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# ESTIMATION OF DIFFUSIVE RELAXATION PROPERTIES AND STRUCURE OF UHMWPE-COMPOSITES, OBTAINED BY METHOD OF SOLID-PHASE EXTRUSION

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**Key words and phrases:** diffusive properties; electron probe microanalysis; plastic deformation; relaxation properties; Solid phase extrusion; submicroscopic structure; X-ray diffraction technique.

**Abstract:** Terms of the research on diffusive, relaxation and structural properties of UHMWPE-composites, obtained by method of solid phase extrusion (**SPE**), were indicated the regularities of change in moisture content, thermal resistance and other properties of the amorphous-crystal polymer. The experimental results are explained scientifically by virtue of X-ray diffraction technique, electron probe microanalysis and other physical research techniques of the UHMWPE SPE process.

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The problem of high-tension polymeric materials and wares obtaining is being under close attention of scientists [1]. Successful ways of the problem solution are concerned with the use of pressure shaping of polymers in solid phase (ram, angled and screw-shaped extrusions) and polymer’s properties modification. Modification of the polymer’s properties by insertion of organic and inorganic admixtures is a perspective way for the creation of composites having crucially new technological and performance characteristics [2].

Ultra-High Molecular Weight Polyethylene (**UHMWPE**) has unique physical and chemical properties and is widely used as a structural material having high-tension characteristics, shock and wear resistance, low index of friction, high cold endurance and a wide range of other important performance characteristics. The extensive use of UHMWPE is complicated by the complexity of its processing due to high viscosity of the hot melt. At the present time the basic method of UHMWPE processing is the hot pressing that is concerned with a prolonged technological cycle and high energy consumption. Taking into account the fact that the marketing area of polymeric wares is intensively growing the problem of the new methods for UHMWPE processing has become essential.

The application of solid-phase technologies enables us to exclude the demerits of the traditional liquid-phase technology. Processing of polymers by methods of plastic deformation in solid phase demands the research on the material structure and the engineering process peculiarities. The present paper is concerned with the structure parameters analysis of UHMWPE polymeric composites and wares obtained by method of solid phase technology.

In the capacity of modifying agents were used:

– carbon nano-materials (**CNM**) «Taunit» (nano-fibers, multiwall nano-tubes) – one-dimensional nano-scaled thread-shaped nano-formations of polycrystalline graphite in the form of granular powder manufactured by LLC «NanoTechCenter» (Tambov);

– titanium carbide (**TiC**), particles with dimensions of 20 mkm;

– titanium diboride (**$TiB_2$**), particles with dimensions of 60 mkm.

TiC and $TiB_2$ were obtained by method of self-propagating high-temperature synthesis (**SHS** technology) by the Institute of Structural Macrokinetics and Material Science of RAS (Chernogolovka).

The experiments on solid phase ram extrusion of UHMWPE polymeric systems at the temperatures lower than the melting point $T_{melt}$ were conducted using the experimental plant that includes the high pressure cell that is the type of capillary viscosimeter designed in the Tambov state technical university and having the with diameter of the loading chamber of 0.005 m (Fig. 1) [2].

Equal channel multi-angular extrusion (**ECMAE**) is a type of solid phase technology that is based on a simple shear. A cylindrical billet is pushed through the device, consisting of a few pares of channels of the same diameter intersecting at certain angles (Fig. 2) [3]. Experimental research was carried out using the plant consisting of 4 working parts. The matrix has $n = 5$ angles of deformation. Inlet and outlet angles of the channel are $\theta_1 = \theta_5 = 80°$. One-half-angle of the channel segments intersection is $\theta_2 = \theta_3 = \theta_4 = 70°$.

In order to define the diffusive properties of the polymeric samples was used the zone method that is the method of non-steady behavior and enables us to solve both direct and inverse diffusive problems [4]. In accordance with the method calculation of the dependence of moisture diffusion coefficient in polymeric composites from concentration demands the curve construction of isothermal dehydration kinetics within the whole range of concentration change at conditions excluding external diffusive resistance.

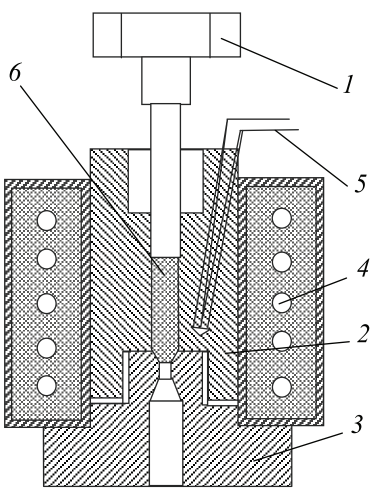


**Fig. 1. The experimental cell for ram solid phase extrusion of polymers:**
*1* – plunger; *2* – matrix; *3* – die;
*4* – heater; *5* – thermocouple;
*6* – polymeric sample

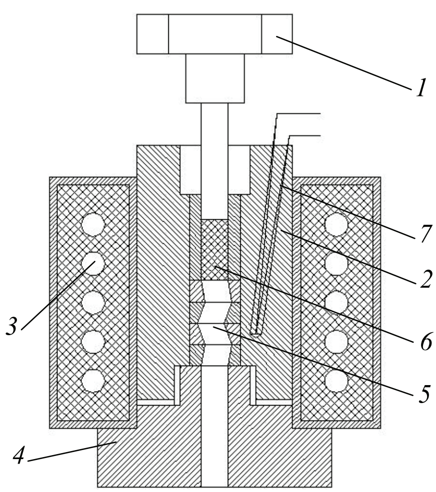


**Fig. 2. The experimental cell for equal channel angular solid phase extrusion of polymers:**
*1* – plunger; *2* – pilot bush; *3* – heater; *4* – base;
*5* – deformation matrix; *6* – polymeric sample;
*7* – thermocouple

X-ray spectrum microanalysis was carried out by the instrumentality of electronic sonde. The main advantages of the method are its locality and possibility to define chemical constitution of a substance in microscopic volume without destruction of the substance [5].

X-ray spectrum research of UHMWPE composite samples was carried out by method of reflection for different ranges of diffraction angles ($CuK_{\alpha}$-rays) monochromated with Ni-filter using the X-ray diffractometer DRON-3.0. For the diffractometric research was used Kepler original beam focusing X-ray optics that allowed to regard the samples as isotropic. In order to avoid the vertical divergence a Soller slit with divergence of 1.5 was used.

In order to define residual orientation stress in the extrudates obtained by solid-phase extrusion of polymeric composites and estimate the temperature limits of their application the method of isometrical heating diagrams was used [6].

The parameters of solid-phase ram extrusion and the factors that effectively influence the quality of a finished extrudate are the temperature of material processing, the expelling pressure $P_f$, geometrical parameters of the die and the presence of modifying admixtures.

Forming pressure $P_f$ is defined as the value of specific axial pressure that causes continuous extrusion of the material through the orifice when the pressure itself remains constant. The pressure $P_f$ depends on the type and proportion of the admixtures to the polymeric matrix, temperature, the rate of forcing and geometrical parameters of the die.

Fig. 3 shows the histogram of the forming pressure changing depending on the UHMWPE + NCM composite structure. The optimal temperature of solid-phase polymer processing can be defined by Boyer correlation [2, 7].

$$T_{extr} = (0.75 \pm 0.15) T_{melt}.$$

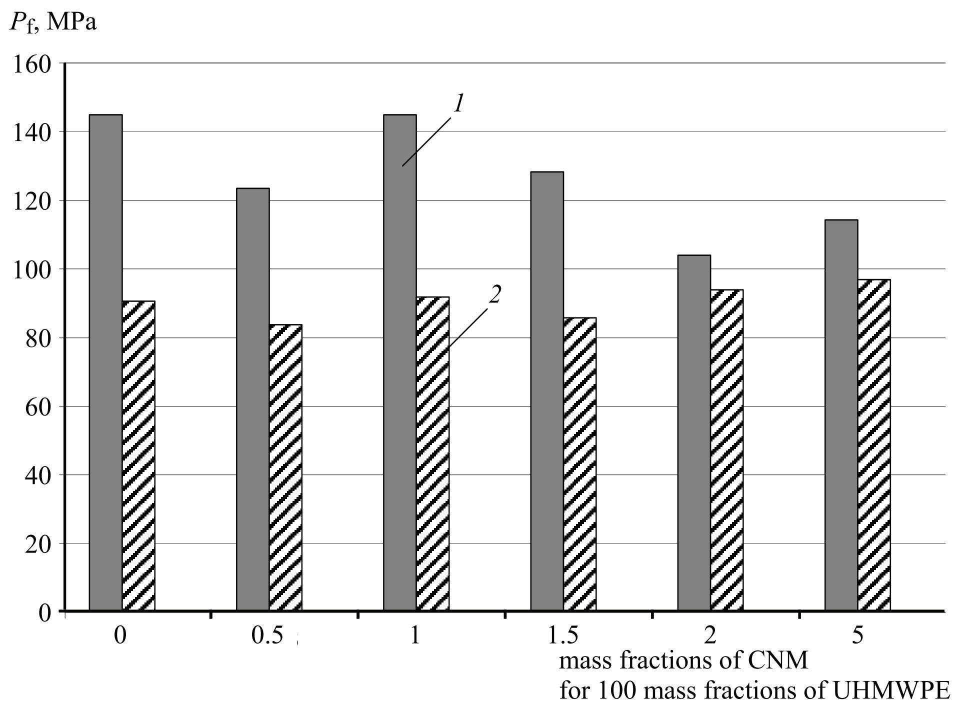


**Fig. 3. Concentration dependences of the forming pressure for polymeric system UHMWPE + CNM, the degree of deformation $\lambda_{extr}$ = 2.07, $T_{extr}$ = 295 K (*1*) and $T_{extr}$ = 363 K (2)**

The decrease in the forming pressure us observed at the optimal temperature $T_{extr}$ = 363 K due to the plastic yielding of the composite and the sliding motion of the material along the channel of the cell.

Fig. 4 shows a common kinetic curve of a diffusive process (the process of moisture desorbtion for a single lamel-shaped UHMWPE + TiC polymer composite sample with variable portion of the modifying admixture).

The analysis of the kinetic curves of the UHMWPE desorbtion process shows the existence of rectangular regions of the curve that slip to the convex regions. Such a shape of the kinetic curves shows that the process of moisture diffusion in the polymeric composites under investigation follows the Fick's law of diffusion [4].

The data obtained (Fig. 5) represent the decrease in the maximal moisture absorption by liquid-phase polymer composite UHMWPE + TiC that can be explained

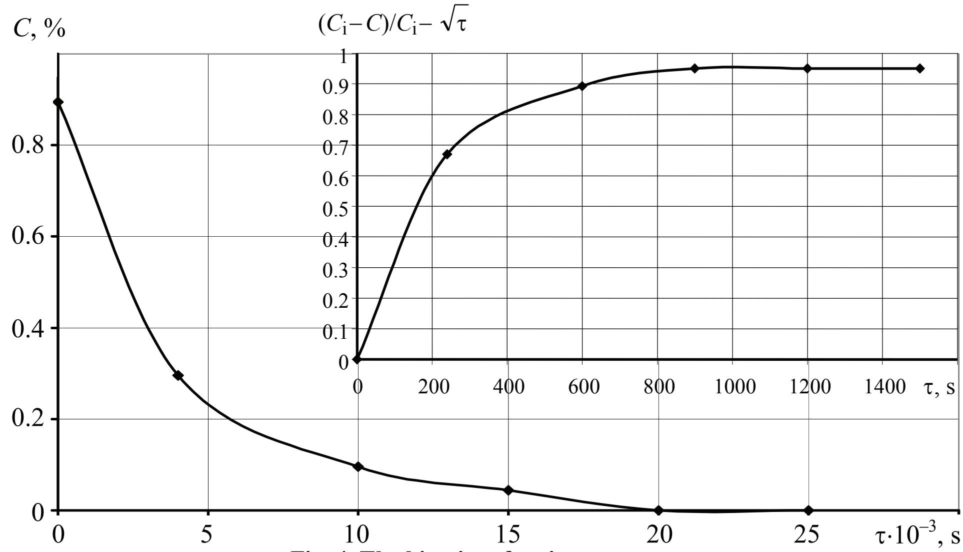


**Fig. 4. The kinetics of moisture content of UHMWPE-composite containing 5 mass fractions of TiC:**

$C_i$ – initial moisture content of the material; $C$ – local moisture content of the material; $\tau$ – time

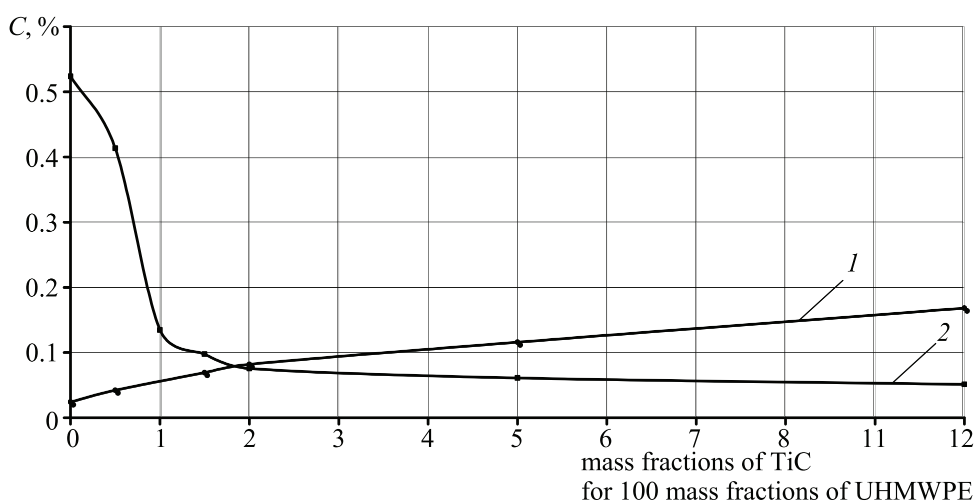


**Fig. 5. The dependence of the maximal moisture absorption of UHMWPE composite from the mass fraction of TiC modifying admixture:**

*1* – solid-phase technology; *2* – liquid-phase technology by considerable hydrophobic properties of titanium carbide. This fact is a positive factor of titanium carbide influence that decrease the plasticization effects of water in polymeric matrix of the composite and allows to retain high tension properties of the material under severe operational environment. The small increase in the maximal moisture absorption of solid-phase UHMWPE composite can be explained by a few defects in the oriented structure of the material caused by the insertion of titanium carbide.

It is common knowledge that the size of admixture inclusions significantly exceed the cross sectional dimensions of the macromolecules of the polymer. However, according to the structural analysis, the sizes are comparable with that of supermolecular features and located on the boundaries of the features (Fig. 6).

The presence of the equal mass fractions of TiC and $TiB_2$ differently change the value of maximal moisture absorption (Fig. 7) of UHMWPE-composite sample, processed by equal channel multi-angular extrusion (ECMAE). This can be explained by the fact that the TiC particles are smaller in size than that of $TiB_2$ and has larger contact area with molecules of the polymeric matrix.

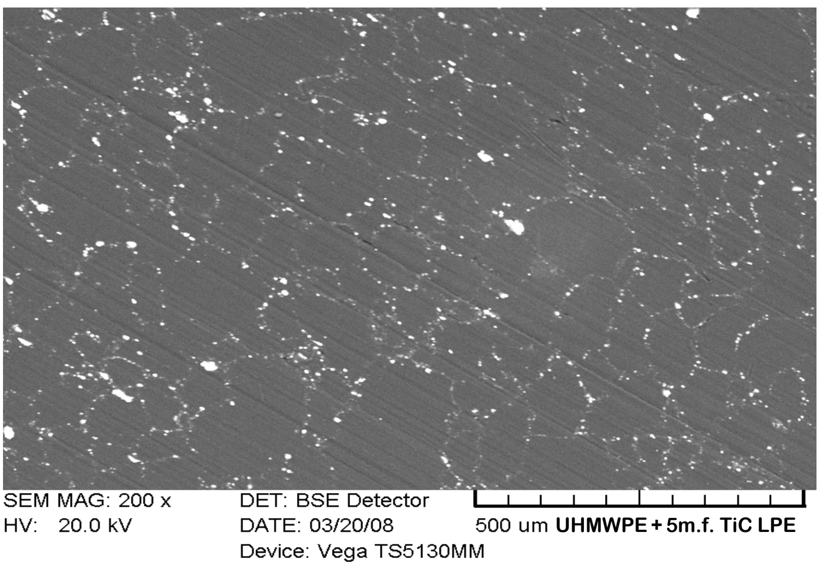


**Fig. 6. Structural picture of UHMWPE+5 mass fractions of TiC polymeric system, obtained by method of electron probe microanalysis**

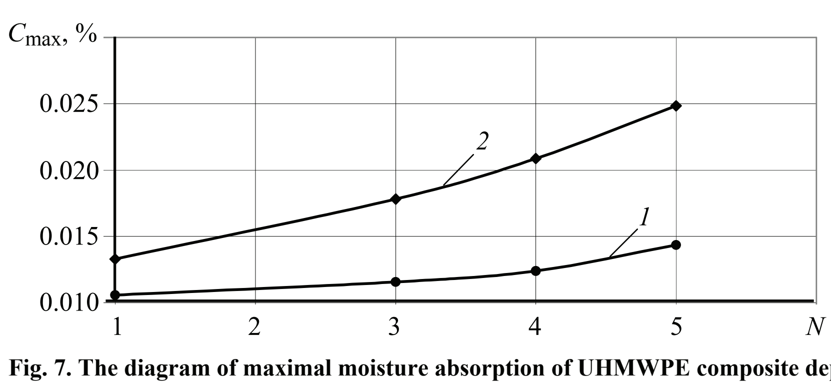


**Fig. 7. The diagram of maximal moisture absorption of UHMWPE composite depending on the number of deformation cycles at equal channel angular extrusion:**
*1* – UHMWPE + 1 $TiB_2$ mass fraction; *2* – UHMWPE + 1 TiC mass fraction

X-ray diffraction analysis of the samples containing various percentage of TiC and $TiB_2$ testifies the previously obtained results of diffusive research and shows that the increase in the amount of admixtures influence mostly the parameters of the UMWPE amorphous phase rather than the crystal phase.

The changes in the crystal phase of UHMWPE (Fig. 8) result mostly in the insignificant stretching of the crystal lattice ($\Delta d$ = 0.001 nm). In this case the half-width of the crystal reflexive actions remains virtually unchanged. This fact indicates that the size of crystallites and the parameters of the crystalline component of the polymer remain virtually unchanged.

The estimation of crystallinity degree of the composites showed that the increase in the percentage of the admixtures leads to the insignificant drop (4–6 %) in crystallinity degree (Fig. 9) and the impact can be noticed beginning with 0.5 % TiC mass fraction.

It was established that introduction of the admixtures impacts mostly on the change of X-ray parameters of the amorphous phase component. The angular position of the amorphous halo (Fig. 9) shows that even a small percentage of the admixture results in an 0.02 nm increase in the average intermolecular distance in non-crystal phase that significantly exceeds the corresponding changes in crystalline phase. In this case the half-width of the diffusive maximum also depends on the TiC и $TiB_2$ admixtures. The insertion of the admixtures causes a small increase in half-width of the amorphous halo at small percentage (not more than 2 %) of TiC and $TiB_2$ components. This indicates the increase in heterogeneity of the amorphous phase (the degree of order in the amorphous component decrease that can be explained by the admixture impact).

Thus, according to the X-ray diffraction technique analysis, the largest structural changes are observed for the samples containing 0.5–2 % TiC and $TiB_2$ admixtures. In this case the crystalline phase remains virtually unchanged, while in the amorphous phase is observed the decrease in the average intermolecular distance and simultaneous decrease in the degree of order. The degree of crystallinity also changes – the fraction of amorphous phase in the polymeric material increases. Further growth of the admixture concentration does not lead to a significant impact on the structural parameters of the composite. The degree of order of the amorphous component grows a bit that may indicate the claster distribution in the volume of the admixtures beginning with ~2 %.

The X-ray diffraction analysis of UHMWPE samples, containing various percentage of CNM showed that the increase in of the admixtures concentration impact mostly on the parameters of the amorphous phase of UHMWPE rather than the crystalline phase of the polymer just as it is occurs in case of TiC и $TiB_2$ admixtures.

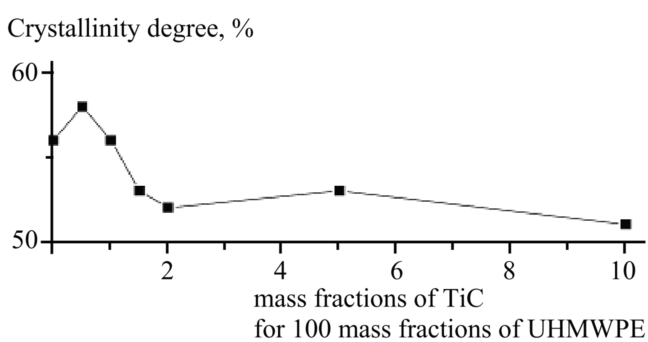


**Fig. 8. The degree of crystallinity of UHMWPE + TiC composites**

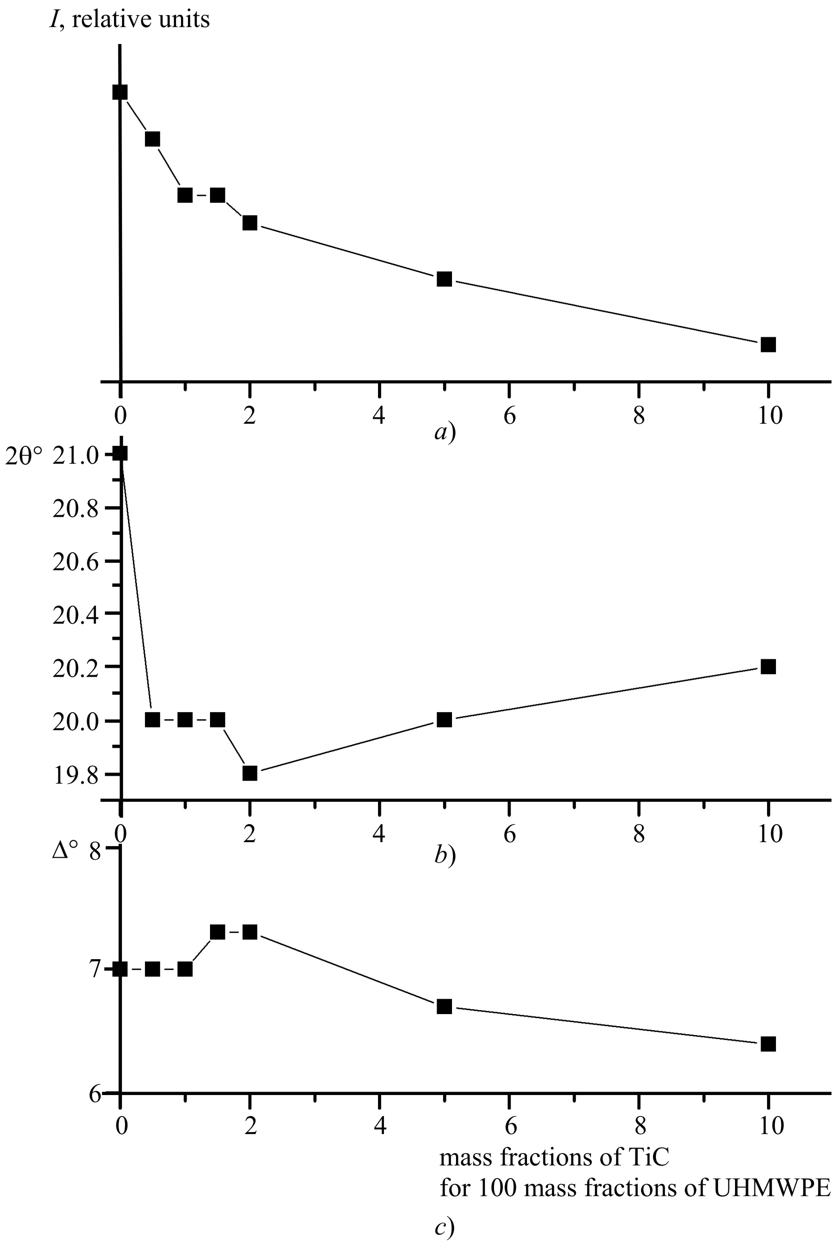


**Fig. 9. The dependences of intensity (*a*), angular position (*b*), half-width (*c*) of an amorphous halo from the percentage of TiC for UHMWPE + TiC polymeric system**

The angular position of the amorphous halo indicates that even a small percent of the admixtures causes the 0.002 nm increase of intermolecular distance in non-crystal phase that exceeds the changes in crystal phase. In this case the half-width of diffusive maximum also react to the CNM adding. The introduction of admixtures increase the half-width of an amorphous halo at small percentage of CNM (less than 2 %) that demonstrates a large increase of heterogeneity of the amorphous phase (the crystallinity of the amorphous component drops that is caused by presence of the admixtures).

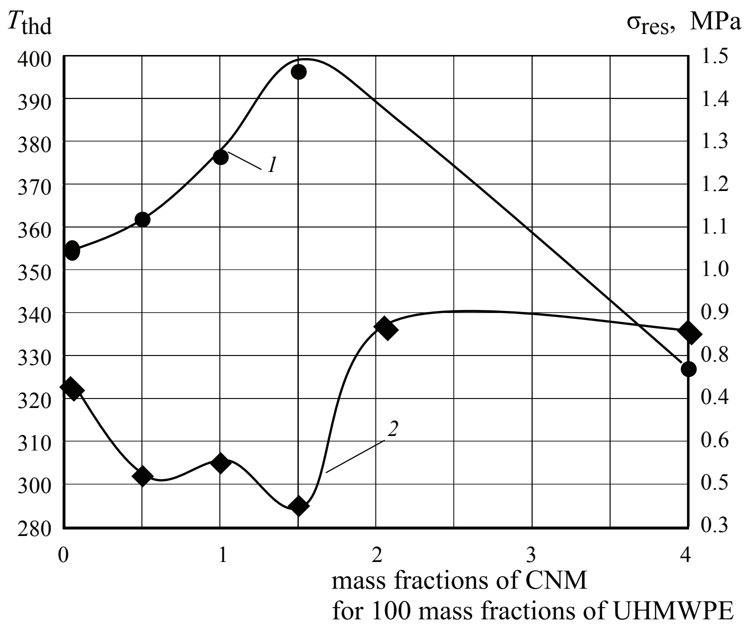


**Fig. 10. The dependence of the heat distortion value $T_{thd}$ (*1*) and the level of residual stress $\sigma_{res}$ (*2*) of solid-phase UHMWPE + CNM samples from CNM percentage in polymeric matrix, the degree of deformation $\lambda_{extr}$ = 2.07 and $T_{extr}$ = 363 K**

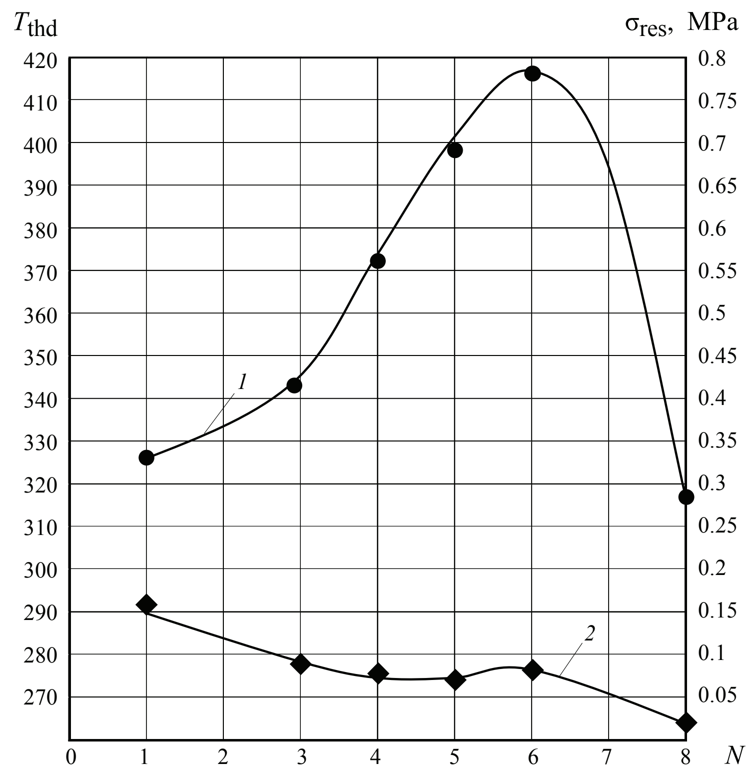


**Fig. 11. The dependence of the thermal resistance (*1*) and the llevel of residual stress (*2*) of UHMWPE + 1 TiC mass fraction samples, processed by ECAE at $T_{extr}$ = 363 K from the number of deformation cycles**

For estimation of the optimal concentration of modifying admixtures in UHMWPE were investigated the properties of a few composites containing various mass fractions of CNM. Diagrams demonstrating the dependence of heat distortion temperature $T_{\text{ht}}$ (*1*) and the level of residual stress $\sigma_{\text{res}}$ (*2*) of the UHMWPE+CNM composites obtained by SPE from the CNM fraction in polymeric matrix (Fig. 10). The fact of 1.5 times decrease in the level of residual stress and 15…20° increase in the value of thermal resistance of the UHMWPE polymeric nano-composite was observed for insertion of 1.5 mass fraction of CNM. The data, obtained by construction of isometric heating diagrams of UHMPE samples processed by ECMAE prove the effectiveness of the technology application. In this case the maximal increase in thermal resistance of the material was obtained after multiple processing of polymeric material (Fig. 11).

## Conclusions

1. Were analyzed the diffusive, relaxation and structural characteristics of UHMWPE-composites, processed by ram and equal channel multi-angular solid phase extrusion.
2. The research data on the diffusive properties testify the decrease in the maximal moisture absorption of the liquid-phase polymeric composite UHMWPE + TiC, and insignificant increase of moisture absorption of the solid-phase composite.
3. Structural research by method of electron probe microanalysis shows that the size of TiC and $TiB_2$ particles are comparable with that of the submolecular features of the polymeric matrix and located mostly on the boundaries of the features.
4. The fact of 1.5 times decrease in the level of residual stress and 15…20° increase in the value of thermal resistance of the UHMWPE polymeric nano-composite was observed for insertion of 1.5 mass fraction of CNM after its processing by pressure in solid phase.
5. The investigation of the schrinkable processes at isometric heating of the UHMWPE samples processed by method of ram equal channel angular extrusion indicated the effectiveness of the technology.

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## Оценка диффузионных, релаксационных свойств и структуры СВМПЭ-композитов, полученных твердофазной экструзией

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**Ключевые слова и фразы:** диффузионные свойства; надмолекулярная структура; пластическое деформирование; релаксационные свойства; рентгеноспектральный микроанализ; рентгеноструктурные исследования; твердофазная экструзия.

**Аннотация:** На основе изучения диффузионных, релаксационных свойств и структуры СВМПЭ-композитов, полученных твердофазной экструзией, выявлены закономерности изменения влагосодержания, температуры теплостойкости и других свойств аморфно-кристаллического полимера. Экспериментальные результаты объяснены с позиций научных представлений, полученных анализом данных рентгеноструктурного анализа, рентгеноспектрального микроанализа и других физических методов изучения технологического процесса твердофазной экструзии СВМПЭ-композитов.

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## Einschätzung der Diffusions- und Relaxationseigenschaften, und der Struktur von der Hartphasenextrusion erhaltenen UHMWPE- Kompositen

**Zusammenfassung:** Auf Grund der Erlernung der Diffusions- und Relaxationseigenschaften, und der Struktur von der Hartphasenextrusion erhaltenen UHMWPE-Kompositen sind die Gesetzmäßigkeiten der Veränderung des Feuchtegehaltes, der Temperatur der Wärmefestigkeit und der anderen Eigenschaften des amorph-kristallischen Polymeres gezeigt. Experimentalergebnisse sind mit Hilfe der Angaben, die durch die Analyse der Angaben von der Röntgenstrukturanalyse, der röntgenspektralischen Mikroanalyse und den anderen physikalischen Methoden der Erlernung des technologischen Prozesses der Hartphasenextrusion der UHMWPE-Kompositen erhalten sind, erklärt.

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## Estimation des propriétés de diffusion, de relaxion et de la structure des UHMWPE-composites obtenus par la méthode de l’extrusion de la phase solide

**Résumé:** A la base de l’étude des propriétés de diffusion, de relaxion et de la structure des UHMWPE-composites obtenus par la méthode de l’extrusion de la phase solide sont indiquées les régularités du changement du contenu de l’humidité, de la température, de la rigidité thermique et d’autres propriétés du polymère cristallique amorphe. Les résultats expérimentaux sont expliqués du point de vue des représentations scientifiques obtenues par l’analyse des données de l’analyse radiocristallographique, de la microanalyse par les rayons X et d’autres méthodes de l’étude du processus technologique de l’extrusion de la phase solide des UHMWPE-composites.

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