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STRUCTURE AND PROPERTIES

Description of Stress–Strain Curves of Polymer Glasses

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Abstract—An approach to description of stress–strain curves in the uniaxial stretching of polymer glasses to the forced elasticity limit is proposed. The equation of the stress–strain curve is a power dependence of reduced stress on reduced strain, where exponent n is the ratio of the elastic modulus of a polymer (at the specified rate of loading and temperature) and the modulus corresponding to the forced elasticity limit at the same temperature. Temperature-time dependences of exponent n for poly(methyl methacrylate) and polycarbonate are measured under the hard regime of loading, at the strain rate from 10^{-2} to 10^{-5} s^{-1}, and at temperatures from 60 to 100°C and from 20 to 120°C, respectively. It is shown that exponent n is sensitive to the temperature and the time of loading (strain rate).

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At present, polymeric materials are used extensively in various branches of industry and are employed not only for functional [1–3] but also for constructional purposes [4–7]. In the latter case, severe requirements are imposed on them with respect to the level of physicomechanical properties [8] and specific features of the relaxation behavior, in particular, temperature–strain–time relationships for the development and decay of rubbery deformation [9–11], and their conservability under exposure to heat-and-humidity and climatic effects.

The solution of tasks aimed at creating new engineering polymeric materials with the desired level of physicomechanical properties and relaxation behavior and at forecasting the characteristics necessary for strain–strength calculations [12–14], including for nonstandard testing conditions [15], calls for gaining insight into the specific features of deformation of these materials.

There are currently various approaches to describing the relaxation behavior (nonlinear properties) of polymeric materials: differential equations of multielement models; ancestral-type equations; Boltzmann–Volterra equations; principles of temperature–time or stress–time analogs; theories of statistical segmental state, flow, and viscoelasticity; logistic-type equations; etc. [16–22].

A considerable contribution to understanding of the nature and mechanism of the physicomechanical behavior of polymer glasses as a class of materials was made in [23–26], where the concept of the generalized physicomechanical behavior of polymer glasses was presented. The authors of [23–26] obtained the generalized stress–strain curve in reduced coordinates (stress and strain were normalized to values corresponding to the forced elasticity limit) and proposed the following ratio:

$$\frac{\varepsilon_{\text{f.el}}}{\sigma_{\text{f.el}}}E_0 = 1.6, \qquad (1)$$

where $\varepsilon_{\text{f.el}}$ is the strain corresponding to the forced elasticity limit, $\sigma_{\text{f.el}}$ is the stress corresponding to the forced elasticity limit (MPa), and E_0 is the elastic modulus (GPa), which is constant, with an accuracy of ±8%, for all the glassy polymers regardless of their chemical nature, rate, temperature, and deformation mode.

Equation (1) may be written as

$$\frac{\varepsilon_{\text{f.el}}}{\sigma_{\text{f.el}}}E_0 = 1.6 = \frac{\varepsilon_{\text{f.el}}}{\sigma_{\text{f.el}}}\frac{\sigma}{\varepsilon} = \frac{\sigma}{\sigma_{\text{f.el}}}\bigg/\frac{\varepsilon}{\varepsilon_{\text{f.el}}} \qquad (2)$$

and may be treated as a special case of Hook's law defining the linear dependence with a coefficient of 1.6 between stress and strain (in the given case, between the reduced values). However, this equation describes only the initial quasi-elastic portion of the generalized stress–strain curve approximately to $\varepsilon/\varepsilon_{\text{f.el}} \sim 0.5$ and the portion of the diagram for $0.5 < \varepsilon/\varepsilon_{\text{f.el}} \le 1$ remains uncovered.

In this study, an approach to describing stress–strain curves of polymer glasses to the forced elasticity limit ($0 < \varepsilon/\varepsilon_{\text{f.el}} \le 1$) is proposed. The collected data are of interest to engineering applications and are also of importance for gaining insight into the relaxation behavior of polymer glasses.

EXPERIMENTAL

The objects of research in this study were an organic glass based on PMMA with a glass-transition temperature of $T_g = 120°C$ and an organic glass based on PC with $T_g = 150°C$.

All tests were performed on a Zwick/Roell Z050 electromechanical universal testing machine with a nominal load of 50 kN. Longitudinal strain was measured by a strain macrosensor with an accuracy rating of 1.0 in accordance with EN ISO 9513. The sensor knives were pressed to the surfaces of the sample with a force not above 1 N. The base of strain measurements was 70 mm. The tests were performed using trowel-shaped samples with a cross-sectional area of 10 × 10 mm^2 and a base length of 90 mm. Tests at reduced and increased temperatures were conducted in a thermal cryocabinet; the time of storage of the sample in it before testing was no less than 60 min.

The uniaxial stretching of PMMA and PC samples in the hard regime of loading was performed at the specified strain rate of 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} s^{-1} (the strain control). The testing temperature for PMMA samples was from 60 to 100°C; for PC samples, from 20 to 120°C. The uniaxial stretching tests of PC samples were conducted at a rate of 7, 25, and 70 mm/min (the displacement control). In this case, the strain rate was determined by the linear regression method on a portion of the time–strain diagrams from $0.3\varepsilon_{\text{f.el}}$ to $0.7\varepsilon_{\text{f.el}}$. This parameter was from 8.2×10^{-3} to 5×10^{-5} s^{-1}. The testing temperature was varied from –60 to 150°C.

In all cases, the samples were loaded to a strain 10–20% higher than the strain corresponding to the forced elasticity limit. The stress–strain diagrams under all loading regimes for both polymers showed local maxima corresponding to the onset of development of a forced elasticity limit (necking). Portions of diagrams before forced elasticity limits were involved in the analysis.

The values of modulus E_0 were determined from the experimental data by the least-squares procedure for two strain ranges of 0.01–0.2 and 0.01–0.3%. The initial strain in both cases was taken to be 0.01% to exclude the noisy part of the data corresponding to the onset of testing (loading). The values of modulus $E_{\text{f.el}}$ were calculated from the experimental data by the method of secant passing through the origin and the point corresponding to the forced elasticity limit (the local maximum at which necking begins on the test portion). Exponent n in the exponential dependence of reduced stress on reduced strain proposed in this study was determined by approximation of the experimental stress–strain diagrams to the forced elasticity limit in reduced coordinates according to the least-squares procedure.

RESULTS AND DISCUSSION

It is known that the temperature and rate of testing exert a marked effect on the pattern of stress–strain diagrams of polymer glasses. At the same time, their rearrangement in reduced coordinates, where stress and strain are normalized to the values corresponding to the forced elasticity limit, yields the generalized stress–strain curve [26] having a common view for different straining conditions.

The experimental study of the deformation of polymer glasses to the forced elasticity limit showed that, even in reduced coordinates, the patterns of diagrams are appreciably different. This phenomenon is especially pronounced on the diagrams obtained at the same rate of testing but at different temperatures (Fig. 1a). Note that the elastic modulus E_0 on the initial portion may go beyond the introduced limitation (±8%) of Eq. (1).

In order to describe the experimental curves obtained in the uniaxial stretching of polymer glasses to the forced elasticity limit, it is proposed to use equation of the stress–strain curve that is a power dependence of reduced stress on reduced strain:

$$\frac{\sigma}{\sigma_{\text{f.el}}} = 1 - \left(1 - \frac{\varepsilon}{\varepsilon_{\text{f.el}}}\right)^n. \qquad (3)$$

Equation (3) makes it possible, with a high accuracy, to describe the stress–strain curves of polymer glasses for various rates of testing and temperatures. Figure 2 presents the experimental diagrams measured for PC at a strain rate of 10^{-3} s^{-1} and a temperature of 24, 100, and 150°C and their approximating curves with exponent $n = 2.5$, 2.0, and 1.72.

Exponent n in Eq. (3) has a physical meaning of the reduced elastic modulus at the specified temperature and rate of loading. This assumption can be easily proved if we write the equation of the tangent to the plot of Eq. (3) at the origin:

$$\frac{\sigma}{\sigma_{\text{f.el}}} = n\frac{\varepsilon}{\varepsilon_{\text{f.el}}}, \qquad (4)$$

or

$$n = \frac{E_0}{E_{\text{f.el}}}, \qquad (5)$$

where $E_{\text{f.el}} = \sigma_{\text{f.el}}/\varepsilon_{\text{f.el}}$, GPa.

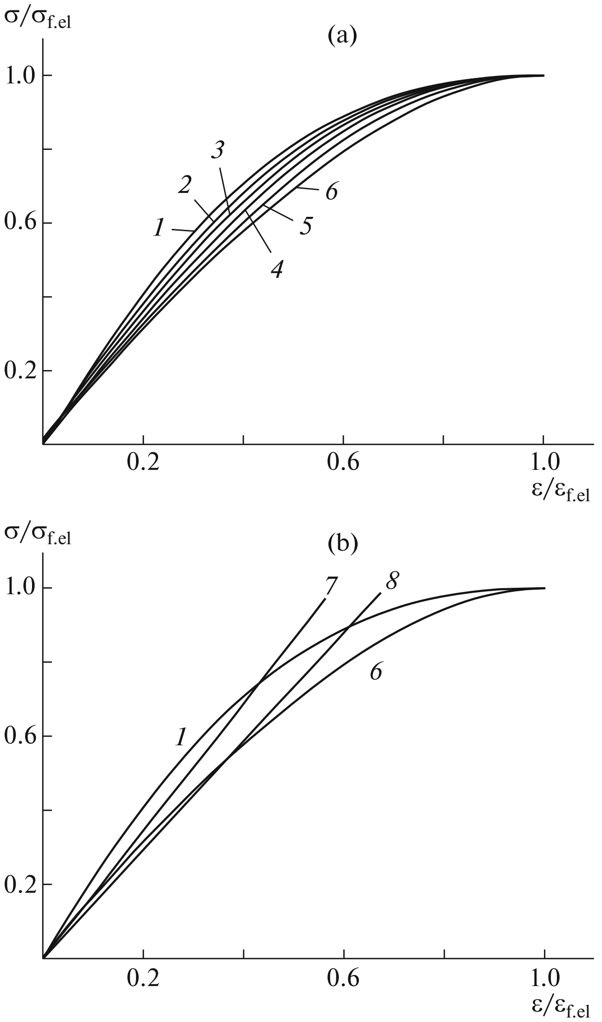

Fig. 1. (a) Plots of reduced stress vs. reduced strain for PC samples at a temperature of (*1*) 24, (*2*) 60, (*3*) 80, (*4*) 100, (*5*) 130, and (*6*) 150°C and a strain rate of 10^{-3} s^{-1}; (b) (*7*, *8*) initial portions of generalized stress–strain curve in accordance with Eq. (1) with allowance for a deviation of ±8%.

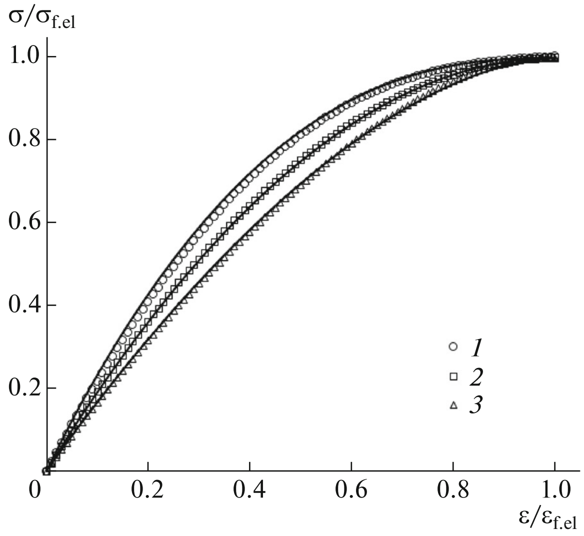

Fig. 2. Approximation of the experimental data for PC at $n = 2.5$, 2.0, and 1.72 and temperature of (*1*) 24, (*2*) 100, and (*3*) 150°C, respectively.

It is seen that all the parameters of Eq. (3) have a physical meaning: stress, strain, the modulus corresponding to the forced elasticity limit, and the elastic modulus of the polymer for the specified rate of loading and temperature.

Note that Eq. (1) written as

$$\frac{E_0}{E_{\mathrm{f.el}}} = 1.6 \qquad (6)$$

may be derived from Eq. (4) as a particular case of the tangent at the origin to the plot of Eq. (3) at $n = 1.6$.

Dependence (1), in accordance to the dissertation by M.S. Arzhakov [26], holds for polymers formed by such synthetic procedures as polymerization, including copolymerization and polycondensation, among which are PMMA, PVC, PS, PC, copolymers based on methyl methacrylate with methacrylic acid and butyl methacrylate, etc. The application of Eq. (1) to describing initial quasi-elastic deformation of the mentioned polymers also opens wide prospects to apply the proposed equation of the stress–strain curve (3) for describing full (to the forced elasticity limit) stress–strain curves with allowance for nonlinearity related to the development of rubbery deformation.

In the general case, exponent *n* may be calculated from the experimental data by two methods: using the least-squares procedure to approximate the stress–strain diagram by Eq. (3) and as the ratio of the elastic modulus of the polymer calculated from the stress–strain diagram on some final portion at the specified rate of loading and temperature and the modulus corresponding to the forced elasticity limit, which is estimated by the secant method using two points, namely, the origin and the forced elasticity limit.

Because of nonlinearity of the stress–strain diagram which manifests itself from the very beginning of the loading process, exponent *n* calculated by the second method will always be lower than exponent *n* determined by the first method, when *n* is calculated for a certain "initial" portion of the stress–strain diagram rather than for the time (point) of the onset of straining.

Because the software of modern testing machines makes it possible to fairly easily calculate exponent *n* via the second method, avoiding the labor-consuming approximation of the diagram portion to the forced elasticity limit through Eq. (3), the accuracy of determining exponent n by these methods was estimated (Fig. 3).

Averaged over all testing regimes, the accuracy of determining exponent n by the second method with respect to the first one was 12% for $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.2$ and 16% for $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.3$ regardless of the type of polymer and the character of loading. The above data demonstrate that the values of exponent n are considerably underestimated in the case of the second method. This finding should be taken into account when the second method is used in the engineering practice.

On the basis of the data considered above, exponent n in Eq. (3) was found to be sensitive to the temperature and rate of straining. Figure 4 shows its temperature–rate dependences under the hard regime of loading for PMAA (the strain control) and PC (the strain and displacement controls). The table presents the ranges of variation in exponent n.

A comparison the temperature–rate dependences obtained for PC in the temperature range from 20 to 120°C under two testing regimes, namely, the strain control and the displacement control (Figs. 4b, 4c), shows that there is good agreement between them.

An analysis of the obtained 3D surfaces makes it possible to conclude the following. First, for both polymers, there is the tendency toward a decrease in exponent n with an increase in the strain rate from 10^{-5} to 10^{-2} s^{-1}, especially in the case of strain control. Second, for PC at all loading rates (the displacement control), the maximum of n values is observed at a temperature of 20°C. Hence, it follows that for PC there are values of temperature and rate of loading at which the curvature of the stress–strain diagram shows a maximum.

Thus, the proposed stress–strain equation (3) describes the dependence of stress on strain with a high accuracy and holds much promise. It provides an opportunity to build a smooth curve devoid of disadvantages of the experimental stress–strain diagram, among which the presence of noises is the principal one. Moreover, it makes it possible to enhance the accuracy of calculations, for example, the stress–strained state of polymer articles [14], by using continuous stress–strain dependences instead of discrete values. Finally, this approach offers a way to construct the stress–strain diagram under testing regimes (temperature, loading rate, etc.) different from the experimental ones by means of determining the values of n via interpolation on the surface exponent n–temperature–rate of loading (Fig. 4).

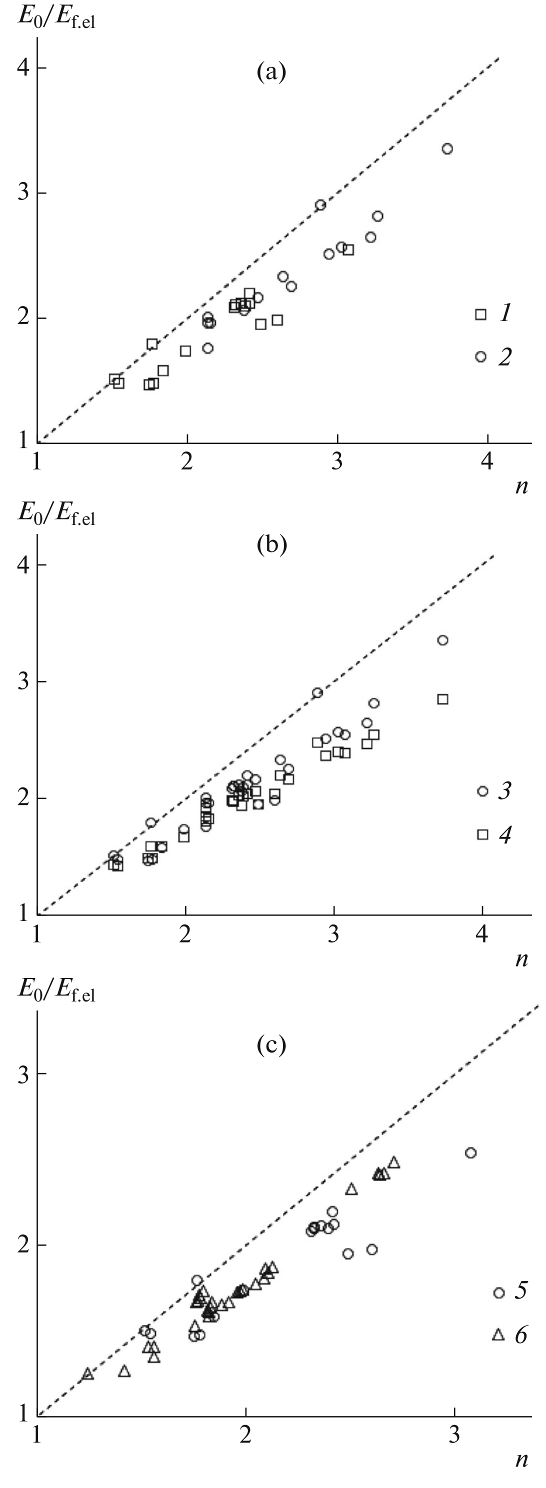

Fig. 3. Dependences of the ratios of elastic moduli $E/E_{\mathrm{f.el}}$ estimated from the stress–strain diagram on exponent n obtained by approximation of the stress–strain diagram by Eq. (3) (a) at $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.2$ for (*1*) PMMA and (*2*) PC and (b) at $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.2$ (*3*) and $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.3$ (*4*) for both materials; (c) under loading with (*5*) the strain control and (*6*) the displacement control for PC at $\varepsilon/\varepsilon_{\mathrm{f.el}} < 0.2$; the dotted curve refers to Eq. (5).

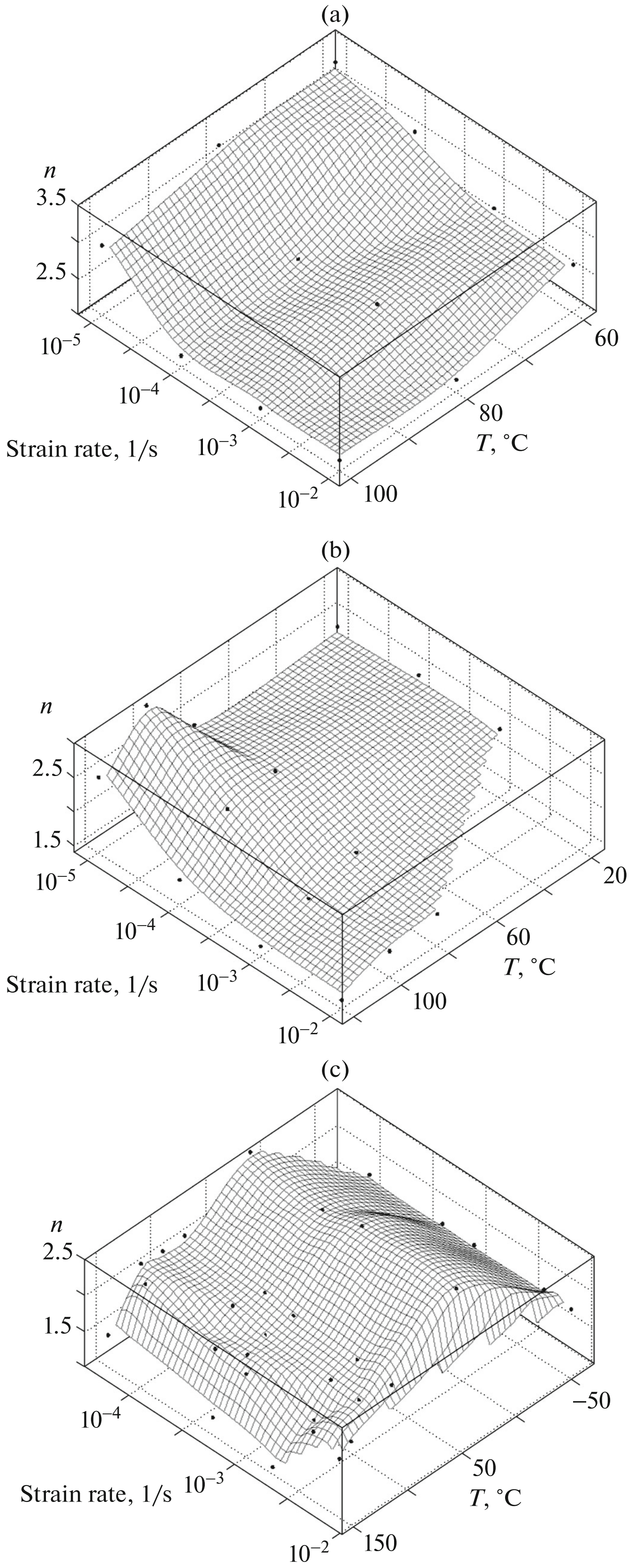

Fig. 4. Temperature–rate dependences of exponent *n* during loading with the strain control for (a) PMMA and (b) PC and (c) with the displacement control for PC.

Values of exponent n

Polymer	T_g, °C	N	T, °C	Controlling signal
PC	150	1.52–3.08	20–120	Strain
PC	150	1.10–2.71	–60 to 150	Displacement
PMMA	120	2.14–3.27	60–100	Strain

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REFERENCES

1. E. N. Kablov, Aviats. Mater. Tekhnol., No. 1 (34), 3 (2015).
2. E. N. Kablov, Ross. Khim. Zh. **54** (1), 3 (2010).
3. I. V. Mekalina, E. G. Sentyurin, S. F. Klimova, and V. A. Bogatov, Aviats. Mater. Tekhnol., No. 4, 45 (2012).
4. Yu. P. Gorelov, T. G. Chmykhova, and I. A. Shalaginova, Plast. Massy, No. **12**, 20 (2009).
5. I. V. Mekalina, V. A. Bogatov, T. S. Trigub, and E. G. Sentyurin, Tr. VIAM, No. **11**, 4 (2013).
6. E. N. Kablov, Vopr. Materialoved., No. 1, 64 (2006).
7. E. N. Kablov, Vestn. Ross. Akad. Nauk **72** (1), 3 (2002).
8. V. A. Bogatov, T. S. Trigub, I. V. Mekalina, and M. K. Aizatulina, Aviats. Mater. Tekhnol., No. 1, 21 (2010).
9. N. O. Yakovlev, Aviats. Mater. Tekhnol., No. S4, 50 (2014).
10. N. O. Yakovlev, E. G. Sentyurin, and G. M. Kharitonov, Tr. VIAM, No. **9**, 12 (2015).
11. G. M. Kharitonov, O. I. Khitrova, N. O. Yakovlev, and V. S. Erasov, Aviats. Prom-st, No. **3**, 7 (2011).
12. N. O. Yakovlev, I. V. Mekalina, and E. G. Sentyurin, Inorg. Mater.: Appl. Res **6** (4), 336 (2015).
13. N. O. Yakovlev, V. S. Erasov, E. G. Sentyurin, and G. M. Kharitonov, Aviats. Mater. Tekhnol., No. 2 (23), 66 (2012).
14. E. N. Kablov, N. O. Yakovlev, G. M. Kharitonov, and I. V. Mekalina, Entsikl. Sprav., No. 9, 2 (2016).
15. N. O. Yakovlev, V. S. Erasov, E. G. Sentyurin, and G. M. Kharitonov, Entsikl. Sprav., No. 10, 6 (2013).
16. K.-X. Hu and K.-Q. Zhu, Polym. Test. **30**, 797 (2011).
17. A. A. Askadskii, V. A. Markov, O. V. Kovriga, O. L. Lependina, V. V. Kazantseva, M. I. Buzin, A. A. Korlyukov, A. V. Golovanov, O. V. Pakhneva, and M. N. Popova, Polym. Sci., Ser. A **51** (5), 576 (2009).
18. P. M. Ogibalov, N. I. Malinin, V. P. Netrebko, and B. P. Kishkin, *Constructional Polymers* (Mosk. Gos. Univ., Moscow, 1972) [in Russian].
19. K. A. Adylkhanov, A. N. Titov, and V. N. Shcherbakov, Zavod. Lab., Diagn. Mater. **65** (8), 48 (1999).
20. K. Chen, K. S. Schweizer, R. Stamm, E. Lee, and J. M. Caruthers, J. Chem. Phys. **129**, 184904 (2008).
21. N. O. Yakovlev, Plast. Massy, Nos. 1–2, 36 (2015).
22. N. O. Yakovlev, Zavod. Lab., Diagn. Mater. **81** (5), 57 (2015).
23. M. S. Arzhakov, A. E. Zhirnov, G. M. Lukovkin, and S. A. Arzhakov, Russ. Metall. (Metally) **2010** (10), 851 (2010).
24. M. S. Arzhakov, G. M. Lukovkin, and S. A. Arzhakov, Dokl. Phys. Chem. **384** (4-6), 119 (2002).
25. G. M. Lukovkin, M. S. Arzhakov, A. E. Sal'ko, and S. A. Arzhakov, Deform. Razrushenie Mater., No. 6, 18 (2006).
26. M. S. Arzhakov, Doctoral Dissertation in Chemistry (MGU, Moscow, 2003).

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