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Specificity of statistics of elastic and strain-strength properties of high-strength polypropylene fibers

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Regularities of statistical distributions of a complex of mechanical properties, including the modulus of elasticity (E), strength (σ) and strain at break (ε_b), high-strength industrial oriented polypropylene (PP) fibers have been analyzed using the Weibull and Gauss models based on a large array of measurements (50 identical samples in each series). The values of the statistical Weibull modulus (m) — a parameter characterizing the scatter of the measured values of the data arrays of E , σ and ε_b have been estimated for the PP samples of two types: single fibers (monofilaments) and multifilament fibers consisting from several hundred single fibers. For the PP multifilament fibers, a more correct description of the distributions of E , σ and ε_b has been received both in the framework of the normal distribution (Gaussian distribution) and in the framework of the Weibull distribution in comparison with the description of such distributions for the PP monofilaments. The influence of the polymer chain conformation on the regularities of the statistical distributions of E , σ and ε_b for the high-strength oriented polymeric materials with different chemical chain structures and the correctness of their descriptions in the framework of the Gauss and Weibull models have been analyzed. For this purpose, the values of m calculated in this work for PP with a helical chain conformation have been compared with the values of m determined by us earlier for ultra-high molecular weight polyethylene and polyamide-6 with the chain conformations in the form of an in-plane trans-zigzag.

Keywords: polypropylene, mechanical properties, statistical analysis, Weibull distribution, Gaussian distribution.

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1. Introduction

High-strength high-modulus polymeric materials are promising reinforcing materials for application in various current technical fields that require increased mechanical characteristics (armor protection, missiles, aircraft and shipbuilding etc.), since high values of strength ($\sigma = 2\text{--}6$ GPa) [1–5] and modulus of elasticity ($E = 230$ GPa) [6], comparable with characteristics of inorganic materials, can be achieved for them [7–16]. A distinctive feature of certain polymeric materials (as a rule, highly-oriented) is the fact that the specific characteristics of their mechanical properties, standardized according to material density (ρ), are record-breaking as compared to all other materials. For instance, the ratio of σ to ρ for high-strength steel with the currently attained largest values of $\sigma = 1\text{--}2$ GPa [14–16] with the density of $\rho \approx 8000$ kg/m³ is $\sigma/\rho = (0.13\text{--}0.25) \cdot 10^{-3}$ GPa · m³/kg, while the value of σ/ρ for ultra-oriented gel-fibers of ultrahigh-molecular weight polyethylene (UHMWPE) with $\sigma = 6$ GPa [1–3] and $\rho \approx 1000$ kg/m³ can attain $6 \cdot 10^{-3}$ GPa · m³/kg, i.e. be in $\sim 25\text{--}50$ times greater than the one for steel. The value of this specific characteristic for UHMWPE may decrease as compared to other types of high-strength inorganic materials, e.g., quartz fibers

with $\sigma = 6$ GPa [9]. It remains rather noticeable even in this case, because the values of σ/ρ for quartz fibers at $\rho \approx 2600$ kg/m³ will be $\sigma/\rho = 2.3 \cdot 10^{-3}$ GPa · m³/kg, which is still ~ 3 times lesser as compared to the value of σ/ρ for UHMWPE.

However, an inevitable consequence of attained record-high values of polymeric material strength (up to 6 GPa) is an increase of their rigidity and, consequently, occurrence of surface structural defects of the rotation type under slightest bends and compressions (the so-called deformation bands that generate localized micro- and macrocrack [1–3]). These defects were shown in [3] to cause a significant increase in the scatter of experimental strength values, revealed during testing of a large number of identical samples. In such cases, determination of a statistically reliable averaged value of σ (σ_{av}) requires the obtaining of a large data array (several tens of parallel measurements) [3,7–13] instead of testing of maximum five samples usually used in practice [17–22]. This approach makes it possible not only to determine reliably the value of σ_{av} , but also to establish the type of statistical distribution σ , which seems to be very important for deeper understanding of material fracture mechanisms.

A number of papers showed (see, for instance, [3,5,7–13]) that the most correct description of strength distribution for brittle and quasi-brittle ultrastrong materials is provided by the Weibull statistics, initially suggested exactly for this material class [23]. At the same time, a Gauss model, most frequently used to describe the statistics of a wide range of properties, phenomena and processes of different natures, may turn out to be incorrect when describing the mechanical properties of ultrastrong quasi-brittle materials. In our opinion, the reason of suitability of this or that statistical model is based on the difference of approaches that underlie the notions of fracture mechanisms for high-strength oriented and conventional isotropic materials. In fact, while a Gaussian distribution (often called a normal distribution) (see, for instance, [24,25]) presupposes an equal-probability breakdown pattern in the whole sample volume, the key factor in a Weibull model [3,5,7–13] is the presence of dangerous defects (micro- and macroscopic cracks localized on the sample surface). Moreover, as has been shown in our previous papers [3,26–30], the correctness of applicability of this or that statistical model is determined by the material's deformational resource, i.e. the material brittleness/plasticity ratio. Actually, in some cases (for more plastic materials) we have demonstrated the manifestation of „statistical dualism“, which means that one and the same array of experimental strength values can be described using both a Gauss model and a Weibull model [27–29]. It must also be noted that, in this case, the type of the sample of a high-strength oriented polymeric material turned out to be critical, in particular, whether the sample is a single monofiber having a sufficiently large (for fibers) cross-section diameter ($\sim 100\text{--}200\ \mu\text{m}$) or a combination of several hundred thinner single fibers (having a diameter $\sim 1\ \mu\text{m}$) in the form of a bundle which, as such, is a statistical object. We think that this circumstance is a favorable factor for correct applicability of Gaussian statistics for a multifilament sample, even if the sample is quasi-brittle.

It must also be noted that the applicability of the Weibull model is not limited solely to a description of strength distribution, but can be extended also to a description of statistics of other equally important mechanical characteristics — elasticity modulus and strain at break (ϵ_b) [27,29]. Consequently, there is a possibility for a more complete characterization of high-strength oriented polymeric materials by extending the number of analyzed statistical mechanical properties.

A series of our previous papers [3,26–30] outlines a detailed study of statistical regularities in mechanical behavior of high-strength oriented polymeric materials based on linear polymers, UHMWPE and polyamide-6 (PA-6), having a chain conformation (mutual arrangement of chain sections in space) in the form of a flat trans-zigzag [31]. However, to our knowledge, polymer-based high-strength materials with a significantly different type of chain conformation have not been studied in this context. One of such

polymers is polypropylene (PP) with a heliciform chain conformation [31]. It can be expected that a change in chain conformation type can significantly affect the pattern of statistical distribution of PP-based materials' mechanical properties.

Thus, the goal of this paper is an analysis of statistical distribution of a complex of elastic and deformation-strength properties of oriented single and multifilament polypropylene fibers while using the Gauss and Weibull statistical models.

It should be noted that the Gauss model is the most widespread one in statistical analysis of databases of different natures, while the Weibull model is less frequently used for these purposes. Therefore, let us consider the main provisions of the Weibull model in more detail.

2. Weibull statistics

In a statistical Weibull model, the fracture probability for identical samples at a given or lower value of applied mechanical stress σ is determined as

$$P(\sigma) = 1 - \exp[-(\sigma/\sigma_0)^m], \quad (1)$$

where m is the so-called Weibull modulus, a statistical parameter which is a measure of dispersion of measurement results, σ_0 is the scale parameter which has the physical meaning of an average strength value (σ_{av}) [7–13,32]. To perform an analysis, the obtained array of test results for n samples is arranged in an increasing order of the value of σ and is converted into an experimental distribution of probabilities with assignment of the total fracture probability P_j to the j -th result. The value of P_j is determined by means of rather simple equations $P_j = f(j, n)$, the most correct of which is the equation (2) [32]:

$$P_j = (j - 0.5)/n. \quad (2)$$

After double logarithmation of the left and right members of the equation (1) and replacement of $P(\sigma)$ by P_j we get the equation (3):

$$\ln \ln[1/(1 - P_j)] = -m \cdot \ln \sigma_0 + m \cdot \ln \sigma. \quad (3)$$

Equation (3) is rather a simple linear equation

$$y = a + bx, \quad (4)$$

where $y = \ln \ln[1/(1 - P_j)]$, $a = -m \ln \sigma_0$, $b = m$ and $x = \ln \sigma$. Having determined m as the inclination angle of dependence $\ln \ln[1/(1 - P_j)] = f(\ln \sigma)$ using the standard linear regression analysis procedure, we can determine the parameter σ_0 by solving the equations (5) and (6):

$$\ln \sigma_0 = -a/m, \quad (5)$$

$$\sigma_0 = \exp(-a/m). \quad (6)$$

The distributions ε_b and E can be analyzed in a similar way [27,29]:

$$\ln \ln[1/(1 - P_j)] = -m \cdot \ln \varepsilon_0 + m \cdot \ln \varepsilon_b, \quad (7)$$

$$\varepsilon_0 = \exp(-a/m), \quad (8)$$

$$\ln \ln[1/(1 - P_j)] = -m \cdot \ln E_0 + m \cdot \ln E, \quad (9)$$

$$E_0 = \exp(-a/m). \quad (10)$$

Equations (7) and (9), where $x = \ln \varepsilon_b$ or $\ln E$, and $a = -m \cdot \ln \varepsilon_0$ or $-m \cdot \ln E_0$, also represent a simple linear equation (4), which makes them attractive for analyzing large arrays of measurements of ε_b and E .

3. Experimental part

3.1. Samples

The samples for the study were high-strength oriented industrial monofibers with a sample diameter of 0.17 mm and multifilament PP fibers (made in Russia) having a linear density of 1600 tex (this corresponds to an effective sample diameter of 0.05 mm).

3.2. Mechanical tests

To estimate strength, the samples of mono- and multifilament fibers having a length of 50 cm were elongated on an Instron-1122 tensile testing machine at room temperature at a cross-head speed of 200 mm/min in compliance with GOST 6611.2-73, i.e. with a deformation rate of 0.4 min^{-1} . Special cylindrical clamps from the manufacturer were used for the studied samples; the clamps were used to fasten and wind several fiber turns onto the cylinders' surface in order to prevent sample's slipping from the clamps. To obtain statistically reliable results, we tested 50 identical samples of PP mono- and multifilaments each, i.e. 100 samples in total.

4. Results and discussion

Figure 1 shows the typical stress-strain curves for samples of PP mono- and multifilaments. It is seen that the value of strain at break ε_b is about 10% for the samples of two types, which in the first approximation makes it possible to classify them as quasi-brittle materials, for which fulfillment of the equation (3) for strength can be anticipated within the Weibull model framework. For this purpose, the strength measurement results were arranged in an increasing order of their values depending on sample number n (see Fig. 2, *a*) and then rebuilt in coordinates $\ln \ln[1/(1 - P_j)] = f(\ln \sigma)$ (see Fig. 2, *b*). The results of analysis of the obtained data are given in Table 1. Linear approximations of each of the dependencies given in Fig. 2 during computer processing with the use of one straight approximating line (standard Weibull distribution function) were obtained with rather

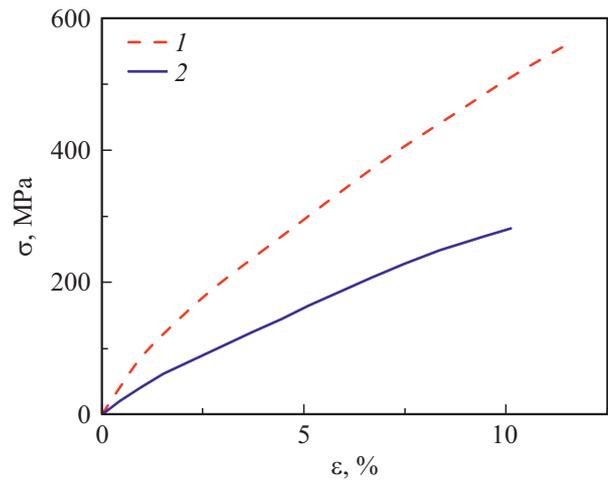


Figure 1. Stress-strain curves for high-strength oriented mono- (1) and polyfilament PP fibers (2).

high values of the determination coefficient $R^2 > 0.95$. Consequently, the results of the performed approximation seem to be correct. Thereat, it can be noted that the approximation for the multifilament ($R^2 = 0.973$) seems to be more correct as compared to the monofilament ($R^2 = 0.954$). Moreover, it is also necessary to note a twofold increase in the value of m for the multifilament ($m = 23.02$) as compared to the monofilament ($m = 12.02$), which means a significantly more narrow distribution of the experimental values for the multifilament samples.

In principle, during a more detailed consideration of the curves $\ln \ln[1/(1 - P_j)] = f(\ln \sigma)$, given in Fig. 2, *b*, each of the considered dependences, in particular the monofiber curve, can be described using two approximating lines with different inclinations: $m = 20.38$ and $m = 8.20$ for the monofiber and $m = 29.80$ and $m = 15.20$ for the multifilament sample. In this case, the results of computer processing of experimental strength values with $R^2 = 0.980$ and 0.986 (as compared to $R^2 = 0.973$ while using a straight line with one inclination) and $R^2 = 0.960$ and 0.975 (as compared to $R^2 = 0.954$ for a straight line with one inclination) for multi- and monofilament samples, respectively, turn out to be more correct. It should be noted that steeper sections, by definition corresponding to a smaller data spread, are typical for lower values of σ for the samples of two types.

Figures 2, *c* and 2, *d* show the histograms of the probability density function (PDF), obtained using the universally adopted approach (see, for instance, [24,25]), for the strength of a single fiber (*c*) and multifilament (*d*), analyzed with computer processing of the data given in Fig. 2, *a*, using the Gaussian function. The approximation results are shown by solid lines. It follows from the obtained processing results that, on the whole, the histograms for the samples of two types can be satisfactorily described by means of enveloping bell-shaped curves. However,

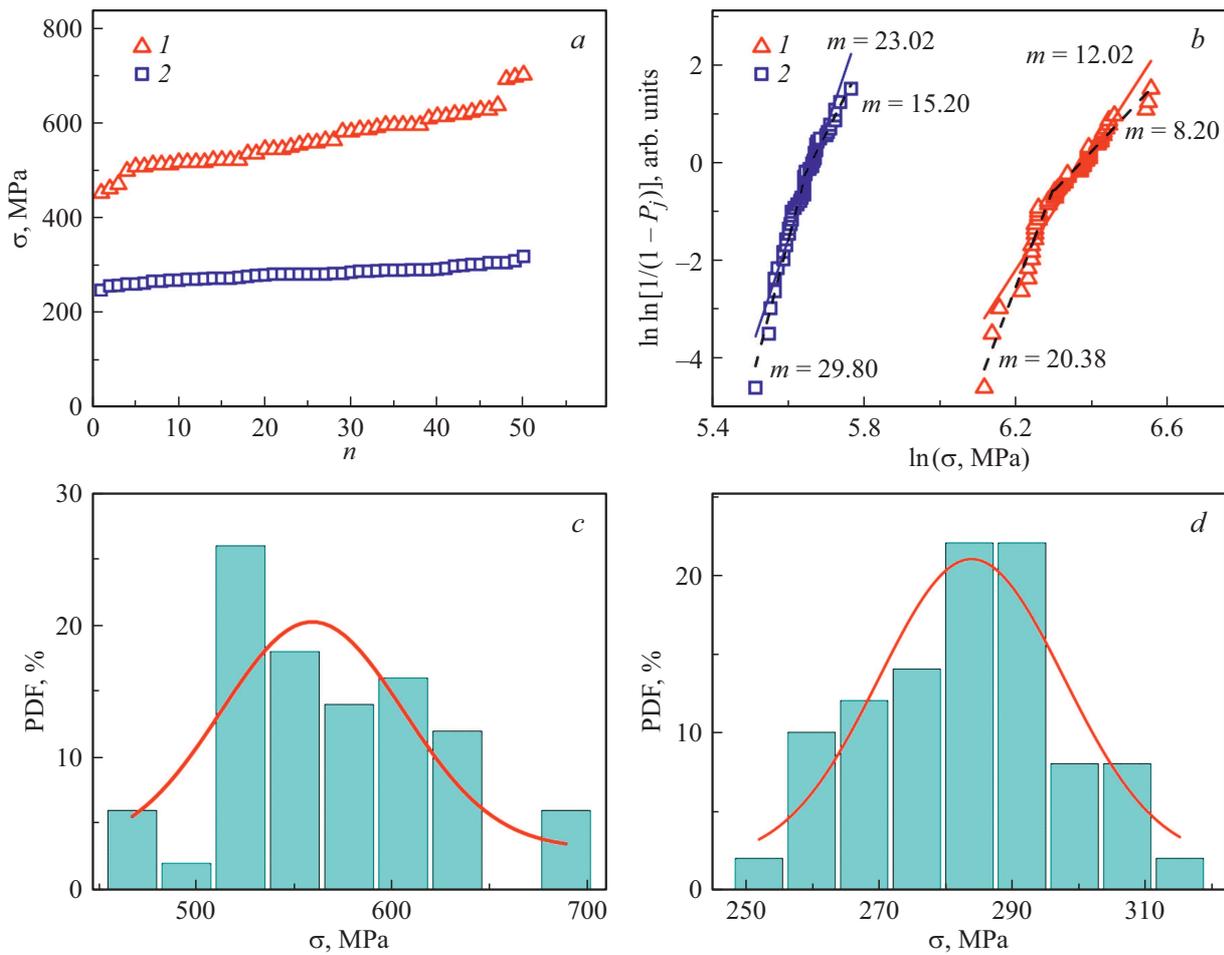


Figure 2. *a* — tensile strength σ in the increasing order of its value depending on sample number n for single (1) and multifilament fibers of oriented PP (2); *b* — Weibull diagrams plotted using the data presented in (*a*); the solid and dashed lines show the results of linear approximation in case of the use of a straight line with one inclination and two straight lines having different inclinations, respectively; *c, d* — histograms of the probability density function (PDF) for strength of a single (*c*) and multifilament PP fiber (*d*) and their description with the use of the Gaussian function (solid bell-shaped curves).

Table 1. Results of strength distribution analysis for high-strength mono- and multifilament polypropylene fibers within the Weibull model framework

Sample type	$y = a + bx$	R^2	m	σ_0 , MPa	σ_{av} , MPa	σ_0/σ_{av}
Monofilament	$y = -76.68 + 12.02x$	0.954	12.02	590	570	1.04
	$y = -128.89 + 20.38x^*$	0.960	20.38	560	570	0.98
	$y = -52.29 + 8.20x^*$	0.975	8.20	590	570	1.04
Multifilament	$y = -130.45 + 23.02x$	0.973	23.02	290	280	1.04
	$y = -168.44 + 29.80x^*$	0.980	29.80	286	280	1.02
	$y = -85.99 + 15.20x^*$	0.986	15.20	287	280	1.03

Note. * approximation in case of the use of two linear sections having different inclinations.

the theoretical distribution curve for the multifilament (see Fig. 2, *d*) more correctly describes the experimental data ($R^2 = 0.751$), as compared to the monofilament curve (see Fig. 2, *c*, $R^2 = 0.563$). Consequently, a description of strength distribution for oriented PP fibers in the form of multifilaments is more correct as compared to a description

of strength distribution for oriented PP fibers in the form of monofilaments when using both the Weibull function and the Gaussian function. In other words, the sample type considerably affects the degree of strength distribution homogeneity. Such behavior can be due to the following reasons.

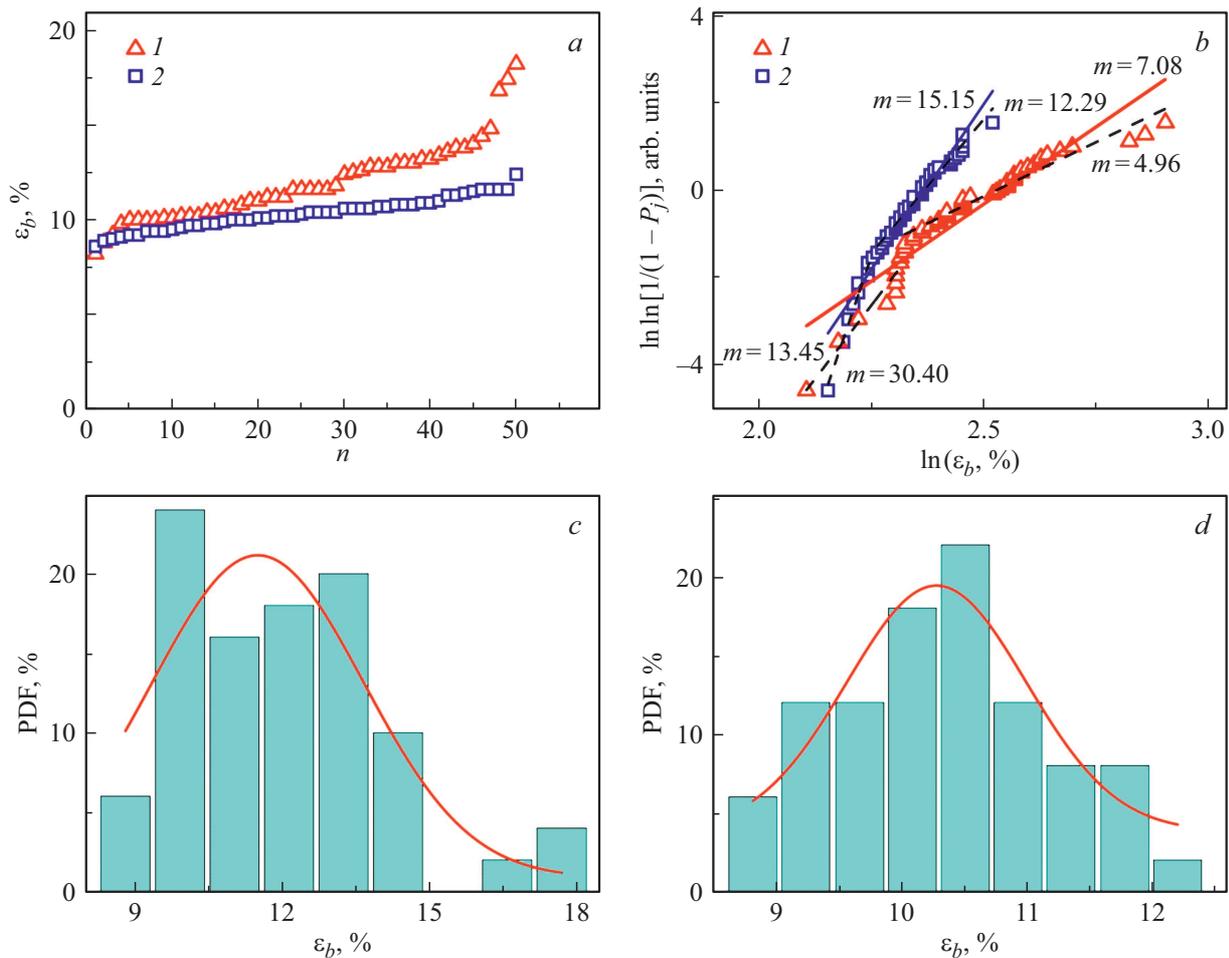


Figure 3. *a* — strain at break ε_b in the increasing order of its value depending on sample number n for single (1) and multifilament fibers of oriented PP (2); *b* — Weibull diagrams plotted based on the data presented in (a) (the same designations); the solid and dashed lines show the results of linear approximation in case of the use of a straight line with one inclination and two straight lines having different inclinations, respectively; *c, d* — histograms of the probability density function (PDF) for strain at break of a single fiber (*c*) and multifilament PP fiber (*d*) and their description with the use of the Gaussian function (solid bell-shaped curves).

As already noted, the multifilament sample (cord), comprising several hundred (~ 200) thin monofibers (filaments), is an object, a priori endowed with a statistical nature and is statistically more homogeneous as compared to the monofiber. Integral mechanical load applied to the cord will be distributed comparatively uniformly among its multiple filaments. Therefore, the presence of single dangerous structural defects (surface microcracks that initiate the fracture process) in some monofibers of such a cord will not necessarily cause the fracture of the whole sample, because a crack in one filament will stop propagating when it encounters another filament. This situation is fundamentally different from deformation of the monofiber, for which even a single dangerous defect (one microcrack) may initiate the fracture of the whole sample.

It should be also noted that the linear approximation results obtained using the Weibull model ($R^2 > 0.95$) seem to be more correct as compared to the approximation results obtained using the bell-shaped Gaussian curves

($R^2 < 0.76$). The obtained result means that, despite the more complex nature of bell-shaped dependences as compared to linear dependencies, which presupposes a lesser convergence of data (decrease of R^2) in the first case, the fracture mechanism for the studied mono- and multifilament PP fibers to a greater extent corresponds to quasi-brittle materials than to plastic ones.

While using the above-mentioned approaches, let us analyze the nature of the statistical distributions of another mechanical characteristics at fracture of oriented PP multifilaments (strain at break ε_b). For this purpose, the two large arrays with the measured values of ε_b (50 values for each of the two sample types), considered in Fig. 3, *a*, were rebuilt in Weibull coordinates $\ln \ln[1/(1 - P_j)] = f(\ln \varepsilon_b)$ (see Fig. 3, *b*). Then they underwent linear approximation by computer processing in order to find out their compliance with the equation (7). The analysis results are given in Table 2. It is seen that, when an approximating line with one inclination is used (standard Weibull distribution function),

Table 2. Results of strain at break distribution analysis for high-strength mono- and multifilament polypropylene fibers within the Weibull model framework

Sample type	$y = a + bx$	R^2	m	$\varepsilon_0, \%$	$\varepsilon_{av}, \%$	$\varepsilon_0/\varepsilon_{av}$
Monofilament	$y = -18.01 + 7.08x$	0.937	7.08	12.7	11.7	1.09
	$y = -32.89 + 13.45x^*$	0.966	13.45	11.6	11.7	0.99
	$y = -12.54 + 4.96x^*$	0.974	4.96	12.6	11.7	1.08
Multifilament	$y = -35.88 + 15.15x$	0.971	15.15	10.7	10.3	1.04
	$y = -69.86 + 30.40x^*$	0.988	30.40	9.97	10.3	0.97
	$y = -29.09 + 12.29x^*$	0.988	12.29	10.7	10.3	1.00

Note. * approximation in case of the use of two linear sections having different inclinations.

the obtained dependence is characterized by determination coefficients $R^2 = 0.94$ and 0.97 for mono- and multifilament fibers, respectively.

This means that the approximation result seems to be correct for the multifilament, but for the monofilament it is better to use two tangent lines, since the value of R^2 upon transition from a single inclination to two inclinations increases from 0.94 to 0.97 . A similar procedure for analysis of a multifilament curve makes it also possible to considerably increase approximation reliability (increase of R^2 from 0.97 to 0.99). Consequently, in any case, when we compare the results of approximation both using two segments of straight lines having different inclinations and one straight line with a single inclination, values of m for the multifilament is always 2–2.5 times greater than the corresponding values of m for the monofilament.

Thus, as in the previously considered case for breaking strength, the distribution of strain at break for the samples of multifilament PP fibers is significantly narrower as compared to its distribution for single PP fibers.

Let us also note that the ratio of the parameter ε_0 , calculated using the equation (8), to the average value of ε_b , ε_{av} , in all the considered cases is $\varepsilon_0/\varepsilon_{av} \approx 1$ (see Table 2), which also confirms the correctness of Weibull model application for analyzing the statistical distribution ε_b of high-strength PP mono- and multifilaments.

The results of the statistical analysis for the values of ε_b within the Gauss model framework are given in Figs. 3, *c* and 3, *d*. It is seen that the distribution curve for the multifilament (see Fig. 3, *d*) is more symmetrical as compared to the curve for the monofilament (see Fig. 3, *c*). Moreover, approximation for the multifilament is characterized by a higher value of $R^2 = 0.766$ as compared to the monofilament ($R^2 = 0.593$). Consequently, a description of the distribution ε_b within the Gauss model framework for the multifilament is more correct than for the monofilament.

A comparison of the results of computer processing of values ε_b with the use of two different statistical models shows that the linear approximation results obtained using the Weibull model ($R^2 > 0.93$) seem to be more correct as compared to the approximation results obtained using bell-shaped Gaussian curves ($R^2 < 0.77$), as in the strength case considered above. They confirm the above-mentioned

conjecture on correspondence of the fracture mechanism for the studied mono- and multifilament PP fibers to the fracture mechanism for quasi-brittle materials, where the main role in the sample fracture plays surface cracks.

Let us consider the peculiarities of statistical distributions for another very important mechanical characteristic during practical application of high-strength oriented PP fibers — their elasticity modulus E . For this purpose, the two arrays of the values of E for PP mono- and multifilaments, shown in Fig. 4, *a*, were analyzed in compliance with the Weibull model (see Fig. 4, *b* and Table 3) and Gauss model (see Figs. 4, *c* and 4, *d*). As is seen from the results of computer processing for the Weibull diagrams given in Fig. 4, *b* and in Table 3, approximation of a straight line with one inclination can be considered as satisfactory only for PP multifilaments ($m = 21.54$, $R^2 = 0.939$). It is unsatisfactory for PP monofilaments ($m = 11.20$, $R^2 = 0.866$), which requires approximation using two tangent straight lines to the analyzed curve. This procedure yields the values of $m = 125.75$ and $m = 7.71$ for regions with lower and higher values of E , respectively.

It should be noted that the very high value of $m \approx 126$, calculated for the given statistical characteristic in the region of lower values of $E < 8$ GPa, does not seem to be unrealistic, since it is comparable to the values of $m = 74$ – 76 and $m = 98$, obtained for ultrastrong ($\sigma = 4$ – 6 GPa) fibers of the organic (UHMWPE [3,26]) and inorganic natures [7–13], respectively. The fact of a considerable exceedance (by more than one order of magnitude) by value $m = 126$ of value $m \approx 8$, calculated for the region of higher values of $E > 8$ GPa, means an abrupt decrease of the data spread for PP monofilament in the region of lower values of E . One is inclined to think that a certain part of the tested PP monofilaments ($\sim 25\%$), owing to the comparatively large fiber diameter ($170 \mu\text{m}$), underwent less homogeneous deformation along the sample cross-section in the course of manufacture. This caused the attainment of lower, but better reproducible values of E .

If we analyze the dependence $\ln \ln[1/(1 - P_j)] - \ln E$ in Fig. 4, *b* for multifilaments by approximation with the use of two tangent lines, then the value of $m = 29.06$ obtained at lesser values of E will be also greater than the value of $m = 17.98$ for greater values of E , as in the monofilament case. However, the ratio of these two

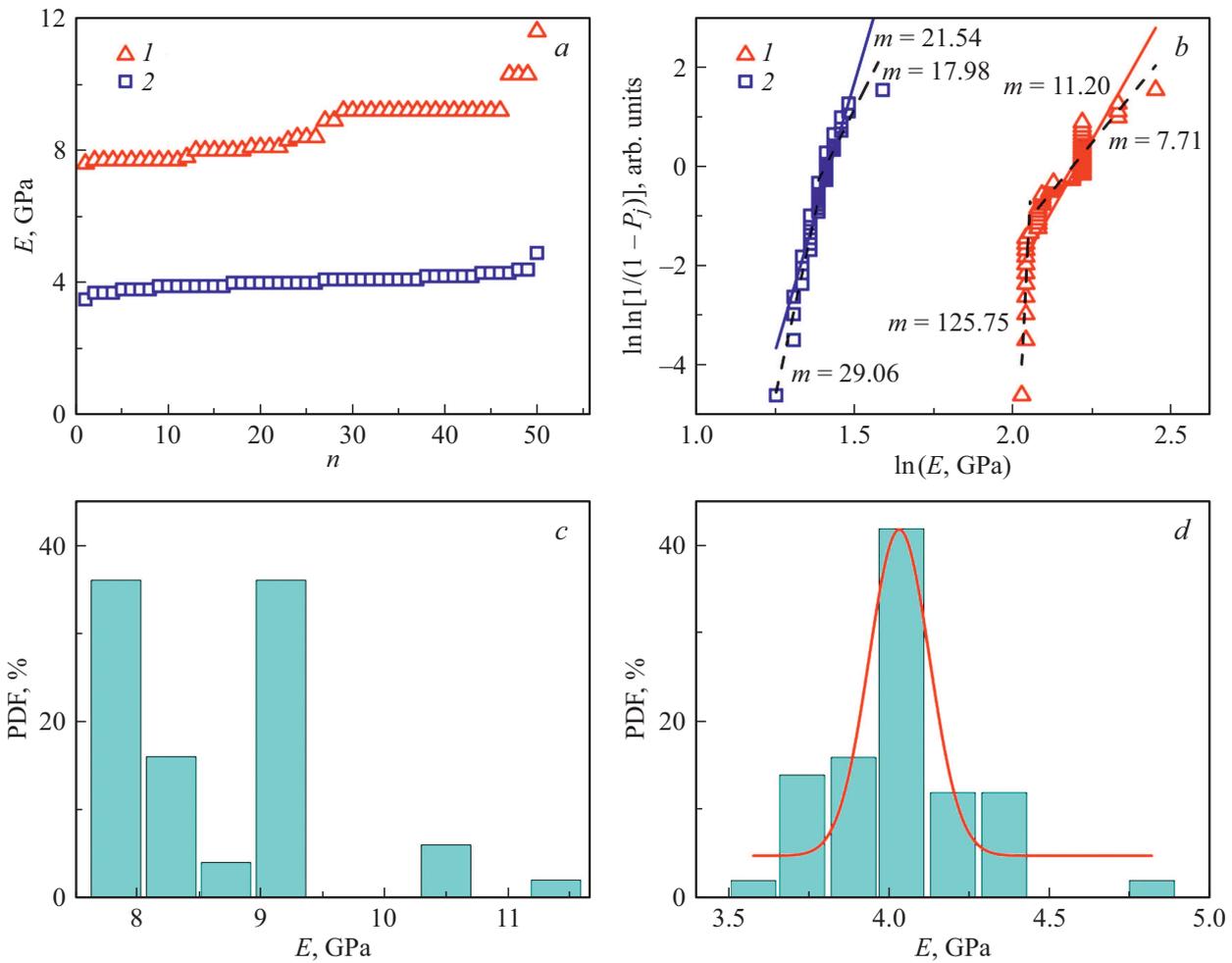


Figure 4. *a* — elasticity modulus E in the increasing order of its value depending on sample number n for single fibers (1) and multifilaments of oriented PP (2); *b* — Weibull diagrams plotted using the data presented in (*a*); the solid and dashed lines show the results of linear approximation in case of the use of a straight line with one inclination and two straight lines having different inclinations, respectively; *c, d* — histograms of the probability density function (PDF) for the elastic modulus of a single fiber (*c*) and polyfilament PP (*d*); solid bell-shaped curve on (*d*) — result of computer processing when using the Gaussian function.

Table 3. Results of analysis of elasticity modulus distribution for high-strength polypropylene mono- and multifilaments within the Weibull model framework

Sample type	$y = a + bx$	R^2	m	E_0 , GPa	E_{av} , GPa	E_0/E_{cp}
Monofilament	$y = -24.67 + 11.20x$	0,866	11.20	9.06	8.64	1.05
	$y = -259.02 + 125.75x^*$	0.723	125.75	7.85	8.64	0.91
	$y = -16.88 + 7.71x^*$	0.927	7.71	8.94	8.64	1.03
Multifilament	$y = -30.64 + 21.54x$	0.939	21.54	4.15	4.00	1.04
	$y = -40.95 + 29.06x^*$	0.969	29.80	4.10	4.00	1.02
	$y = -25.38 + 17.98x^*$	0.964	17.98	4.11	4.00	1.03

Note. * approximation in case of the use of two linear sections having different inclinations.

values of m is considerably lesser than ($\sim 29/18 < 2$) as compared to the corresponding ratio of the values of m for monofilaments ($\sim 126/8 > 10$). It means that scatter of the values of E for multifilaments is more homogeneous as compared to monofilaments.

Let us also note the closeness of the average measured values of E , E_{av} , and theoretical values of E_0 , calculated using the equation (10), for all the cases considered above. The observed fulfillment of the condition $E_0 \approx E_{av}$ (see Table 3) confirms the correctness of the performed analysis

Table 4. Values of statistical Weibull modulus m , calculated from the distribution curves of σ , ε_b and E for high-strength mono- and multifilament polypropylene fibers in linear approximation using one inclination

Sample type	Characteristic		
	σ	ε_b	E
Monofilament fiber	12.02	7.08	11.20
Multifilament fiber (cord)	23.02	15.15	21.54

of the statistical distributions of E within the Weibull model framework.

In conclusion, let us consider the PDF histograms depending on the value of E (see Figs. 4, *c* and 4, *d*) to find out their correspondence to the Gaussian distribution. It follows from the data in Fig. 4, *c* that an enveloping bell-shaped curve cannot be obtained for a single fiber with computer processing of the experimental data. At the same time, such a curve, typical for a normal distribution (or Gaussian distribution), is observed for the multifilament (see Fig. 4, *d*). The revealed difference can be due to the following reasons. It appears that in the case of multifilaments, consisting of several hundreds of very fine ($\sim 1 \mu\text{m}$) monofiber threads (monofilaments), the applied integral mechanical tensile load is averaged among a large number of monofilaments, thereby preventing the detection of an abrupt boundary of a crossover of a change in E , revealed for a single fiber. Such behavior can be also explained by more perfect orientation drawing when producing monofilaments (PP) as compared to the technology of PP multifilament production, which is confirmed by higher (in 2 times) values of E and strength for monofilaments as compared to the values of E and σ for multifilaments (see Fig. 4, *a* and Fig. 2, *a*).

The summary Table 4 summarizes the statistical analysis results for the distribution curves of σ , ε_b and E for high-strength mono- and multifilament PP fibers, obtained by linear approximation of Weibull diagrams with the use of one inclination. It is necessary to note that, the value of m for multifilaments is always ~ 2 times greater than the corresponding value of m for monofilaments for all the three studied mechanical characteristics. In other words, the established difference between the values of m for the samples of two types is a constant, both for the elasticity modulus (E) and for mechanical breaking characteristics (σ and ε_b). This circumstance seems to be rather unexpected because these two different types of mechanical characteristics are controlled by different molecular-structural mechanisms. As is known [3,7–12], the critical role in case of breaking characteristics is played by surface cracks, while in case of determination of E , at the initial deformation stages, the cracks' role is negligible, and the main role is played by rigidity of an individual chain.

The higher values of m for multifilaments, which mean a lesser data scatter, can be related to the already noted statistical nature of the multifilament sample, which ensures

a more uniform (as compared to the monofiber) distribution of the applied mechanical load among multiple filaments.

Regarding the approximation results for the distribution curves of σ , ε_b and E within the Gauss model framework, the bell-shaped curves, typical for the given distribution type, for PP multifilaments were obtained for all the three studied mechanical characteristics (see Figs. 2, *d*, 3, *d* and 4, *d*). At the same time, such curves for PP monofilaments can be obtained only for strength and strain at break (see Figs. 2, *c* and 3, *c*), thereat, their shape is considerably more asymmetric as compared to multifilaments. In other words, on the whole, the computer processing results for monofilaments seem to be less correct than for multifilaments.

Thus, the statistical distributions of all the three studied mechanical characteristics (strength, strain at break and the elastic modulus) for PP multifilaments can be described correctly both within the Weibull model framework and within the Gauss model framework when analyzing the same experimental results. In our opinion, in this case the „dualism“ of statistics of σ , ε_b and E manifests itself; we have observed it earlier for the strength of multifilament fibers of PA-6 [28] — a polymer with a different chain conformation type: in-plane trans-zigzag.

The revealed manifestation of the statistical dualism in the distribution of elastic and deformation-strength mechanical characteristics for PP-based materials can be caused by the following factors. On the one hand, though the values of $\varepsilon_b = 8\text{--}17\%$ for the studied plastic polypropylene materials exceed the values of $\varepsilon_b < 5\%$ for quasi-brittle materials, for which the Weibull model was the most efficient, both deformation intervals ε_b are same-order values. Therefore, applicability of the Weibull model is also possible in the interval ε_b from 8 to 17%. On the other hand, it has turned out that the Gaussian statistics is also applicable for multifilament samples, because this material is statistically more homogeneous (several hundreds of single fibers deform simultaneously). This system corresponds to a normal distribution of the fracture process along the sample cross-section, regardless of the fracture mechanism. Moreover, multifilament PP fibers are characterized by relatively small values of the elasticity modulus $E = 3\text{--}5 \text{ GPa}$ and greater values of strain at break (8–17%), i.e. they have a certain plasticity resource. This circumstance is also a favorable factor for correct description of the statistical distribution of mechanical characteristics within the Gauss model framework.

The values of $m = 7\text{--}23$ determined in this paper for high-strength mono- and multifilament PP fibers (see Table 4), in particular for multifilaments ($m = 15\text{--}23$), are higher as compared to the values of m from the literature for ultrastrong ultra-oriented (drawn in 120 times) UHMWPE samples ($m = 7\text{--}10$) [26,27,30], quartz ($m = 12$) [9], ceramic ($m = 8\text{--}9$) [7], glass and carbon fibers ($m = 3\text{--}11$) [8,13], as well as carbon nanotubes ($m = 3\text{--}7$) [11]. This means a lesser scatter of the experimental data in the case of PP-based materials;

it can be explained by the more pronounced plasticity of the studied PP fibers (greater strain at break $\varepsilon_{av} = 10\text{--}11\%$) as compared to quasi-brittle ultrastrong materials ($\varepsilon_{av} < 5\%$). This argument correlates with the observation of higher values $m = 43\text{--}45$ for strength of a rather plastic soft high-strength material — polyamide-6 ($\varepsilon_b = 16\%$) [28,29]. Moreover, the strength of PP plastic fibers ($\varepsilon_{av} = 0.3\text{--}0.6$ GPa) is significantly, by an order of magnitude, lower as compared to the strength of brittle ultrastrong materials ($\varepsilon_{av} = 2\text{--}6$ GPa), which may also lead to an increase in the data scatter (a decrease in the values of m) for the latter ones.

It should be also noted that the Weibull modulus values $m = 7\text{--}23$ for the PP-based materials (heliciform chain conformation) are intermediate between the values of $m = 7\text{--}10$ and $m = 43\text{--}45$ [3,26–30], calculated by us for the materials based on UHMWPE and PA-6, respectively, that have the conformation of in-plane trans-zigzag. Consequently, the impact of the chain conformation type on the value of scatter of mechanical characteristics of polymers' oriented fibers is ambiguous. Its clarification requires further additional studies involving polymeric materials having other types of the chain chemical structure.

5. Conclusion

Using the example of high-strength polymeric materials (multifilament PP fibers with a heliciform chain conformation) it has been shown that the distributions of elastic (E) and deformation-strength mechanical characteristics (σ and ε_b) can be correctly described using two statistical approaches, the Weibull and Gauss approach, which are based on different concepts for describing the probability of material mechanical fracture. The obtained data confirms the occurrence of statistical dualism in the distribution of mechanical properties, which we have found earlier [26–30] for high-strength materials based on other polymers (UHMWPE and PA-6 with the chain conformation of the in-plane trans-zigzag type).

The parameters of the Weibull distribution for the oriented mono- and multifilament PP fibers have been determined based on a large statistical data array (50 measurements of identical samples for each material type). It was established that the values of the statistical Weibull modulus m (data scatter characteristics) for each of the three studied mechanical properties of the multifilament fibers are 2 times greater than the corresponding values of m for the single fibers. This means that the data scatter during mechanical tests of multifilament fibers is much lesser than for the monofibers. This result is related to a more pronounced statistical homogeneity of the multifilament fibers composed of several hundreds of thin single fibers. The results of this paper confirm the significant impact of the sample type on the specificity of experimental data scatter, found previously for the UHMWPE-based ultrastrong materials [30]. It was shown that the impact of the chain conformation on the

value of mechanical characteristics scatter is ambiguous and requires further clarification.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] V.A. Marikhin, L.P. Myasnikova. Structural basis of high-strength high-modulus polymers. In: *Oriented Polymer Materials* / Ed. S. Fakirov. Huthig & Wepf Verlag-Zug, Heidelberg (1996). P. 38–98.
- [2] V. Marikhin, L. Myasnikova, Y. Boiko, E. Ivan'kova, E. Radovanova, P. Yakushev. Role of Reactor Powder Morphology in Producing High-strength High-modulus UHMWPE Fibres. In: *Reactor Powder Morphology* / Ed. L. Myasnikova, P. Lemstra. Nova Publishers, Hauppauge, N.Y, Ch. 10 (2011). P. 235–294.
- [3] Yu.M. Boiko, V.A. Marikhin, L.P. Myasnikova, O.A. Moskalyuk, E.I. Radovanova. *J. Mater. Sci.* **52**, 3, 1727 (2017).
- [4] Yu.M. Boiko, V.V. Kovriga. *Intern. J. Polym. Mater.* **22**, 1–4, 209 (1993).
- [5] R. Marissen, D. Wienke, R. Homminga, R. Bosman, K.M. Veka, A. Huguet. *Mater. Sci. Appl.* **7**, 5, 238 (2016).
- [6] Yu.M. Boiko, V.A. Marikhin, O.A. Moskalyuk, L.P. Myasnikova. *Physics of the Solid State* **61**, 1, 182 (2019).
- [7] D.M. Wilson. *J. Mater. Sci.* **32**, 10, 2535 (1997). doi: 10.1023/A:1018538030985.
- [8] F. Tanaka, T. Okabe, H. Okuda, I.A. Kinloch, R.J. Young. *Composites A*, **57**, 2, 88 (2014).
- [9] L.G. Baikova, T.I. Pesina, M.F. Kireenko, L.V. Tikhonova, C.R. Kurkjian. *Technical Physics* **85**, 6, 83 (2015).
- [10] K.-H. Nitta, C.-Y. Li. *Physica A* **490**, 1076 (2018). doi: 10.1016/j.physa.2017.08.113.
- [11] A.H. Barber, R. Andrews, L.S. Shaudler, H.D. Wagner. *Appl. Phys. Lett.* **87**, 203106 (2005).
- [12] G. Sun, J.H.L. Pang, J. Zhou, Y. Zhang, Z. Zhan, L. Zheng. *Appl. Phys. Lett.* **101**, 131905 (2012).
- [13] M.R. Gurvich, A.T. Dibenedetto, A. Pegoretti. *J. Mater. Sci.* **32**, 14, 3711 (1997).
- [14] M. Aguiari, M. Palombo, C.M. Rizzo. *Welding World* **65**, 289 (2021).
- [15] C. Maraveas, Z.C. Fasoulakis, K.D. Tsavdaridis. *Fire Sci. Rev.* **6**, 3, 1 (2017).
- [16] Y. Huang, X. Jin, G. Cai. *J. Mater. Res.* **32**, 20, 3894 (2017).
- [17] Yu.M. Boiko, I.G. Kuznetsova, V.V. Kovriga, A.Ya. Goldman, A.M. Tarasov, V.A. Artemyev, G.D. Myasnikov. *Mekh. komp. mater.* **23**, 2, 202 (1987) (in Russian).
- [18] Yu.M. Boiko, V.V. Kovriga, A.Ya. Goldman. *Polymer Science A* **33**, 9, 1972 (1991).
- [19] Yu.M. Boiko, W. Brostow, A.Ya. Gol'dman, A.C. Ramamurthy. *Polymer* **36**, 7, 1383 (1995).
- [20] L. Laiarinandrasana, Y. Nziakou, J.L. Halary. *J. Polym. Sci. B* **50**, 1740 (2012).
- [21] Yu.M. Boiko, M.Ya. Sherman. *Polymer Science A* **40**, 2, 279 (1998).
- [22] Yu.M. Boiko, I.G. Kuznetsova, S.A. Unezheva, V.V. Kovriga, L.A. Gann. *Mekh. komp. mater.* **29**, 1, 3 (1993) (in Russian).
- [23] W. Weibull. *J. Appl. Mech.* **18**, 9, 293 (1951).
- [24] E.I. Kulikov. *Prikladnoy statisticheskiy analiz* (2008). 464 p. (in Russian).

- [25] J.K. Patel, C.B. Read. Handbook of the Normal Distribution. 2nd ed. Statistics: Handbooks and Monographs. **150**, N.Y. Marcel Dekker, Inc (1996). 456 p. ISBN 0-8247-9342-0.
- [26] Yu.M. Boiko, V.A. Marikhin, O.A. Moskalyuk, L.P. Myasnikova, E.I. Radovanova. Physics of the Solid State **58**, *10*, 2065 (2016).
- [27] Yu.M. Boiko, V.A. Marikhin, L.P. Myasnikova, E.I. Radovanova. Colloid Polym. Sci. **296**, *10*, 1651 (2018).
- [28] Yu.M. Boiko, V.A. Marikhin, O.A. Moskalyuk, L.P. Myasnikova, E.S. Tsobkallo. Technical Physics Letters **45**, *8*, 37 (2019).
- [29] Yu.M. Boiko, V.A. Marikhin, O.A. Moskalyuk, L.P. Myasnikova, E.S. Tsobkallo. Technical Physics Letters **45**, *14*, 20 (2019).
- [30] Yu.M. Boiko, V.A. Marikhin, O.A. Moskalyuk, L.P. Myasnikova. Physics of the Solid State **62**, *4*, 590 (2020).
- [31] P. Flory. Statistical mechanics of chain molecules. Mir, M. (1971). 440 p. (in Russian).
- [32] J.D. Sullivan, P.H. Lauzon. J. Mater. Sci. Lett. **5**, 1245 (1986).