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Dynamical Young's Modulus and Internal Friction in Ultra-High Molecular Weight Polyethylene Composites

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Abstract

This work is devoted to the acoustic spectroscopy investigation of self-reinforced ultra-high molecular weight polyethylene composites made of pressed unidirectional sheets stacked orthogonally to each other. The studied samples demonstrate excellent mechanical properties in a wide temperature range from –5 °C to 50 °C. The relative change in the modulus of longitudinal elasticity for all samples in the studied temperature range did not exceed 1.6%. Depending on pressure value that is used at the stage of fabrication, the studied samples demonstrated dynamic Young's modulus values up to 17.8 GPa and internal friction up to $16\cdot10^{-2}$. Quasi-static mechanical properties are measured using the specimens of various shapes by tensile test. The values of Young's modulus, determined in the elastic part of the tension curves, reach 16.9 GPa.

Keywords: Ultra-high molecular weight polyethylene; UHMWPE; Self-reinforced composite; Young's modulus; Internal friction

1. INTRODUCTION

The first research works on ultra-high molecular weight polyethylene (UHMWPE) can be dated to the 1980s [1]. The difference between UHMWPE and high-density polyethylene is high average molecular weight and average chain length, more than 10^6 g/mol and 10^5 bonds, respectively. The properties of this material depend on the bonds between the amorphous and orthorhombic crystalline phases provided by tie molecules, volumetric percentage of crystallites and their alignment. The melting point of UHMWPE depends on the crystallinity and ranges from 142 °C to 147 °C [2]. In addition to being used in the form of an isotropic material reinforced with other materials or mechanically activated, UHMWPE is actively used in the form of fibers.

The fibers of UHMWPE have excellent tensile properties — modulus and strength, due to a highly oriented crystalline microstructure with a large number of secondary bonds. They are used as a reinforcing component in composite materials due to their high strength-to-weight ratio, good toughness and high wear resistance [3]. Achieving the required high parallel orientation and crystallinity of the long chains in these fibers is made possible by a special semi-melt spinning process [4]. In this method, a solvent of polyethylene polymer molecules is heated and mixed thoroughly, after which it is squeezed out through spinnerets into a cooling solvent. The strength of such fibers is ten times higher than that of steel, but it is still far from the theoretical strength of the C–C covalent bond. UHMWPE fiber family include Spectra® (Honeywell Specialty Materials, USA), Dyneema® (DSM, Netherlands). Claimed performance for Dyneema SK77 is 4.0 GPa tensile strength, 140 GPa tensile modulus, and 3.7% ultimate strain. Spectra 2000 fibers have similar performances: 3.7 GPa, 132 GPa and 2.9% for the respective properties. With a density of 0.97 g/cm^3, the specific properties of fibers from both manufacturers are the best achieved so far [5].

Various surface modification techniques are used to optimize the adhesion and improve other properties of

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fibers after extrusion [6]. As a result, regular micro- and macrostructures increase the high specific surface area of the UHMWPE fibers at different scales and promotes mechanical adhesion to the matrix of composite materials reinforced by them. Unidirectional (UD) material from UHMWPE is produced by winding yarn from the fibers onto a flat mandrel and pressing them into single-ply plate. With the use of such plates, it is possible to create self-reinforced polymer composites with different layers stacking and the technology of their consolidation.

The wide range of applications of composites based on UHMWPE is due to their special properties, which allow them to be used under extreme conditions. Known for their use in medicine, mechanical and electrical engineering, shipbuilding, but they have the greatest potential as ballistic protection materials. UHMWPE composites are used in bulletproof vests [7], vehicle protection as a standalone armor plates [8], or as a backing layer for composite ceramics armor plates [9]. They are used to create hard shells of ballistic helmets [10]. In the last decade, significant progress has been made in the research and development of UHMWPE composites used to optimize ballistic impact and overall dynamic deflection feature [11].

Mechanical behavior of UHMWPE composites under high-velocity impact is critical for the design of any armor application. The tensile strength of fibers follows a certain statistical distribution and is usually described by the Weibull function [12]. Single-oriented composite tensile strength can be calculated within the framework of the micromechanics approximation determined by the rule of mixtures if the parameters for UD material are known [13]. This approach, however, is difficult to apply when alternating the stacking orientation of individual layers. Orthogonal stacking of adjacent layers, in comparison with parallel stacking, leads to a decrease in the anisotropy of mechanical properties on a macroscale. However, it leads to a significant change in the microstructural characteristics of the interface between the fiber and the matrix and a decrease in crack resistance during delamination [14]. In several publications, attempts were being made to create combined experimental – numerical methods for predicting the change in the ballistic limit in UHMWPE composites with different stacking sequences [11,15]. There exist constitutive models that describe the behavior of such materials based on experimental results including stress-strain curves in different planes in tension and compression, out-of-plane load curves, strain rate, delamination phenomena, and strain based on failure criteria [16–18]. Thus, precise experimental data are needed to describe the basic elastic and plastic properties of UHMWPE composites.

Quasi-static tensile testing of UHMWPE multilayer composite is difficult to perform due to low interlayer shear strength. Low-frequency methods for measuring the Young's modulus, like dynamic mechanical analysis, for these materials show a large scatter of values associated with the significant influence of macroscopic defects, sample sizes and the method of preparation. The interpretation of the effect of high frequency elastic wave propagation in UHMWPE composites can become a fundamental basis for confirming their properties and constructing models for their destruction. The most important of the mechanical parameters describing this process are Young's modulus and damping of elastic waves in the material (internal friction). They can be measured using the piezoelectric ultrasonic oscillator method [19].

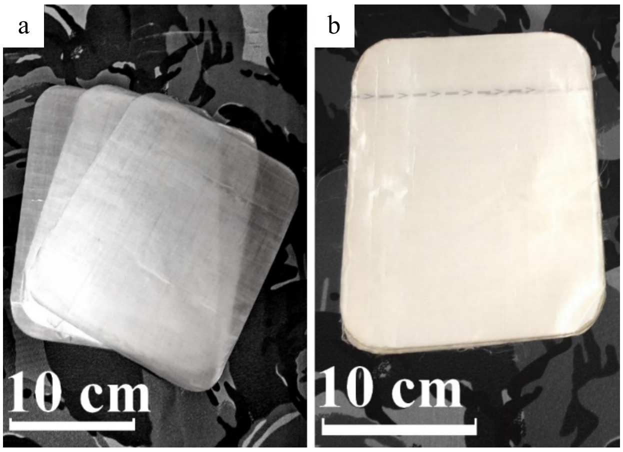

Fig. 1. The UD layers (a) and molded slab (b) of UHMWPE composite.

2. METHODS

The materials studied in this work were so-called cross-ply UHMWPE composites. Fig. 1a shows the UD layers before the molding process. To ensure the required mechanical properties of the manufactured composites during the molding process, the temperature was precisely maintained. Its values do not exceed 140 °C. UD plates were welded from 23 orthogonal layers at various pressures. With a variation in a small range of exposure time of about two hours, phased degassing was carried out. The slabs of the finished multilayer composite (Fig. 1b) had dimensions of about 165×165×4 mm with a mass up to 0.085 kg and other characteristics given in Table 1.

Young's modulus and damping of elastic waves in the studied materials were determined using the piezoelectric ultrasonic oscillator method at a frequency close to 100 kHz [19]. For the resonant frequency of samples f the following equation was used:

$$m_q f_q \cdot \mathrm{tg}\frac{\pi f_c}{f_q} + m_s f \cdot \mathrm{tg}\frac{\pi f_c}{f} = 0, \quad (1)$$

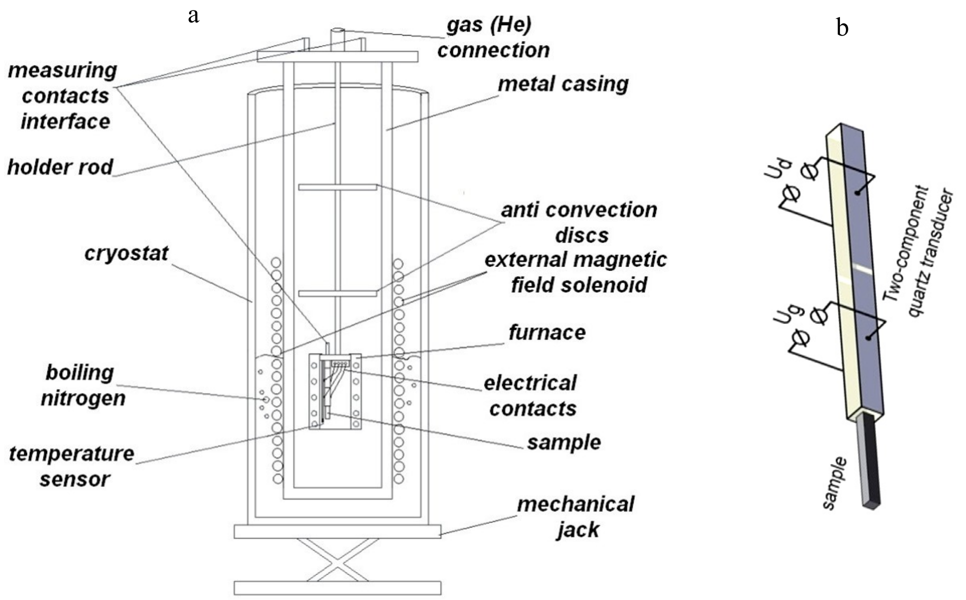

Fig. 2. Functional diagram of the measuring cell (a) and a quartz oscillator with a sample (b).

where m_q and m_s are the masses of the quartz transducer and of the sample, f_q and f_c are the resonant frequencies of the quartz transducer alone and with the sample attached, respectively. The Young's modulus of the materials E was calculated from the resonant frequency of the longitudinal oscillations f in the sample of length l and density ρ:

$$E = 4\rho \frac{f^2 l^2}{n^2}. \quad (2)$$

In the case of the initially unknown value of Young's modulus, its search was carried out in a certain admissible range, while the resonant length of the sample could correspond to different harmonics $n = 1, 2, 3\ldots$ The scheme of the measuring cell and the quartz oscillator with the sample are shown in Figs. 2a and 2b, respectively. To study the Young's modulus and the damping of elastic waves (δ), samples of a rectangular section of about 3×4 mm were cut out from the composite slab.

Precise experimental determination of the Young's modulus by this method is possible with a known density of the material. These values were measured by standard displacement method using a GH-252 (A&D Company) analytical balance with accurate temperature control by a V7-78/1 (AKIP) meter and isopropanol as a medium. The measured density values are also shown in Table 1.

To compare the data of the dynamic values of Young's modulus with the static ones, tensile tests were carried out using the INSTRON 5966 universal testing system. Specimens of various shapes were conditioned and tested at a temperature of 23 °C, a test speed of 20 mm·min^{-1} and a constant force on pneumatic grips.

3. RESULTS AND DISCUSSION

The length of the samples successively decreased from 50 mm, which at a given density corresponded to the maximum acceptable values of $E < 100$ GPa. By fixing the cut samples on the oscillator (Fig. 3a) and searching for a resonance in the frequency range up to 140 kHz and strain amplitude up to $\varepsilon = 10^{-5}$, the lengths corresponding to condition (2) were determined. In this way, two types of specimens with multiple lengths were prepared (Fig. 3b). The characteristics of the samples used for measurements are given in Table 1.

The values of Young's modulus measured on long samples (Fig. 4) decreased monotonically with temperature change from –5 °C to 50 °C and the maximum slope

Table 1. Dimensions and characteristics of the samples.

№ of plate	Number of layers	Pressure (MPa)	Plate mass (kg)	Plate thickness (mm)	Density (kg/m^3)	First resonant length (mm)	Second resonant length (mm)
N1	23	15	0.084	3.5	0.975	18.45	36.68
N2	23	7	0.083	3.7	0.973	17.81	35.77
N3	23	2	0.084	3.8	0.972	11.55	23.52

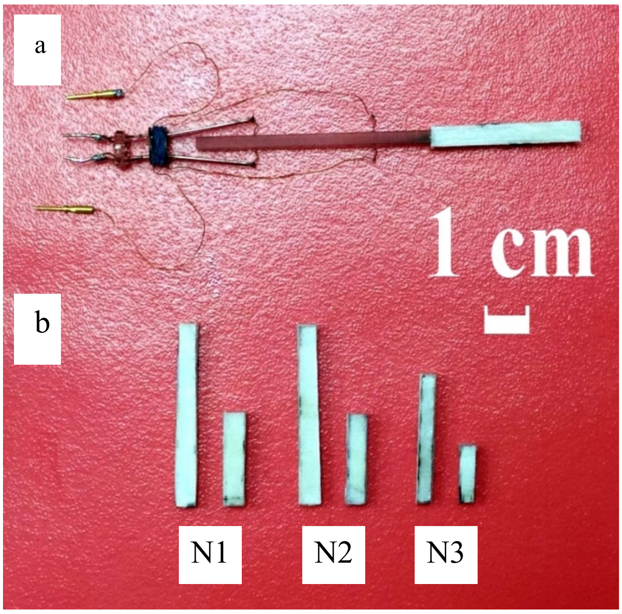

Fig. 3. Quartz oscillator with a glued sample cut from a N2 plate (a) and other samples with a resonant length at the first (short) and second (long) harmonics (b).

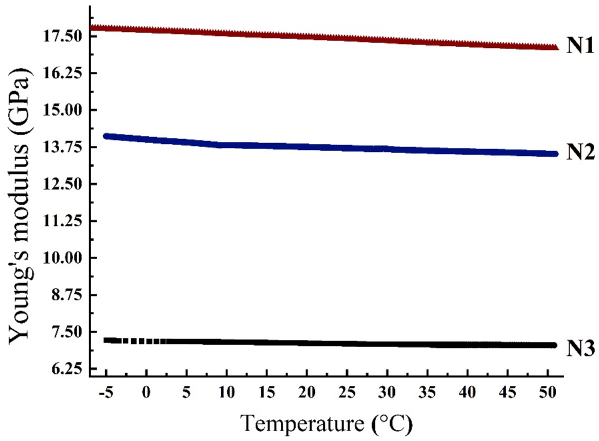

Fig. 4. Temperature dependences of Young's modulus measured in long samples (second harmonics).

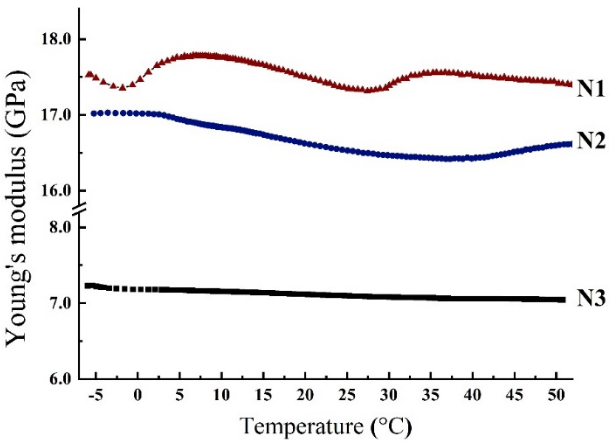

Fig. 5. Temperature dependences of Young's modulus measured in short samples (first harmonics).

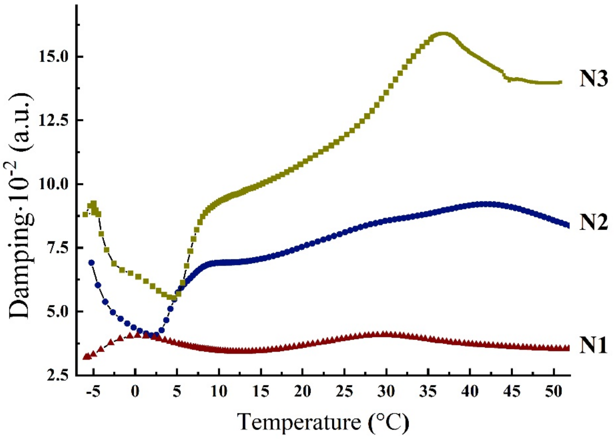

Fig. 6. Temperature dependences of damping of elastic waves measured at the first harmonics.

corresponded to a N1 sample of material pressed at 15 MPa. The elasticity increased at high sintering pressures. The relative change in Young's modulus is also maximum for sample N1 and in the temperature range under consideration is up to 1.6%. The temperature dependences of Young's modulus measured in short samples were more non-linear (Fig. 5). However, for these samples, a lower value of damping and a higher measurement repeatability were observed. The dynamic values of Young's modulus measured in both types of samples at frequency of 100 kHz are shown in Table 2.

All samples showed a high level of internal friction $\delta > 10^{-2}$. The attenuation of elastic waves in a material pressed at a lower pressure (N3) depended especially strongly on temperature. It had the highest values and a pronounced maximum at about 37 °C (Fig. 6). The internal friction in the material sintered under the highest pressure had the least temperature non-linearity. In general, for all materials under study, elastic effects (Young's modulus) and internal friction showed a standard inverse relationship.

Samples after tensile tests are shown in Fig. 7. On straight-sided specimens with small cross section (38.5 mm^2), delamination and breakage of the upper layers were observed. The fibers at the fracture surfaces were cut off uniformly perpendicular to the tensile loading direction in accordance with the creep failure (Fig. 7a). In the width-tapered specimens with a similar cross section the delamination was less pronounced. However, the integrity of the upper layers was violated from the grip section in the gauge direction. In such specimens, the destruction occurred from the surface to the inner layers of the gauge section with the pulling out of the fibers (Fig. 7b). Samples with large cross section (81.3 mm^2) and straight shape (Fig. 7c) showed the best result in measurements repeatability inside the elastic region. The values of Young's

Table 2. Young's modulus and internal friction in samples at room temperature.

№ of plate	Young's modulus in short samples at 100kHz (GPa)	Young's modulus in long samples at 100kHz (GPa)	Young's modulus tensile testing (GPa)	Internal friction in short samples at 100kHz (a.u.)·10^{-2}
N1	17.3	17.4	16.9	11.6
N2	16.5	13.7	—	7.9
N3	7.0	7.1	6.5	3.9

Fig. 7. Specimens after tensile testing: straight-sided (a), width-tapered (b) and large cross section (c).

modulus obtained by tensile tests for specimens N1 and N2 were less than dynamic ones (Table 2).

Up to now, there exist no values of Young's modulus and internal friction measured by the composite piezoelectric oscillator method. However, it is known that the tensile modulus and its loss in self-reinforced UHMWPE composite can undergo a number of relaxation processes [20]. These processes depend on the stacking orientation and method of consolidation of adjacent layers. The so-called β-relaxation temperature for cross-linked UHMWPE is below 0 °C, while the α-relaxation temperature is above 50 °C. Features of the behavior of curves of this type can be observed in short samples (Figs. 5 and 6). Due to the high-frequency measurement method used in this work, some relaxation processes may have no time to finish. Thus, an increase in the strain rate can lead to the avoiding of the effects of twisting, kinking and pulling out of the fibers [18,21]. It leads to an increase in the values of the dynamic Young's modulus and to a decrease in internal friction compared to quasi-static ones. It is also worth bearing in mind that the thermal activation nature of some processes makes a greater contribution at high frequencies of elastic waves.

4. CONCLUSIONS

The piezoelectric ultrasonic oscillator method has been used to measure the mechanical characteristics of UHMWPE composites. It has been demonstrated that it is necessary to account for the high attenuation of elastic waves in the samples and correctly select their length in accordance with the mode of longitudinal vibrations. The best repeatability measurements have been obtained for the first harmonic. In general, these values correspond to quasi-static ones at room temperature. The lower level of damping of elastic waves in short samples makes it possible to measure their parameters in the range of low strain amplitudes up to $\varepsilon = 10^{-6}$. The temperature dependences of Young's modulus and internal friction in short samples change in the opposite way, which is typical for composites reinforced with high-modulus fibers. In the second mode, the measured values are subjected to averaging at several nodal points. However, the use of higher harmonics in this method is still possible to study relative properties of UHMWPE composite and to avoid delamination in samples.

The investigated UHMWPE composites have high elastic (up to $E = 17.8$ GPa) and damping properties (up to $\delta = 16 \cdot 10^{-2}$). Large values of internal friction and their peak on the temperature dependence for the material pressed at $P = 2$ MPa will adversely affect the initial stage of the impact, when the strain rate is very high, and the failure of the material is associated with fiber breakage [16]. Perhaps this behavior is characteristic of the material due to the small number of binding molecules formed between the fibers of its less homogeneous microstructure or delamination. Composites sintered at the highest pressures ($P = 15$ MPa) with the parameters used in this work are promising for use as ballistic protection materials.

REFERENCES

[1] P. Smith, P.J. Lemstra, *Ultrahigh-strength polyethylene filaments by solution spinning/drawing, 2. Influence of solvent on the drawability*, Die Makromolekulare Chemie, 1979, vol. 180, no. 12, pp. 2983–2986.

[2] D.L.P. Macuvele, J. Nones, J.V. Matsinhe, M.M. Lima, C. Soares, M.A. Fiori, H.G. Riella, *Advances in ultra high molecular weight polyethylene/hydroxyapatite composites for biomedical applications: A brief review*, Materials Science and Engineering C, 2017, vol. 76, pp. 1248–1262.

[3] S. Ma, X. Zhang, B. Yu, F. Zhou, *Brushing up functional materials*, NPG Asia Materials, 2019, vol. 11, no. 1, art. no. 24.

[4] L. Xia, P. Xi, B. Cheng, *A comparative study of UHMWPE fibers prepared by flash-spinning and gel-spinning*, Materials Letters, 2015, vol. 147, pp. 79–81.

[5] B. Fei, *High-performance fibers for textiles*, in: *Engineering of high-performance textile*, Woodhead Publishing, Sawston, 2018.

[6] A.L. Forster, J. Chin, J.S. Peng, K.L. Kang, K. Rice, M. Al-Sheikhly, *Long term stability of UHMWPE fibers*, in: *Mechanics of composite and multi-functional materials, Volume 7*, ed. by C. Ralph, M. Silberstein, P. Thakre, R. Singh, Springer, Cham., 2016, pp. 369–375.

[7] P.J. Hazell, *Armour: Materials. – Theory, and Design*, Taylor & Francis, Oxfordshire, 2015.

[8] G.P. Anastasiadi, M.V. Sil'nikov, *Rabotosposobnost' bronevykh materialov*, Asterion, Saint Petersburg, 2004 (in Russian).

[9] I.F. Kobylkin, V.V. Selivanov, *Materials and structures of light armor protection: textbook*, BMSTU, Moscow, 2014.

[10] Y. Liang, X. Chen, C. Soutis, *Review on manufacture of military composite helmet*, Applied Composite Materials, 2021, vol. 29, pp. 1–19.

[11] R. Zhang, B. Han, J.-Y. Zhong, L.-S. Qiang, C.-Y. Ni, Q. Zhang, Q.-C. Zhang, B.-C. Li, T.J. Lu, *Enhanced ballistic resistance of multilayered cross-ply UHMWPE laminated plates*, International Journal of Impact Engineering, 2022, vol. 159, art. no. 104035.

[12] W. Huang, Y. Wang, Y. Xia, *Statistical dynamic tensile strength of UHMWPE-fiber*, Polymer, 2004, vol. 45, no. 11, pp. 3729–3734.

[13] K. Kartikeya, H. Chouhan, A. Ahmed, N. Bhatnagar, *Determination of tensile strength of UHMWPE fiber-reinforced polymer composites*, Polymer Testing, 2020, vol. 82, art. no. 106293.

[14] I. Meshi, I. Amarilio, D. Benes, R. Haj-Ali, *Delamination behavior of UHMWPE soft layered composites*, Composites Part B: Engineering, 2016, vol. 98, pp. 166–175.

[15] J. Peinado, L. Jiao-Wang, Á. Olmedo, C. Santiuste, *Influence of stacking sequence on the impact behaviour of UHMWPE soft armor panels*, Composite Structures, 2022, vol. 286, art. no. 115365.

[16] K. Krishnan, S. Sockalingam, S. Bansal, S.D. Rajan, *Numerical simulation of ceramic composite armor subjected to ballistic impact*, Composites Part B: Engineering, 2010, vol. 41, no. 8, pp. 583–593.

[17] M. Zakeri, H. Mansoori, M. Sadeghian, M. Guagliano, *Impact response of fiber metal laminates based on aluminum and UHMWPE composite: Numerical simulation*, Thin-Walled Structures, 2022, vol. 172, art. no. 108796.

[18] B.D.H. Utomo, *High-speed impact modelling and testing of dyneema composite*, Ipskamp Drukkers, Netherlands, 2011.

[19] S. Kustov, A. Saren, B. D'Agosto, K. Sapozhnikov, V. Nikolaev, K. Ullakko, *Transitory ultrasonic absorption in "domain engineered" structures of 10 M Ni-Mn-Ga martensite*, Metals, 2021, vol. 11, no. 10, art. no. 1505.

[20] S. Ratner, A. Pegoretti, C. Migliaresi, A. Weinberg, G. Marom, *Relaxation processes and fatigue behavior of crosslinked UHMWPE fiber compacts*, Composites Science and Technology, 2005, vol. 65, no. 1, pp. 87–94.

[21] L. Chen, K. Zheng, Q. Fang, *Effect of strain rate on the dynamic tensile behaviour of UHMWPE fibre laminates*, Polymer Testing, 2017, vol. 63, pp. 54–64.

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Динамический модуль Юнга и внутреннее трение в композитах на основе сверхвысокомолекулярного полиэтилена

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Аннотация. В данной работе при помощи акустического метода исследованы механические свойства самоусиленного композита на основе сверхвысокомолекулярного полиэтилена. Листы однонаправленного материала в нём расположены ортогонально и объединены термическим прессованием. Относительное изменение модуля продольной упругости для всех образцов в интервале температур от –5 °C до 50 °C не превышает 1,6%. В зависимости от величины давления, используемого на этапе изготовления, значения динамического модуля Юнга в исследуемых образцах достигают 17,8 ГПа, при этом внутреннее трение не превышает $16 \cdot 10^{-2}$. Квазистатические механические свойства для образцов различной формы исследованы методом испытаний на растяжение. Значения модуля Юнга, определенные по этим данным в упругой части, достигают 16,9 ГПа.

Ключевые слова: сверхвысокомолекулярный полиэтилен; СВМПЭ; самоусиленный композит; модуль Юнга; внутреннее трение