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Combined method of grinding and homogenization of fine powders rubbers and other polymers

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ABSTRACT

This study presents data on the development and research of cryogenic-vibration grinding process modes which would ensure an efficient grinding process of complex composite systems with a high degree of heterogeneity of components in their composition of products such as fluoroplast, bismuth oxide and tungsten carbide. The general regularities of low-temperature processing and grinding of non-degassed elastomers are established. A method has been tested that establishes the regularities of cryogenic grinding and ultrasonic homogenization of a complex mechanical system, the microstructure and dispersed compositions of the ground material have been determined.

1. Introduction

The need of fine powders obtaining from polymers and their compositions is an urgent task since at present they are widely in demand in various industries including for the production of parts for various purposes using additive technologies (Pietrzykowska et al., 2019; Xi et al., 2020; Allaf et al., 2015; Schultz et al., 2000; Goodridge et al., 2012; Yuan et al., 2019; Yang et al., 2019)Powders based on plastics or rubbers are obtained by very expensive methods which are based on blows, cutting, crushing, grinding, while using all kinds of crushers, mill rollers (Schocke et al., 1999; Smith et al., 2000). When using them sufficiently large polymer particles from 2 to 10 mm are obtained (Chen & Wang, 2001; Wang et al., 2002). These processes are energy-intensive, so in this case there can be no question of energy saving.

The most promising method for obtaining fine powders is cryomilling. For the first time, this method was used to obtain powders of metals and their alloys (Witkin and Lavernia, 2006). Currently, numerous studies have proven the effectiveness of cryomilling (Witkin & Lavernia, 2006; Lavernia et al., 2008; Zhou et al., 2003; Liao et al., 2003) including for the production of fine polymers and composite powders based on them (Zhu et al., 2006; Zhu et al., 2006; Zhu et al., 2006; Robotti et al., 2016). It should be noticed that cryomilling is compatible with any thermoplastics and their compositions. The essence of the method is to cool the material using liquid nitrogen to the brittleness temperature, followed by mechanical action in various grinding units-cryomills. Cryopreservation of polymers and their composites at low temperatures makes it possible to obtain a fine powder with particles up to 2 microns, which makes it possible to create new composite materials with increased physical and mechanical characteristics (Pietrzykowska et al., 2019; Xi et al., 2020; Katiyar et al., 2020). The use of grinding units in combination with cryofreezing makes it possible to ensure high homogeneity of the mixture of both mixed

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(homogeneous) and non-mixed (with a high degree of heterogeneity) polymers and their compositions (Smith et al., 1998; Cavalieri et al., 2002; Lebovitz et al., 2003; Kashibadze et al., 2021).

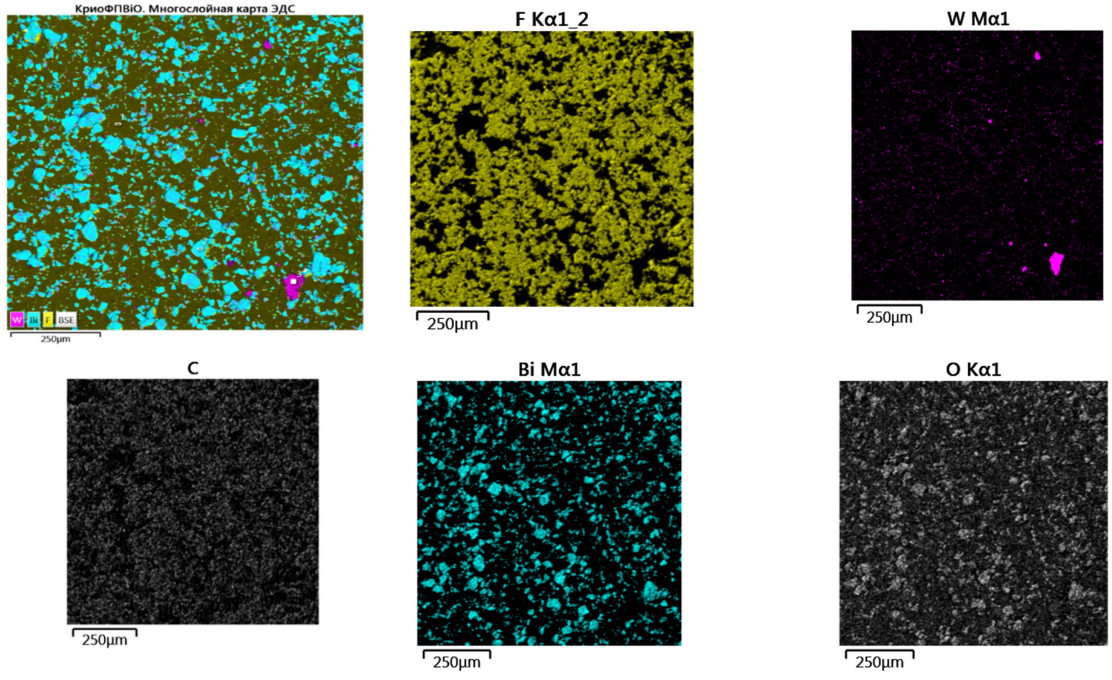
The fineness and quality of the grinding of materials is important for the intensification of various technological processes. In addition, the crushed products acquire new physical and chemical properties that allow reducing the duration of technological processes, reducing the temperatures and pressures accepted in production, reducing material consumption and energy consumption, giving materials and products high strength, heat resistance, activity, etc. (Pietrzykowska et al., 2019; Xi et al., 2020; Lebovitz et al., 2003; Pan and Shaw, 1994). Fine and ultrafine grinding using the cryogenic freezing method can be carried out using mills of various types of action. The most widely studied possibilities of using ball mills for cryogenic grinding are (Delogu et al., 2017; Bai et al., 2000; Smith et al., 2000; Smith et al., 2001; Smith et al., 2000; Macfhionnghaile et al., 2014) there is also data on the use of a jet-vortex mill (Liang et al., 2002). Grinding with the use of vibrating mills in combination with cryofreezing has certain prospects. This is primarily due to the possibility of ensuring sufficient fineness of grinding powders when using this type of mills and this method have found wide application in pharmaceutical grinding (De Cleyn et al., 2021; De Cleyn et al., 2020; Li et al., 2016).

There is a vibration technology for cold grinding of solid, viscous substances in which the materials being ground, for example, thermoplastic plastics, become brittle. At low-temperature processing crushing is performed at temperatures of -50 °C ... -150 °C, at this temperature, the plastic mass is in a pseudo-brittle state. It was established that the direct contact of the milled material with the refrigerant which was used as liquid nitrogen, increases the efficiency of the heat exchange process by using both the boiling heat of liquid nitrogen and the heating of its gaseous phase (Zhuchkov et al., 2009; Zhuchkov et al., 2010). The cryophrashing technology using vibrating mills is very interesting for the study of the grinding of polymers and their compositions in the low temperature region. Due to the improvement of the cryopreservation technology, it is possible to produce qualitatively new products that provide the required technological parameters for the subsequent stages of processing, in particular, homogenization and hot pressing of the final product, in particular, for obtaining radiation-protective composite materials. Thus, the purpose of this study was to develop and study the modes of the cryogenic-vibration grinding process which would ensure an effective process of grinding complex composite systems with a high degree of heterogeneity of components in their composition, such as fluoroplast, bismuth oxide and tungsten carbide, for the subsequent production of radiation-protective composite materials.

2. Materials and methods

2.1. Synthesis

For cryogenic grinding, a composite material based on a fluoroplast polymer, bismuth oxide and tungsten carbide was used (Pavlenko et al., 2012). Fig. 1 and Table 1 show the elemental composition of the material obtained using the OXFORD Instruments energy-dispersion particle microanalyzer on the Tescan MIRA 3 LMU electron scanning microscope (Tescan, Czech Republic).



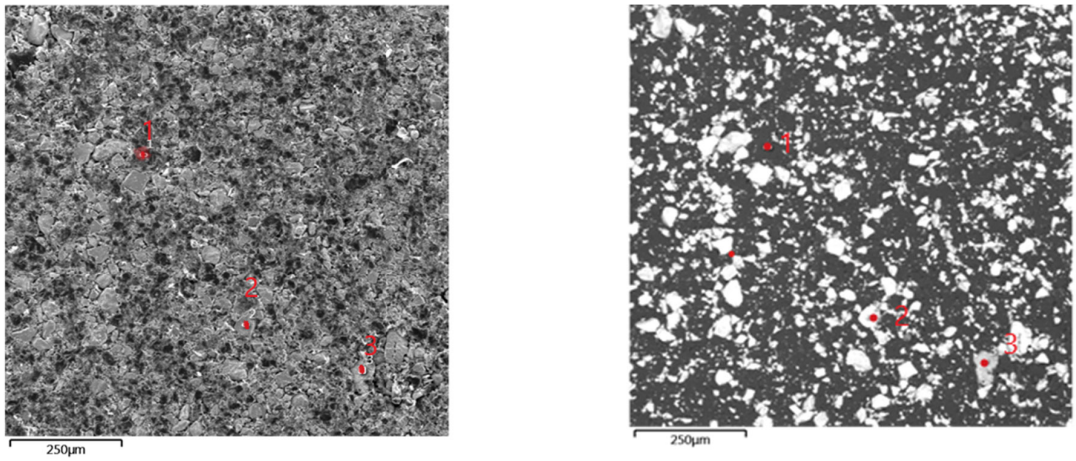


Fig. 1. Map of the distribution of composite material elements

Table 1. The elemental composition of the composite material

The name of the spectrum, at. %	C	O	F	Al	Co	W	Bi
CryoFPViO. K	29.39	4.08	63.69			0.28	2.56
Spectrum 1	42.07		57.85	0.04		0.03	
Spectrum 2	31.99	44.24	1.70				22.07
Spectrum 3	53.01	16.12	4.77		0.58	25.52	
The name of the spectrum, the weight. %	**C**	**O**	**F**	**Al**	**Co**	**W**	**Bi**
CryoFPViO. K	15.94	2.95	54.65			2.32	24.14
Spectrum 1	31.35		68.19	0.07		0.39	
Spectrum 2	6.70	12.34	0.56				80.40
Spectrum 3	11.15	4.52	1.59		0.60	82.15	

2.2. Research methods

The optimal values of the dependences of acceleration (A, g), velocity (V, mm/s) and displacement (S, microns) on the oscillation frequency (f, Hz) were calculated using Eq. (1) and Eq. (2). The speed of vibration movements

$$V=S/T, \tag{1}$$

where S is the movement of the particle in one oscillation; T is the oscillation period. The mentioned speed of movement determines the speed of changing the position of the grinding and grinding bodies.

$$T=1/f. \tag{2}$$

The parameters of the cryogenic grinding process for preliminary selection of the heat exchange mode during cooling of the system consisting of fluoroplast, bismuth oxide and tungsten carbide, containing a certain content of an aqueous solution of methanol, aldehydes and esters after the ultrasonic homogenization stage, were determined using a mathematical apparatus that takes into account the presence of a liquid phase in a porous structure at any temperature (up to -150°C). As the sample temperature decreases the proportion of the liquid phase decreases and the proportion of the solid phase increases.

During the process modeling the following assumptions are made: the temperature of the cooling agent remains constant; the density of the frozen product does not depend on time; the temperature at any point of the product fragment depends only on the current radius and time (symmetric problem).

The amount of the frozen liquid phase is characterized by a value GƆ equal to the ratio of the crystalline phase G_H to the initial mass of the liquid phase G_H:

$$\omega = \frac{G_{л}}{G_{н}} \tag{3}$$

The value GƆ changes from 0 to 1 as it decreases. To determine it, the following dependence was used:

$$\omega = \left(1 - b \cdot \frac{1-W}{W}\right) \cdot \left(1 - \frac{t_{кр}}{t}\right), \tag{4}$$

where b is the content of the liquid phase per unit mass of dry matter, kg/kg; W is the initial content of the liquid phase in the product;

$t_{кр}$ is the cryoscopic temperature, ˚C.

The following form of the thermal conductivity equation was used:

$$c\rho \frac{\partial t}{\partial r} = \frac{\partial}{\partial r}\left(\lambda \cdot \frac{\partial t}{\partial r}\right) + \frac{2\lambda}{r}\frac{\partial t}{\partial r}, \tag{5}$$

where c is the heat capacity, ρ is the density, λ is thermal conductivity. The heat capacity before freezing ($t > t_{kp}$) was determined by the formula:

$$C = Cc(1-W) + Cж(1-\omega)W, \tag{6}$$

where $Cc, Cж$ is the heat capacity of the dry mass and the liquid phase, J/kg·K.

When the periscope temperature is reached, a solid phase appears in the particle the proportion of which increases as the temperature decreases. The heat of the phase transition released during the freezing of the liquid phase is taken into account as an additional heat capacity determined by the ratio:

$$C_{i,j}\rho_{i,j}\frac{t_{i,j+1} - t_{i,j}}{\Delta\tau} \approx \frac{1}{r^2_{i,j}}\left[\frac{\frac{r^2_{i+1/2,j}\lambda_{i+1/2,j}\left(t_{i+1,j} - t_{i,j}\right)}{\Delta r} - \frac{r^2_{i-1/2,j}\lambda_{i-1/2,j}\left(t_{i,j} - t_{i-1,j}\right)}{\Delta r}}{\Delta r}\right], \tag{7}$$

where r is the heat of crystallization of the liquid phase, kJ/kg. The thermal conductivity of the cooled system was determined by the following ratios:

$$\lambda_м = \begin{cases} \lambda_0, & npu\ \ t > t_{кр} \\ \lambda_0 + \omega\Delta\lambda, & npu\ \ t \le t_{кр} \end{cases}, \tag{8}$$

where λ_0 is the heat capacity of unfrozen products, W/m * K, according to the data, $\Delta\lambda$ is the difference in the thermal conductivity of the crystalline phase and the liquid phase (W/m * K). At $t > t_{kp}$, the heat capacity is determined by the ratio (4), at $t \le t_{kp}$ the heat capacity is determined by the ratio (7). The derivative $\frac{d\omega}{dt}$ is determined by the ratio (9):

$$\frac{d\omega}{dt} = -\frac{0.789}{\left[\ln(t_{кр} + 1 - t) + 0.714\right]^2 \cdot (t_{кр} + 1 - t)}, \tag{9}$$

Initial condition: at $\tau = 0 \quad t = t_0$.

Boundary conditions:

At $r = 0 \qquad \frac{\partial t}{\partial r} = 0;$ (10)

At $r = R \qquad \lambda\frac{\partial t}{\partial r} = -\alpha(t - t_x),$ (11)

where α is the coefficient of heat transfer from the particle to the refrigerant, W/m·K; t_x is the temperature of liquid nitrogen, ˚C. Its analytical solution is not possible due to the nonlinear nature of the problem, complex dependencies of thermophysical characteristics on temperature. Therefore, the process is modeled using numerical methods. The values of the thermal conductivity coefficients $\lambda_{i+1/2}, \lambda_{i-1/2}$ in the additional nodes are calculated using their values in the main nodes of the grid according to the formulas:

$$\lambda_{i+1/2,j} = \frac{2\lambda_{i+1,j}\lambda_{i,j}}{\lambda_{i+1,j} + \lambda_{i,j}}, \qquad \lambda_{i-1/2,j} = \frac{2\lambda_{i-1,j}\lambda i, j}{\lambda_{i-1,j} + \lambda_{i,j}}. \tag{12}$$

The discrete analog of the boundary condition (11) has the form:

$$\lambda_{1+1/2}\frac{t_{2,j+1} - t_{1,j+1}}{\Delta r} = \alpha(t_{1,j+1} - t_x) \tag{13}$$

The calculation program provides for the determination of thermophysical parameters at the nodal and intermediate points of the grid. Then the temperature at the outer boundary and at the inner points of the layer is calculated. The use of an explicit scheme for the approximation of the differential Eq. (4) imposes certain restrictions on the choice of the values of the steps in time ($\Delta\tau$) and coordinate (Δr). The stability of the calculation is provided under the condition:

$$F_0 < 0.5, \tag{14}$$

where F_0 is the Fourier grid number:

$$F_0 = \frac{\lambda\Delta\tau}{C\rho(\Delta r)^2}. \tag{15}$$

Since the heat capacity C and the thermal conductivity λ vary widely, the fulfillment of the stability condition for F_0 is checked at each node of the grid.

Earlier the design of the experimental cryomel was developed by the authors (Zhuchkov et al., 2010; Pavlenko et al., 2012). Due to the fact that there are no data on the intensity of the distribution of ultrasonic vibrations in the processed system, a method was used to determine the density of the ultrasonic field using a specially designed device-a cavitometer. The determination method consists in the fact that piezo-elements are installed in the device, connected to the indicating and recording device. The sensors are installed at different heights and distances in the reactor volume, the signals taken from them are processed using a special program and graphically stored in the database of a personal computer (Fig. 2).

Fig. 2. General view of the ultrasound machine

The granulometric composition of the ground powders was determined using the ANALYSETTE 22 NanoTec plus laser particle size analyzer. The TESCAN MIRA 3 LMU electron microscope (TESCAN, Czech Republic) was used for scanning electron microscopy. The samples were pre-sprayed with a layer of chromium 5 nm thick. The microstructure of the surface was studied using an SE detector (secondary electrons) and a BSE detector (back-reflected electrons).

3. Results and Discussion

3.1. The stage of cryogenic grinding and homogenization

Earlier studies conducted by the authors to identify the patterns of cryogenic solidification and grinding of polymers containing up to 30% of monomers, in particular polyiso-butylene, polyoctene, polyhexene and their copolymers, showed that the resistance of polymers to low temperatures depends on the type of polymer (Schultz et al., 2000). When testing polyisobutylene already in the -40° region with the solidification of the prototype is observed and at -60 °C the polymer becomes brittle. If the polymer contains distributed gas phases, in particular phenyl groups, the solidification limit is reduced to -80°C, in the case of a fluoroplast-based system, mixtures containing bismuth oxide and tungsten carbide retain elasticity much longer and require, according to preliminary estimates, cooling below -100°C. The parameters of the cryogenic grinding complex with the characteristics of low potential energies provided by the values of the vibration system presented in Table 2 were selected.

Table 2. The set values of acceleration (A, g), velocity (V, mm/s) and displacement (S, microns) at a voltage of 105 V

Cursor	Frequency ratio f (Hz)	Vibration displacement S(micron)	Vibration velocity V(mm/s)	Vibration acceleration A (g)
C1	50	3,16	0,99575	0,03188
C2	100	2,79	1,75	0,11241
C3	150	0,0549	0,05174	0,00497
C4	200	0,08036	0,10099	0,01293
C5	250	0,03245	0,05097	0,00816
C6	300	0,01927	0,03633	0,00698
C7	350	0,02436	0,05357	0,012
C8	400	0,026	0,06535	0,01674
C9	450	0,00531	0,01503	0,00433

Using mathematical calculations the optimal values of the dependences of acceleration (A, g), velocity (V, mm/s) and displacement (S, microns) on the oscillation frequency (f, Hz) were established. Thus, in the process of cryogenic grinding and homogenization of composite materials consisting of fluoroplast, bismuth oxide and tungsten carbide, the installation made it possible to process the crushed product in the ranges of variable oscillation frequencies at 50-450 Hz which provided vibrational movements of grinding bodies and the crushed product in the aisles of 3-150 microns/s. Fig. 3 shows the results of calculations performed in accordance with the algorithm which described in clause 2.2 (formulas 3-15), presented in the form of graphs.

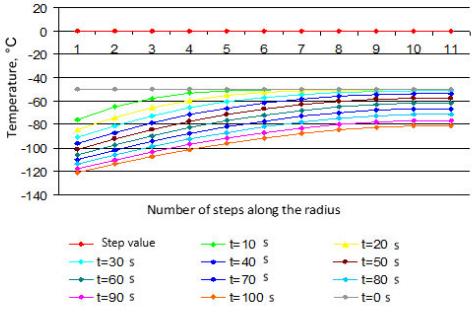


Fig. 3. The temperature distribution over the particle radius over time.

This approach allowed us to develop preliminary characteristics of the process implemented during the exploratory experimental stages of processing the product for its cryogenic grinding and subsequent homogenization.

3.2. The stage of ultrasonic grinding and homogenization

The proposed technology of grinding and homogenization of composite materials in the composition of fluoroplast, bismuth oxide and tungsten carbide includes combined processes of cryogenic and ultrasound grinding and homogenization alternating in a certain pattern. For the ultrasonic stage of the technology, a liquid-phase medium in the form of an aqueous solution of methanol, aldehydes and esters is proposed. This system made it possible to create the best conditions for the distribution of ultrasonic vibrations for processing a mixture of components with very significantly different physical characteristics. Fig. 4 shows the established dependence of the distribution and intensity of the frequencies and amplitudes of the obtained oscillations in the reaction space on a piezoelectric generator of ultrasonic vibrations with a frequency of 22-30 kHz.

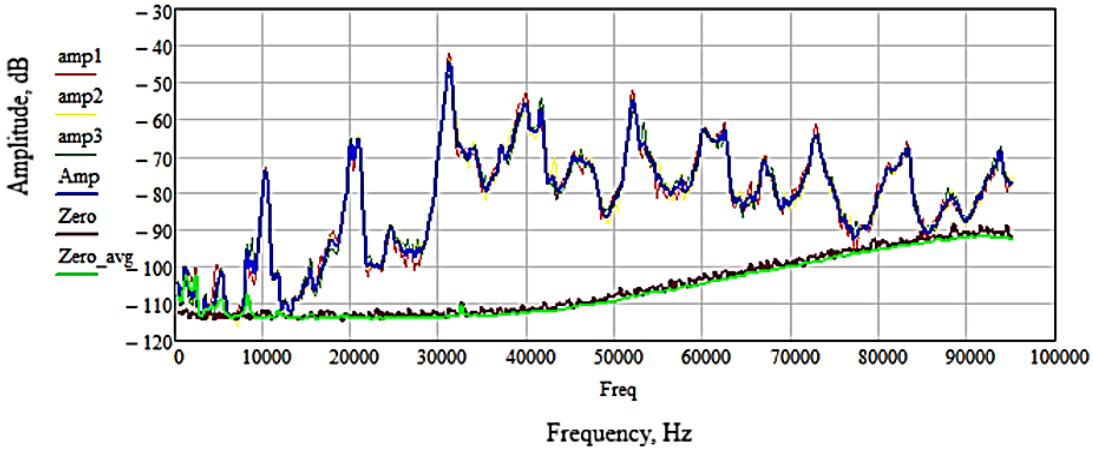


Fig. 4. Dependence of the distribution and intensity of the frequencies and amplitudes of the obtained oscillations in the reaction space

The obtained distribution of the intensity of frequencies and amplitudes of vibrations in the reaction space made it possible to optimize the parameters of the ultrasonic grinding and homogenization process in the volume of an aqueous solution of alcohols, aldehydes and esters of composite materials in the composition of fluoroplast, bismuth oxide and tungsten carbide.

3.3. Changes in the surface structure of the composite material after grinding

The study of the microstructure of the particle surface before and after cryopreservation showed the following. The fluoroplast in its initial form is represented by a fine powder, the particles of which are combined into large agglomerates (Fig. 5).

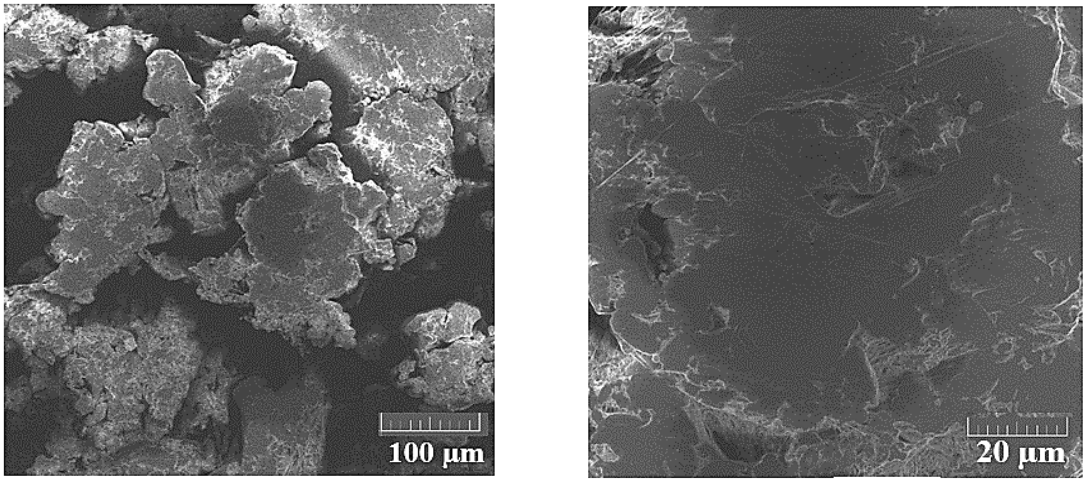


Fig. 5. Microstructure and character of the surface of the fluoroplast particles in their original form

The particles of bismuth oxide in their initial form have a developed surface, an acute-angled shape are represented by aggregated conglomerates of various sizes (Fig. 6).

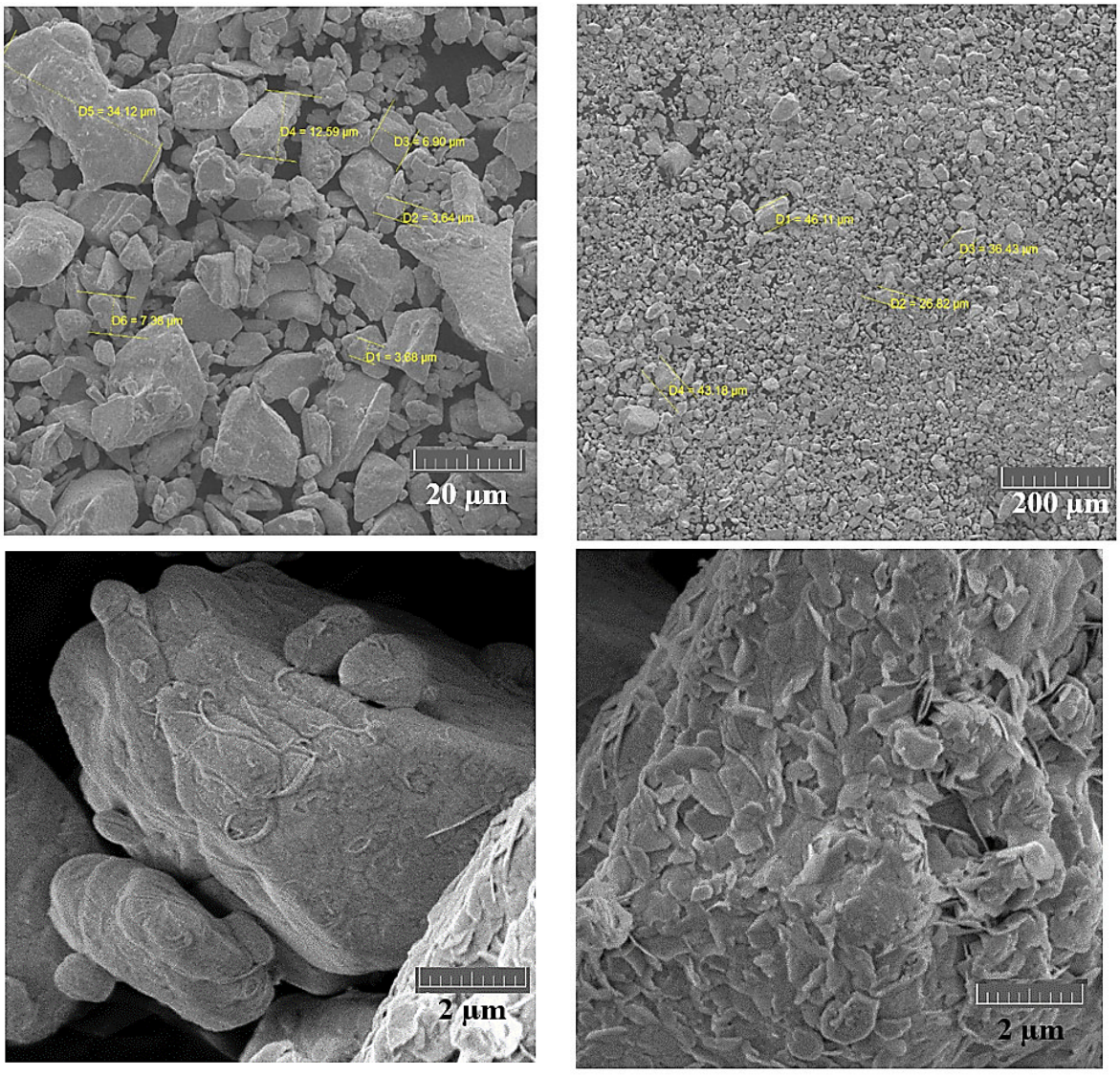
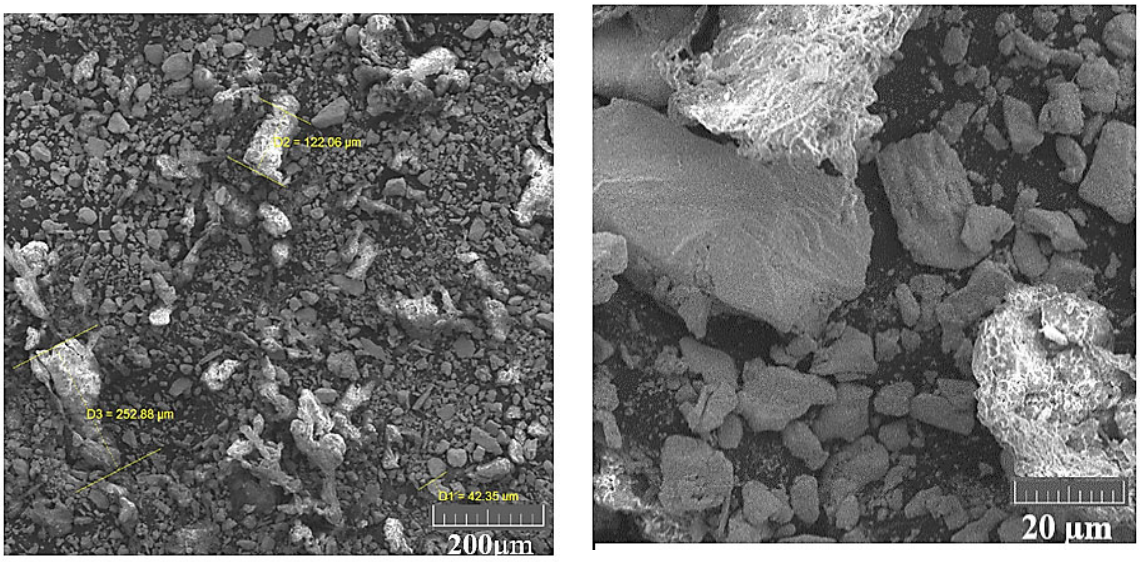


Fig. 6. Micrographs of bismuth oxide particles

After a joint cryomilling according to the established optimal regime a sufficiently homogeneous mixture of the smallest particles was obtained without inclusions of secondary aggregated agglomerates (Fig. 7).



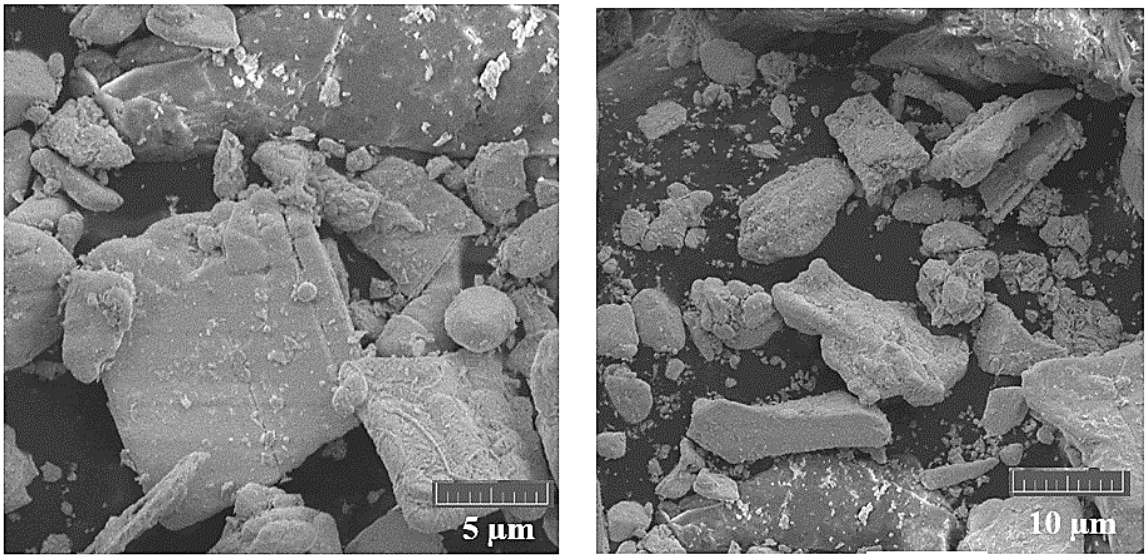


Fig. 7. Microstructure and particle distribution of composite material

The study of the finished samples after pressing showed more uniform distribution of particles over the volume of the composite when using the mixture after cryomilling (Figs. 8, 9).

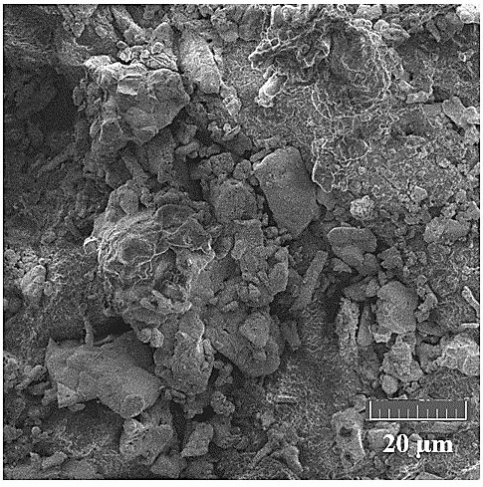
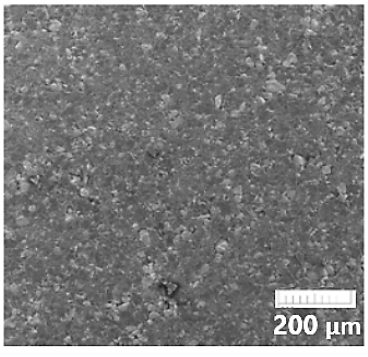
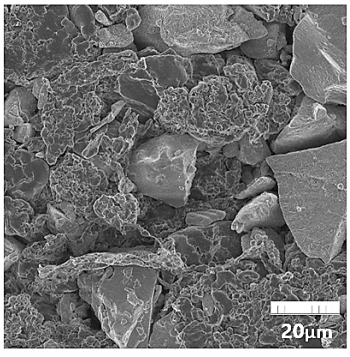


Fig. 8. Microstructure of the composite using a mixture obtained by grinding in a ball mill

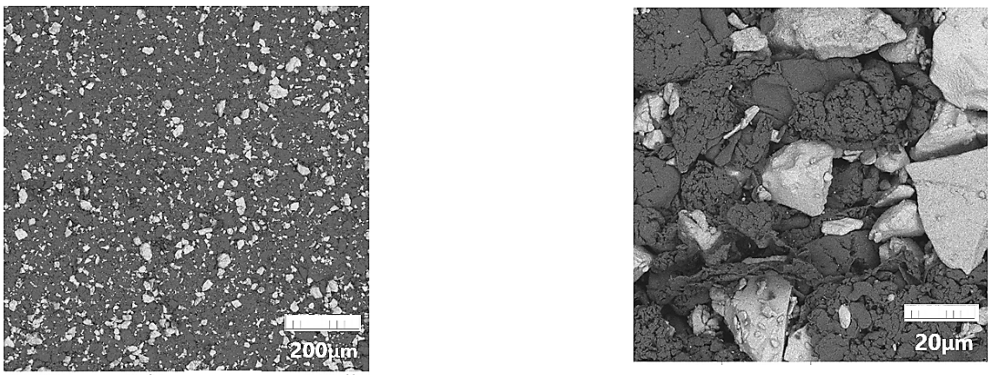
The use of the BSE detector made it possible to obtain a pronounced compositional contrast, clearly marking bismuth oxide particles on microphotographs (Fig. 10). The fraction of reflected electrons is determined by the backscattering coefficient which is a function of the atomic numbers of the elements that make up the sample. The reflection efficiency increases with the atomic number creating a basis for differentiation between different phases. Thus, the sections of the sample containing heavier elements in their composition will look lighter on the electronic BSE image, and the sections containing lighter elements in the composition will look darker.



(a)



(b)



(c) (d)

Fig. 9. The microstructure of the composite material taken with the SE detector (a, b) and taken with the BSE detector (c, d)

3.4. The cryomilling effect on the granulometric composition of samples

Fig. 10 shows a graph of the particle size distribution after grinding.

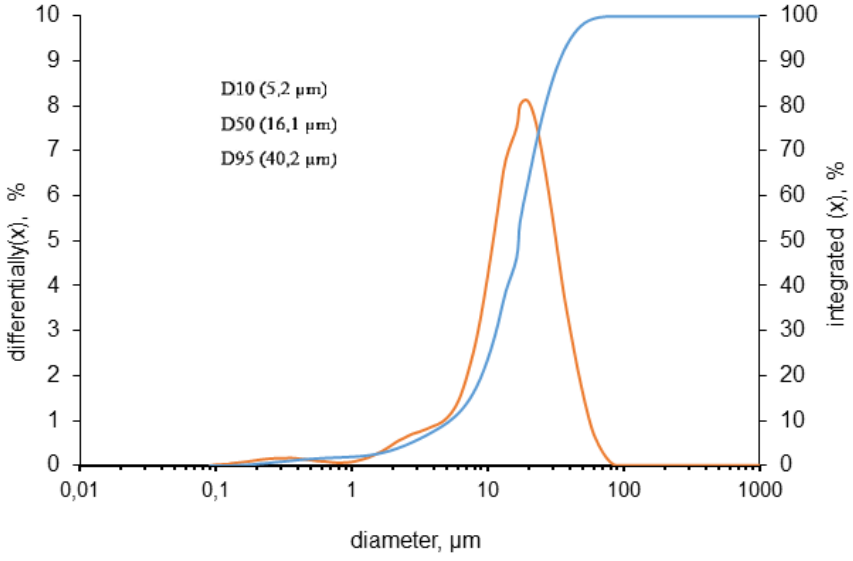


Fig. 10. Particle size distributions of composite material based on fluoroplast polymer, bismuth oxide and tungsten carbide

It was mentioned above that cryopreservation of elastomers at low temperatures makes it possible to obtain a fine powder, which allows you to create new composite materials. The analysis of the results showed that the total range of particles corresponds to the range from 0.1 to 75 microns, 50 % of the substance is less than 16 microns and 95 % is less than 40.2 microns. The bulk of the material is represented by particles from 15 to 20 microns. This generally allows us to conclude about a finer grinding compared to traditional polymer grinding technologies, which produce sufficiently large polymer particles from 2 to 10 mm. More finely ground material is able to acquire new physical and chemical properties that allow you to adjust the duration of technological processes, reduce material consumption and energy consumption, etc.

4. Conclusions

The technology of grinding and homogenization of composite materials in the composition of fluoroplast, bismuth oxide and tungsten carbide is proposed which includes combined processes of cryogenic and ultrasound grinding and homogenization alternating in a certain pattern. In the process of cryogenic grinding and homogenization of composite materials consisting of fluoroplast, bismuth oxide and tungsten carbide, the installation allowed processing the crushed product in the ranges of variable oscillation frequencies at 50-450 Hz which provided vibrational movements of grinding bodies and the crushed product in the aisles of 3-150 microns/s. It is established that in the process of cryogenic grinding a better homogenization of the mixture of materials occurs and the range of particle size distribution is significantly shifted to the region of the smallest particles. The total range of particles corresponds to the range from 0.1 to 75 microns, 50 % of the substance is less than 16 microns and 95 % is less than 40.2 microns. The bulk of the material is represented by particles from 15 to 20 microns, which is significantly smaller than the particle sizes obtained during grinding at a ball mill.

The study of the microstructure of the finished samples confirmed a more uniform distribution of particles over the volume of the composite when using the mixture after cryomilling which in the future will allow obtaining radiation-protective composite materials based on the developed mixture.

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