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POLYMERS

Statistical Analysis of the Strength of Ultra-Oriented Ultra-High-Molecular-Weight Polyethylene Film Filaments in the Framework of the Weibull Model

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Abstract—A statistical analysis of the distribution of the tensile strength σ of ultra-oriented ultra-high-molecular-weight polyethylene (UHMWPE) film filaments has been performed in the framework of the Weibull model using the results obtained from a large number (50) of measurements. The UHMWPE film filaments have been produced by means of high-temperature multistage zone drawing of xerogels prepared from 1.5% UHMWPE solutions in decalin. The Weibull modulus has been determined for this type of materials. It has been shown that, for the ultimate draw ratio λ = 120, the average tensile strength is equal to 4.7 GPa, which is significantly higher than the tensile strength σ = 3.5 GPa for commercial gel-spun UHMWPE fibers manufactured by the DSM Company (The Netherlands) and the Honeywell International Incorporation (United States). It has been demonstrated that, for 20% of the specimens thus prepared, the tensile strength reaches record-high values σ = 5.2–5.9 GPa.

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1. INTRODUCTION

Gel-spun ultra-oriented film filaments and fibers based on ultra-high-molecular-weight polyethylene (UHMWPE), which are characterized by high values of tensile strength (σ > 3 GPa) and elastic modulus (more than 120 GPa) [1], are considered to be very promising materials. More than half of their industrial production has been used for the fabrication of armor protection tools and equipment. These materials have also been used for the manufacturing of ropes, cables, networks, sports equipment, etc.

Usually, mechanical characteristics of polymeric materials, including ultra-high strength gel fibers, are determined by averaging the results obtained from a relatively small number of measurements (about five tests [1, 2]). However, using the example of ultra-high strength high-modulus inorganic materials, which exhibit extremely high tensile strengths σ = 8 GPa (carbon fibers) [3], 6–7 GPa (glass and silica fibers) [4], 3–4 GPa (ceramic fibers) [5], and others, it has been shown that, for a sufficiently large database of measurements of tensile strength σ (up to 50), the statistics of the tensile strength distribution is more adequately described in the framework of the Weibull model [3–22]. At the same time, to the best of our knowledge, this statistical model has not been used to analyze the strength properties of high-strength materials of organic nature. But, since ultra-oriented gel-spun UHMWPE films and fibers are quasi-brittle and characterized by a low strain at break (less than 5%) [1], for these ultra-oriented polymeric materials, as well as for the aforementioned brittle inorganic materials, the Weibull model can also be valid for the description of the tensile strength distribution.

Thus, the purpose of this study was to determine the applicability of the Weibull model [7] to the description of a statistical strength distribution of ultra-oriented gel-spun UHMWPE film filaments using the results of a large number of measurements.

In the Weibull model, the cumulative probability function $P(\sigma)$, which describes the probability of failure of a specimen for this or lower value of the tensile strength σ (the weakest-link statistics), has the following form for completely identical specimens (the standard Weibull model) [3–22]:

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

where m is the so-called Weibull modulus (i.e., it is a parameter, the reciprocal of which characterizes the dispersion of the strength) and σ_0 is a constant.

The simplest estimator of the probability $P(\sigma)$, which will be designated as P_j, is the equation

$$P_j = j/(n+1), \quad (2)$$

where j and n are the serial number of the specimen and the total number of specimens for experimental values of strength in ascending order, respectively. However, using several estimators of this type ($P_j = (j \pm a)/(n \pm b)$, where a and b are numerical coefficients), the authors of [8] showed that the most correct of them is the equation

$$P_j = (j - 0.5)/n. \quad (3)$$

It turned out that the deviations of the Weibull modulus m from the average value, which were obtained using this equation for several test series of identical specimens, have a minimum value, including the deviations of m found from equation (2). Therefore, in the present study, the probability P_j is determined from equation (3).

Usually (see, for example, [5, 7–11]), the distribution of the tensile strength in the framework of the Weibull model is analyzed in the coordinates $\ln\ln[(1/(1-P_j))]$–$\ln\sigma$. This is a consequence of transforming equation (1) and taking a double logarithm of its left-hand and right-hand sides:

$$\ln\ln[(1/(1-P_j))] = m(\ln\sigma - \ln\sigma_0). \quad (4)$$

Further, the statistical distribution of the tensile strength will be analyzed in the framework of this equation using the results of measurements for 50 specimens of ultra-high strength gel filaments formed from 1.5% UHMWPE solutions in decalin. The Weibull modulus m will be determined from the slope of the dependence $\ln\ln[(1/(1-P_j))] = f(\ln\sigma)$.

2. PREPARATION OF SPECIMENS AND THEIR TESTING

In our investigations, we used UHMWPE with the viscosity-average molecular weight $M_\eta = 3 \times 10^6$ g/mol.

A weighed portion of the UHMWPE powder (calculated for a 1.5 mass % polymer solution) in the presence of an antioxidant (di-*tert*-butyl-*p*-cresol, 0.1 mass % with respect to the mass fraction of the polymer) was placed in a vial with a solvent (decalin) and immersed into a heat-transfer liquid in the Huber CC-308 ultrathermostat heated to a temperature of 100°C. Then, the temperature was raised to the dissolution temperature of the polymer (120°C) with continuous stirring. The stirring was stopped as soon as the viscosity of the solution began to increase rapidly due to the transition to a gel state. Thereafter, the stirrer was removed from the solution contained in the vial, and instead of it a reflux condenser with a ground glass stopper was inserted into the vial. The gel solution was heated to 160°C and kept at this temperature for one hour in order to homogenize the solution. The transparent homogeneous gel solution thus prepared was poured into a Petri dish at room temperature. The rapid cooling and subsequent crystallization resulted in the transition of the solution to a liquid-gel state with the formation of a porous structure consisting of randomly oriented interconnected stacks of lamellae. After drying, wet gels transformed into the so-called xerogels, i.e., opaque films that have retained a specific lamellar wet-gel structure. The volume of the solution poured into the Petri dish was chosen so that, after the drying of the gel, the thickness of the xerogel film amounted to 80–100 μm. The xerogel was prepared by the removal of the solvent through the evaporation at room temperature for three days.

The as-prepared xerogel films were cut with a specially designed instrument into narrow strips with a width of approximately 1 mm and then were subjected to high-temperature multistage zone drawing using a contact heater on a laboratory setup according to the method described in [1]. By varying the orientation load and increasing the drawing temperature up to 139–141°C, i.e., up to the melting temperature of the polymer in an unloaded state, we obtained ultra-oriented high-strength UHMWPE film filaments with a ultimate draw ratio $\lambda = 120 \pm 10$.

The ultra-oriented UHMWPE film filaments thus prepared were stretched to failure on an Instron-1122 universal tensile testing machine at room temperature. The drawing rate was 10 mm/min. The distance between the jaws of the tensile testing machine was 10 mm. In order to obtain a reliable statistics, we measured the tensile strength of 50 specimens.

3. RESULTS AND DISCUSSION

The results obtained from measurements of the tensile strength σ for the ultra-oriented UHMWPE film filaments with the draw ratio $\lambda = 120$, which were prepared by means of high-temperature multistage zone drawing of the xerogels, are presented in ascending order of the strengths σ in Fig. 1. The tests performed for the first time for this type of materials with a large number (50) of specimens demonstrated that the tensile strength σ is characterized by a rather wide distribution in the high-strength range from 4.0 to 5.9 GPa. Therefore, in order to obtain reliable mechanical characteristics for this type of materials, it is necessary to analyze a large number of measurements (at least a few tens), rather than to be restricted to 5–10 measurements, which are usually presented in the scientific literature.

It should be noted that the values of σ reached in our measurements are very high, because the arithmetic mean strength $\sigma = 4.7$ GPa is 25% higher than the value of $\sigma = 3.5$ GPa achieved for commercial gel-spun UHMWPE fibers Dyneema (DSM Company, The Netherlands) and Spectra (Honeywell International Incorporation, United States) (see promotional

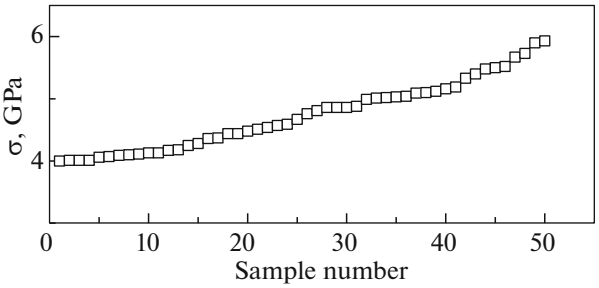

Fig. 1. Tensile strength distribution curve of ultra-oriented UHMWPE film filaments with the draw ratio λ = 120 in ascending order of strengths σ. The film filaments were prepared from the 1.5% solution in decalin.

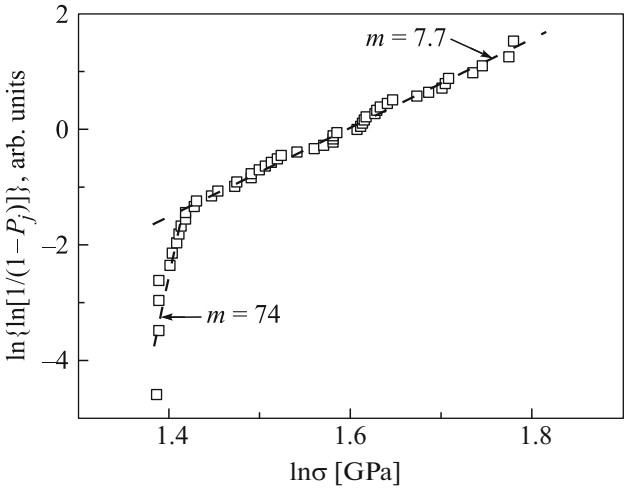

Fig. 2. Data presented in Fig. 1 after their processing using equations (3) and (4). Dashed lines show the results of the least-squares analysis of two parts of the curve.

materials of these companies). Furthermore, for 20% of the fractured specimens, the tensile strength reaches record-high values σ = 5.2–5.9 GPa. This means that the resource of strength of commercial samples prepared from UHMWPE gels has not yet been completely exhausted.

The data presented in Fig. 1 are plotted in Fig. 2 in the coordinates ln ln[(1/(1 – P_j))]–lnσ using equations (3) and (4). It is interesting to note that, for the UHMWPE film filaments under investigation, the obtained curve is characterized by two parts, each having quite different slopes, in contrast to brittle inorganic materials [3–18], the strengths of which are usually approximated by a single straight-line curve obtained by averaging the set of experimental data (although, in some cases, changes in the strength are not fit into a single straight line). We believe that the reliable presence of two parts in the distribution curve of the tensile strength of the UHMWPE film filaments under investigation is due to a good statistics of measurements (50 specimens). The Weibull moduli m were determined, for the first time, from the slopes of two parts of the tensile strength distribution curve using the least-squares method. It was found that m = 74 for 20% of the low-strength specimens with a narrow dispersion of the tensile strength σ and m = 7.7 for 80% of the high-strength specimens with a wide dispersion of σ. In other words, the difference between the values determined above, which amounts to one decimal order, is enormous. This behavior can be explained by the following factors.

As is known [1], extremely oriented high-strength polyethylene specimens are characterized by the formation of defects of a particular type, or, more specifically, macroscopic rotation defects, i.e., the so-called kink bands observed in the near-surface layers. This phenomenon is caused by the disruption of a number of macro- and microfibrils, the release of the entropy energy stored in them, and the development of compressive stresses in the direction opposite to the orientational forces, which result in the formation of kink bands. It is also known [23–25] that, at the boundaries of the kink bands, due to a sharp bend of closely spaced fibrillar elements, there arise submicroscopic discontinuities that coalesce during the loading, which increases the probability of propagation of the main crack in them and the failure of the specimen. Apparently, two sharply different slopes of the distribution curve of the tensile strength σ (Fig. 2) indicate the existence of specimens with very different numbers of "critical" kink bands that facilitate the extension of the main crack in the specimens with lower values of σ under the mechanical loading as compared to higher-strength specimens. It is interesting to note that the narrow distribution of the tensile strength (m = 74) is observed in a very narrow strength range σ = 4.0–4.1 GPa, which is critical for this type of materials. In other words, the negative effect exerted by defects in these specimens on the homogeneity of the structure of their material reaches its apogee. As a result, they exhibit properties typical of quasi-brittle materials.

It should also be noted that the minimum value of the Weibull modulus m = 7.7 determined in the present study is close to the values of m for silica fibers (m = 12) [4], ceramics (m = 8–9) [8], carbon nanotubes (m = 4–7) [6], glass and carbon fibers (m = 3–11) [3, 9], which are brittle materials. This means that the wide tensile strength distribution range for the majority (80%) of specimens studied in this work is also consistent with the mechanism of failure of brittle inorganic materials. This behavior is hardly surprising, because the specimens of ultra-oriented UHMWPE film filaments under investigation can be considered as quasi-brittle materials due to low values of strains during their failure (less than 5%) [1]. Therefore, the brittleness of inorganic and ultra-oriented polymeric materials is primarily caused by surface defects (narrow cracks and kink bands in the former and latter materials, respectively).

4. CONCLUSIONS

It was shown that the use of high-temperature multistage zone drawing makes it possible to obtain extremely oriented gel-crystallized UHMWPE film filaments with the average tensile strength σ = 4.7 GPa, which significantly exceeds the tensile strength of commercial UHMWPE fibers (σ = 3.5 GPa) manufactured by the leading foreign companies using the gel technology. The strength distribution of these materials was analyzed in terms of the Weibull statistics using the results obtained from 50 measurements under the conditions of short-term loading, and the Weibull modulus m was also determined for this type of materials. It was found that the tensile strength distribution exhibits specific features in the form of a narrow dispersion of the tensile strength σ in the low-strength range σ = 4.0–4.1 GPa (m = 74) and a wide dispersion in the high-strength range σ > 4.1 GPa (m = 7.7). It was demonstrated that, for 20% of the fractured specimens, the tensile strength reaches values in the range σ = 5.2–5.9 GPa, which are among the highest values according to the world's scientific and patent literature.

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