Materials Physics and Mechanics 32 (2017) 207-212 Received: July 14, 2017

RELAXATION IN RESINS WITH LOW-FREQUENCY MECHANICAL CYCLING

V.I. Ivlev*, A.F. Sigachyov, N.E. Fomin, V.A. Yudin

Mordovia State University N.P. Ogareva, Bolshevistskaya, 68, Saransk, 430005, Russia

*e-mail: ivlevvi2010@mail.ru

Abstract. Hardened polyester and epoxy resins were tested for the relaxation of mechanical stresses, depending on the initial stress (2.6 ÷ 24 MPa), time and temperature (15 ÷ 45 °C). The dependence of stress on time in the relaxation of resins in the investigated ranges of mechanical stresses is described by the logarithmic function characteristic for stress relaxation in crystalline solids (metals).
Keywords: epoxy resin; polyester resin; relaxation; mechanical stress.

1. Introduction

Relaxation phenomena form a significant part of the properties of materials, including polymers, which may include cured resin. Naturally, the study of this group of properties of new materials is usually started immediately after the receipt of these materials in sufficient quantities.

Polyester and epoxy resins are a universal family of resins, on the basis of which receive composite materials, widely used in various fields of modern technology for more than a hundred years. Relaxation processes in these materials is also studied quite a long time and actively. However, due to the wide variety of composition and grades of these resins, the complexity of the atomic-molecular processes in them, especially when using them for the production of composite materials, there always remain questions requiring further investigation.

One of the manifestations of relaxation is mechanical hysteresis. As a rule, in dynamic experiments is often determined the energy losses of oscillations. In our previous experiments, the dependence of the effective (or conditional) modulus on deformation was studied for low-frequency mechanical cycling [1]. The effective modulus was defined as the tangent of the slope of the strain curve $E = d\sigma/d\varepsilon$ (σ is the mechanical stress, ε is the relative deformation).

In Fig. 1 shows the relationship between the stress and deformation σ (ε) obtained during cycling. A characteristic feature of the obtained dependences σ (ε) is the presence of a hysteresis, especially strong in the first cycle. The dependence of the effective modulus E on the magnitude of the mechanical stress upon loading and unloading the sample is shown in Fig. 2.

The curve σ (ε) obtained during unloading after the first loading is very different from the curve obtained under loading, it is practically monotonic, with the exception of a small section at the lowest loads. At maximum loads, the unloading curve is steeper than the loading curve for low loads, on the contrary, so that the E (σ) curves obtained during loading and unloading, when plotted on the same graph, overlap (Fig. 2). This feature is retained in subsequent cycles. From this we can conclude that the stress relaxation processes prevail at the initial stages of unloading (high stresses), and the deformation relaxation processes prevail at the final (small stresses).

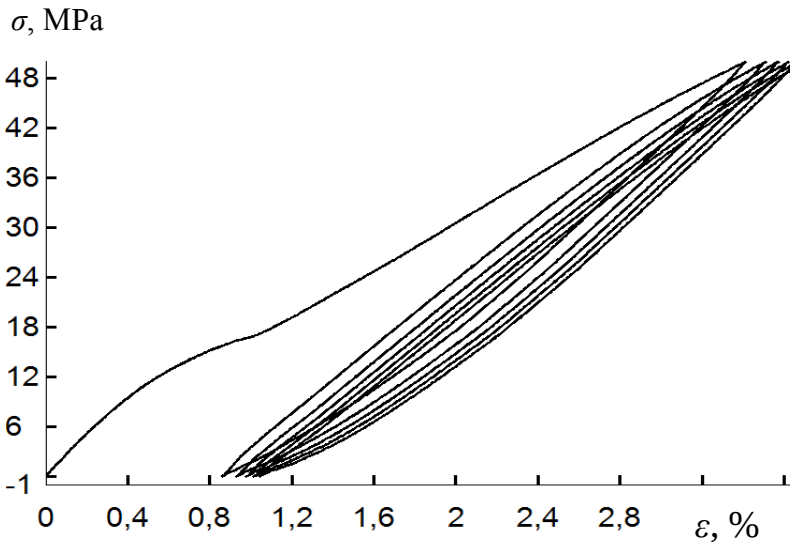

Fig. 1. Hysteresis in epoxy resin during deformation at a rate of $3 \cdot 10^{-4}$ c^{-1}.

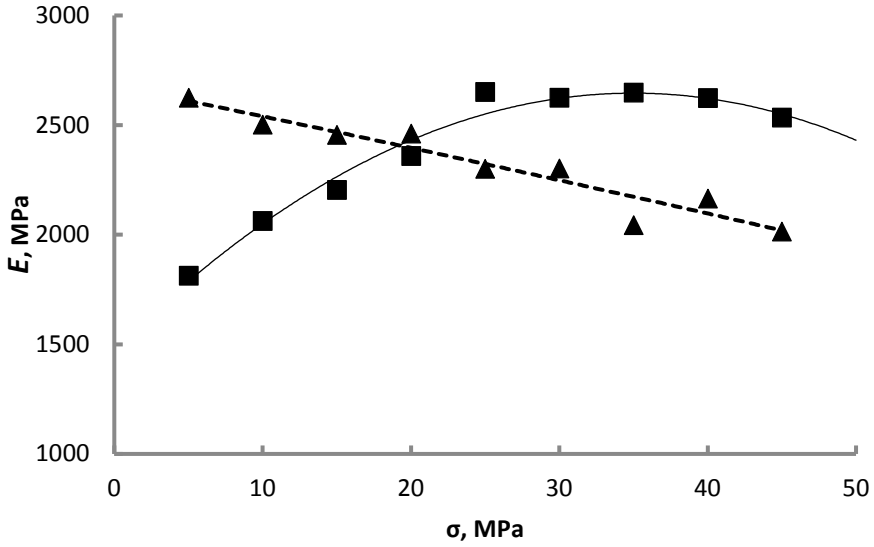

Fig. 2. The dependence of the effective modulus on the magnitude of voltage during cycling (epoxy resin).

The processes of strain relaxation (creep) of resins were investigated by us earlier [2, 3]. The aim of this work is more detailed study of stress relaxation in these materials.

2. Materials and methods of research

Polyester resin PN-1 produced by the enterprise "Combine" Kamensky "(GOST 27952-88). Resin PN-1 is a solution of unsaturated polyester based on diethylene glycol, maleic anhydride and phthalic anhydride in styrene. For curing resin was used hardener Butanox M-60 and the accelerator is OK (1.5 % active). Cure was carried out at 20 °C. The time interval between the preparation of samples and their rupture test and creep was not less than a week.

Epoxy resin ED-20 produced by the company "Karbohim". Samples for the study were prepared by a technique close to the technology for the preparation of building composites

based on epoxy resin: mixing the resin with the hardener Ethal-45M in a 2: 1 ratio, pouring into a mold, holding for 24 hours at room temperature, then 6 hours at 80 °C.

Investigation of the mechanical properties of PN-1 resin was carried out on a universal testing machine Shimadzu Autograph AG-X Series [4]. The samples of rectangular section with the sizes of the working part (between the grippers of the machine) 4 * 10 * 100 mm are used. The control of the test process and preliminary processing of the data obtained on this machine are carried out using the software TRAPEZIUM X * 1 [5].

The stress relaxation in the resin samples was examined at room temperature. The sample was loaded stepwise to a predetermined stress level, then the grippers of the machine were fixed, and the deformation was remained for from half an hour to two hours. Then the load increased to the next level and the record of the relaxation curve continued.

3. Test results and discussion

An example of the obtained in our experiments relaxation curves shown in Fig. 3.

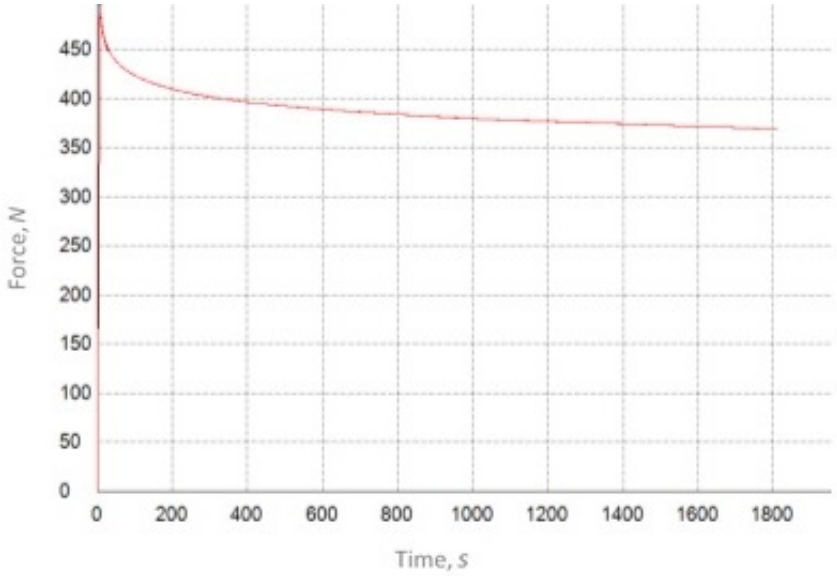

Fig. 3. The relaxation curves for the polyester resin at 12.5 MPa.

As is known, if the relaxation process proceeds through a single simple mechanism, its time dependence can be interpolated by an exponential

$$x = x_0 e^{-t/\tau}, \quad (1)$$

with the constants $x0$ and τ. Then in semilogarithmic coordinates $lnx\ (t)$ this dependence has the form of a straight line.

In Fig. 4 shows the dependence of $ln\sigma(t)$ obtained for sample polyester resin (σ – mechanical stress). As can be seen, this dependence is clearly nonlinear. The analysis showed that the curve in Fig. 2 for any practical purpose can be interpolated by a polynomial of the third degree.

Garofalo notes that in 1904 it was found that the experimental data on relaxation of stresses in metals and alloys are well described by equation of the form

$$\sigma = \sigma_0 - \alpha_p ln(1 + \tau_p t), \quad (2)$$

where σ_p is the initial stress, α_p and τ_p are time-independent constants. [6]

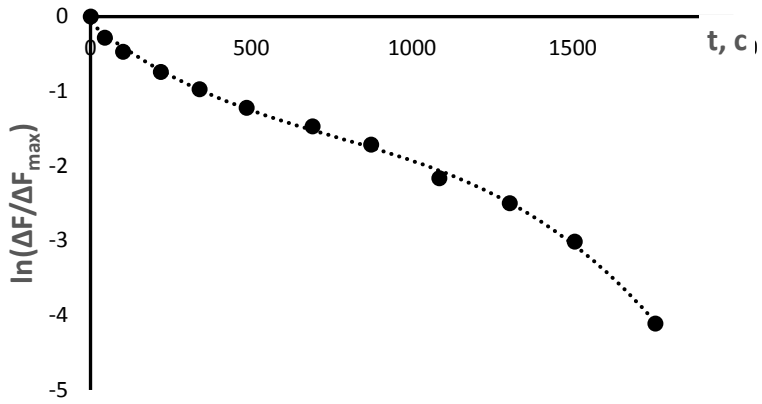

Fig. 4. Relaxation of stress in the resin PN-1 at a voltage of 12.5 MPa.

However, neither [6] nor in later works was not proposed physical mechanisms for this dependence.

In Fig. 5 shows the dependence of the stress on the value of $ln\ (1\ +\ bt)$ obtained for the polyester resin at different initial stresses. It turned out that all the experimental points fit near the common straight line with the criterion of reliability of the approximation $R^2 > 0.996$. This means that the time dependence of the voltage can be described by a function of the form:

$$y = aln(1 + bt), \tag{3}$$

where $y = (\sigma - \sigma_\infty)/(\sigma_0 - \sigma_\infty)$; σ is the stress at time t, σ_∞, σ_0 is the relaxed and initial stress, respectively. The constants a and b are practically independent of the stress and are equal to $a \approx 0.15$ and $b \approx 0.7$. Note that the results are weakly sensitive to the value of the parameter b.

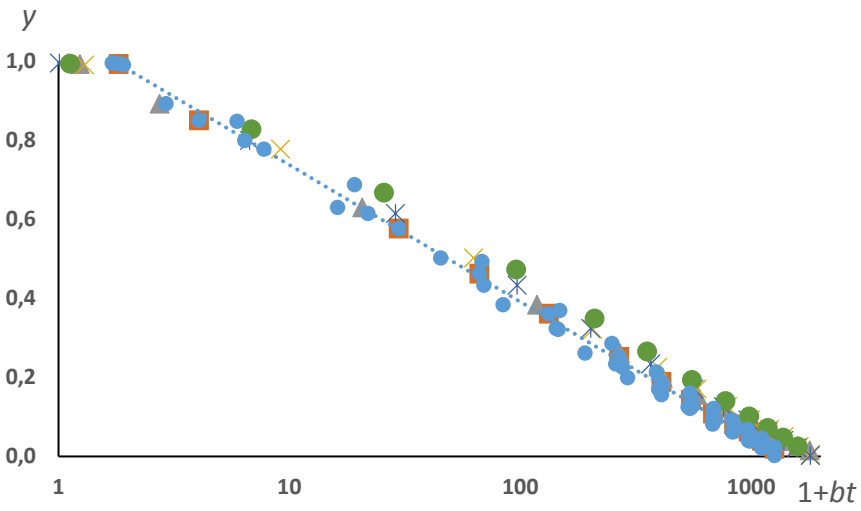

Fig. 5. Results of testing polyester resin for tension at different initial stress values (different markers correspond to different values of the initial stress).

The change in temperature in the interval from 15 to 35 °C did not reveal a noticeable effect on the value of the constants.

In the bending test, data qualitatively similar to those obtained with stretching were obtained, but with slightly different constants (Fig. 6): $a \approx 0.2\ and\ b \approx 0.05$.

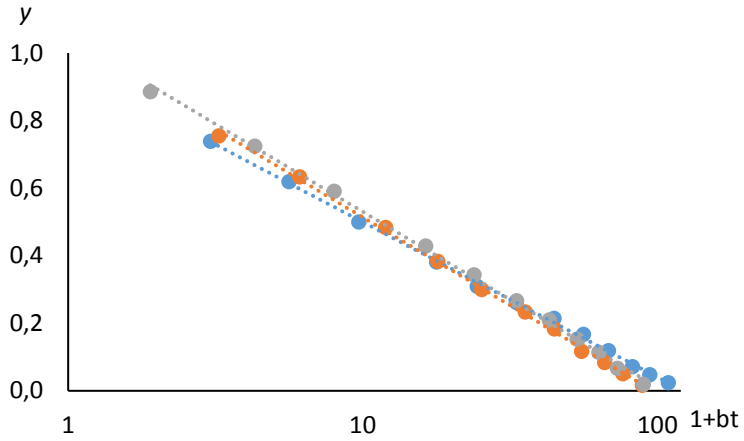

Fig. 6. Results of testing polyester resin for bending at different initial stress values (different markers correspond to different values of the initial stress).

Stress relaxation in epoxy resin occurs similar to the relaxation in polyester resin (Fig .7). Constants for this resin was equal to: $a \approx 0.16$ *and* $b \approx 0.3$.

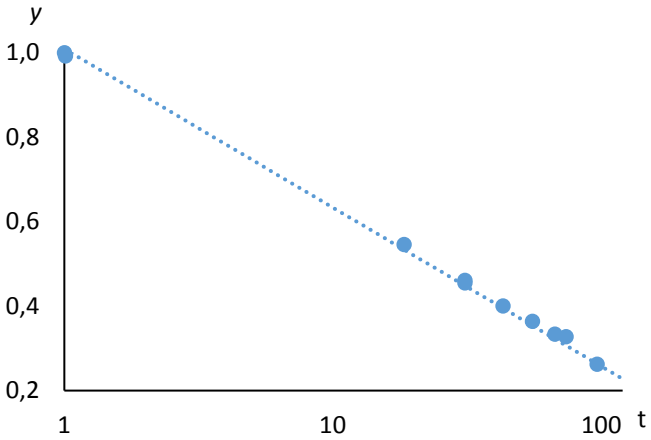

Fig. 7. The test results of the epoxy resin.

Functions (2) and (3) are actually the same. Therefore, stress relaxation in the glassy resin is at least qualitatively (mathematically) can be described in the same way as in crystalline metallic materials.

Our studies of creep in resins [2, 3] showed that it is well described by a logarithmic function of the form

$$\varepsilon = \varepsilon_e + \varepsilon_p + \varepsilon_0 ln(1 + vt), \quad (4)$$

which is mathematically identical to the formula (2). From this we can draw the natural conclusion that the molecular mechanisms of stress relaxation and creep have the same nature.

The derivation of relation (3) for crystals was based on the notion that the material can be divided into elementary volumes with a characteristic size L [7]. It was assumed that this volume can undergo continuous deformation regardless of the deformation of the neighboring elementary volume. If the deformation in a given elementary volume has occurred, then the stresses in the neighboring elementary volumes cannot reduce this deformation.

In principle, there are no contraindications to the use of this model and to non-crystalline materials, especially as, at low temperatures, polymers are mechanically indistinguishable from simple elastic solids [8].

When analyzing the results of the creep study in resins, we made the assumption that some forms of local mobility, which are related to the movement of side groups or small fragments of the main chains [8], which play the same role as dislocations in crystals. Taking into account the similarities in the laws of creep and stress relaxation, it can be assumed that the motion of the same groups or fragments determines the relaxation of stresses.

4. Conclusions

1. Relaxation of mechanical stresses is described by a logarithmic function, which has the same form for both crystalline metals and amorphous cured resins.

2. Quantitative characteristics of stress relaxation in both of the studied resins under tensile test and bending are close, that can be interpreted in favor of the assumption about the similarity of the structural elements responsible for relaxation in these compounds.

3. Identical form of the function, describing the two types of relaxation processes (relaxation of mechanical stresses and creep) for substances of different nature (metals and polymers) and various structures (crystalline and amorphous) leads to the assumption of a deeper unity of the nature of these processes.

References

[1] N.E. Fomin, V.I. Ivlev, A.F. Sigachyov, V.A. Yudin // *Physics and chemistry of material processing* **5** (2015) 66.
[2] N.E. Fomin, V.I. Ivlev, V.A. Yudin, A.F. Sigachyov // *Materials Physics and Mechanics* **22** (2015) 78.
[3] V.I. Ivlev, A.F. Sigachyov, N.E. Fomin, V.A. Yudin // *Materials Physics and Mechanics* **30** (2017) 61.
[4] http://www.ssi.shimadzu.com/products/literature/Testing/C224-E045.pdf
[5] http://www.ssi.shimadzu.com/products/product.cfm?product=trapeziumx
[6] F. Garofalo. *Fundamentals of Creep and Creep-Rupture in Metals* (Metallurgy, Moscow, 1968). (In Russian).
[7] R. Kahn (Ed.), *Physical Metallurgy* Vol. 3. (Mir, Moscow, 1968). (In Russian).
[8] G.M. Bartenev, S.J. Frenkel. *Polymer physics* (Chemistry, Leningrad, 1990). (In Russian).