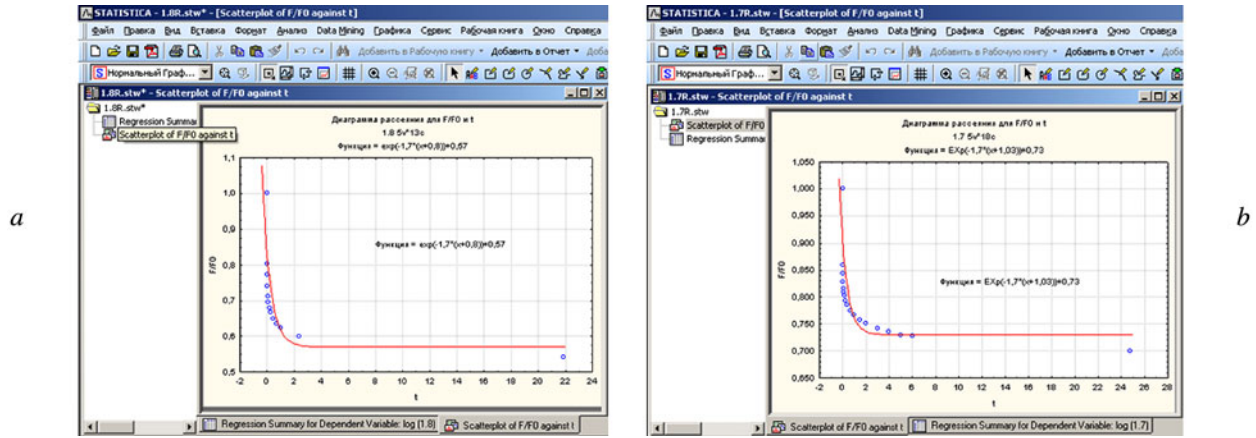


Fig. 3. Stress relaxation of specimens formed from 143R Thermoploy polycarbonate in standard coordinates: a) specimen 1.8R; b) specimen 1.7R.

2) the $F-\Delta l$ curve is nonlinear with the appearance of plastic deformation right up to the maximum load F_{max} , after attainment of which an increase in deformation occurs without an increase in load F , whereupon the section of the specimen is narrowed (1–2);

3) a pronounced reduction in applied load, which is accompanied by development of deformation and the appearance of a neck (2–3);

4) diminishing section of the neck so-formed with its transformation into a strip under a constant load (3–4); and

5) an increase in load to F'_{max} with further development of deformation (4–5) and subsequent failure.

The curve (see Fig. 2) is a typical tension diagram of an amorphous polymer such as polycarbonate.

The tension diagram enabled us to investigate stress relaxation and its rate, i.e., study the dependence of relative load F/F_0 on test time t during a pause between the different tensioning steps, where F_0 is the load at the moment when the machine is shut-down:

- in segment (1–2) when $F < F_{max}$;
- on attainment of $F = F_{max}$;
- in segment (2–3) at the moment of neck formation when F experiences a pronounced reduction;

TABLE 1

Specimen	Stress-relaxation equation
1.3R	$F/F_0 = \exp(-1.84^t(t + 0.75)) + 0.66$
7.1R	$F/F_0 = \exp(-1.94^t(t - 1.46)) + 0.65$
3.1R	$F/F_0 = \exp(-0.85^t(t + 1.8)) + 0.62$

TABLE 2

Specimen	Stress-relaxation equation
1.8R	$F/F_0 = \exp(-1.7^t(t + 0.8)) + 0.57$
7.6R	$F/F_0 = \exp(-1.82^t(t - 1.52)) + 0.59$
3.3R	$F/F_0 = \exp(-3.15^t(t - 1.45)) + 0.59$

- in segment (3–4) when $F = \text{const}$ and the neck develops; and
- in segment (4–5) when the neck is loaded.

The experimental data were processed using the STATISTICA software package (StatSoft, Inc. 2001). This permitted visualization of the data and results of statistical analysis, and automation of processing of the large data file. It should be pointed out that the coefficient of determination R^2 , which characterizes the error generated in the calculations, was no less than 0.8 [4]. The software permitted derivation of formulas for calculation of regression coefficients in conformity with the method of least squares, and construction of plots with calibration of model parameters.

Figure 3 shows plots of stress relaxation in standard coordinates for a sample of the 143R Thermoplay. The specimens were investigated for the case of machine shut-down:

- 1.8R – at the moment of neck formation (segment 2–3) on the tension diagram (see Fig. 3a);
- 1.7R – at the moment of neck development (see Fig. 2, segment 3–4).

It is established from results of statistical processing of the experimental data that the rate of stress relaxation for the polycarbonates of all brands is maximum at the moment the machine shuts down at $F > F_{\text{max}}$ (segment 2–3 on the tension diagram), i.e., during neck formation.

For specimens of the three brands investigated in different stages of tensioning, the STATISTICA software establishes equations that make it possible to describe the experimental stress-relaxation curves obtained. Equations for the case of stress relaxation during shut-down of the testing machine on attainment of F_{max} are presented in Table 1 (see Fig. 2).

According to the experimental plots of the relationship between relative load F/F_0 and test time t , which were obtained for different fixed deformations (shutdown of the machine at various stages of specimen tensioning), it is possible to state that the relaxation process is completed with residual stress retained in the specimen. Thus, the normalized values are 0.66, 0.65, and 0.62 for specimens 1.3R, 7.1R, and 3.1R, respectively (see Table 1).

Equations describing the stress-relaxation process at the maximum rate for the various consignments of polycarbonates are presented in Table 2 (segment 2–3 of the relaxation diagram).

The stress-relaxation curves of the polycarbonates conform to an equation that can be written in the following general form:

$$F/F_0 = \exp(-a^t(t + c)) + b, \quad (3)$$

where a , b , and c are empirical constants.

It is readily established that the curves, which describe the stress relaxation in (3), and which are plotted from the experimental results, satisfy the equation:

$$\frac{dF / F_0}{dt} = -\frac{F}{F_0} a^t [1 + (\ln a)(t + c)] + ba^t [1 + (\ln a)(t + c)], \quad (4)$$

where

$$\lim_{t \rightarrow \infty} \frac{F}{F_0} = b.$$

The derivative $d(F/F_0)/dt$ when $t = 0$ assumes the form:

$$\left. \frac{dF / F_0}{dt} \right|_{t=0} = -\left. \frac{F}{F_0} \right|_{t=0} [1 + (\ln a)c] + b[1 + (\ln a)c]. \quad (5)$$

Equation (3) has the initial condition:

$$F|_{t=0} = F_0(e^{-c} + b). \quad (6)$$

Let us denote the relaxation time by τ_r . From Eq. (3), it follows that τ_r is the solution of the equation

$$(F / F_0 - b)|_{t=\tau_r} = e^{-1}.$$

Hence, it follows that τ_r satisfies the nonlinear equation:

$$1 = a^{\tau_r} (\tau_r + c). \quad (7)$$

Equation (7) does not permit an explicit solution; let us therefore cite its approximate solution:

$$\tau_r \cong \begin{cases} \frac{1-c}{1+\ln a}, & c < 1; \\ \frac{1+\ln a + \sqrt{(1+\ln a)^2 + 2(c-1)(\ln a)^2}}{(\ln a)^2}, & c \geq 1. \end{cases} \quad (8)$$

The experimental investigations performed for the stress relaxation of polycarbonates in various stages of tension confirm that the course of stress relaxation always terminates at a stress σ_∞ . Knowledge of the equilibrium stress is one of the longevity indicators of a polymeric material performing under stress relaxation. Expression (8), which is derived from the experimental curves, makes it possible to determine the most important physical characteristic of the polymer – the time required for stress relaxation.

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