Study of the Effect of Cryogenic Grinding on the Microstructure and Mechanical Properties of Polymer Composites

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Abstract. The paper presents data on the synthesis of polymer composites based on a fluoroplastic matrix and ground titanium hydride. The possibility of mixing the initial components using cryogenic grinding has been studied. The uniformity of distribution of the filler in the polymer matrix was investigated by scanning electron microscopy. For comparison, composites were made in which the mixing of the components was carried out manually in an agate mortar. It is shown in the work that when using cryogenic grinding of components, their distribution is much more uniform than when manually mixing. It has been established that cryogenic milling will prevent the agglomeration of highly dispersed titanium hydride particles obtained during milling, ensuring high homogeneity of the polymer composite. Data on the mechanical properties of the obtained composites are presented. Annealing at 350 °C significantly increased the microhardness of all the samples under study. For pure fluoroplastic, this value increased by 35.7%, and for composites by 35.5% and 30.7% when using grinding in a mortar and cryogenic grinding, respectively.

Keywords: Cryogenic grinding · Titanium hydride · Fluoroplastic · Surface microstructure · Microhardness · Hot pressing

1 Introduction

Scientists from various countries are involved in radiation protection. The most common materials for radiation protection from gamma and neutron radiation are concretes [1–3]. Recently, special attention has also been paid to radiation-protective materials based on polymers [4–6]. Such polymer composites consist of a radiation-resistant polymer matrix and a radiation-shielding filler. Depending on the type of radiation for which protection is created, the type of filler is selected. For example, organosilicon fillers can be used to protect against cosmic radiation in which vacuum ultraviolet radiation is present [7]. In addition, the use of organosilicon fillers significantly increases the resistance of composites to the incident flow of atomic oxygen in space [8, 9].

Biological protection of nuclear reactors requires comprehensive protection from both gamma and neutron radiation. The works [10, 11] present data on the radiation-protective characteristics of a multicomponent material the iron – magnetite – serpentinite cement concrete with high protection. The work [12] summarizes the data on fillers

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used in concrete for biological protection. In [13], using the barite aggregate as an example, it is shown that the type of aggregate is more important than the amount of aggregate used in concrete to protect against γ-radiation.

Metal hydrides [14, 15], in particular titanium hydride, are promising materials for protection against neutron radiation. Titanium hydride possesses not only good protective properties against neutron irradiation, but also high thermal stability [16, 17]. Most of the research is devoted to the introduction of titanium hydride into concrete. This paper presents data on the possibility of introducing titanium hydride into a polymeric fluoroplastic matrix.

The creation of polymer composites is associated with a number of problems. The main one is the uniform distribution of the added filler into the polymer matrix [18, 19]. With an uneven distribution of filler particles, conglomerates are formed, which leads not only to a decrease in physical and mechanical properties, but also to a decrease in radiation-protective characteristics. One of the solutions to this problem is the modification of the added filler, but this is a rather laborious process [20, 21]. In this work, we used a method of mixing fluoroplastic and titanium hydride by means of joint cryogenic grinding of components.

2 Methods and Materials

Fluoroplastic F-4, grade PN-20, was used as a polymer matrix. It was a white press powder with a particle size of 6–20 μm. Fluoroplastic of this brand is used for products with increased reliability. The density of the fluoroplastic used is 2.2 g/cm^3.

Titanium hydride with the chemical formula $TiH_{1.7}$ was used as a filler. The starting titanium hydride was a shot with a diameter of 1–4 mm. To introduce titanium hydride into the polymer matrix, it was preliminarily ground in a jet-vortex mill for 15 min. After grinding, the titanium hydride particle size did not exceed 100 μm.

The mixing of the components (fluoroplastic and titanium hydride) was carried out in a vibrating mill at a cryogenic temperature. To create a cryogenic temperature, liquid nitrogen was used ($T = -196$°C). To obtain composites, the homogenized mixture was molded by hot pressing at a temperature of 200 °C and then annealed at a temperature of 350 °C. To assess the effect of cryogenic grinding on the properties of the final composites, composites were also synthesized without using cryogenic grinding. The mixing of the components was carried out by manual mixing in an agate mortar. The amount of filler in both cases was 60 wt%.

The surface microstructure of the obtained composites was studied using a TESCAN MIRA 3 LMU high-resolution scanning electron microscope.

The Vickers microhardness of the obtained samples was investigated on a NEXUS 4504 device at the same load of 200 g.

3 Results and Discussion

Figure 1 shows the data on the microstructure of the surface of polymer composites obtained by mixing the components manually in an agate mortar (a, c) and using cryogenic grinding (b, d).

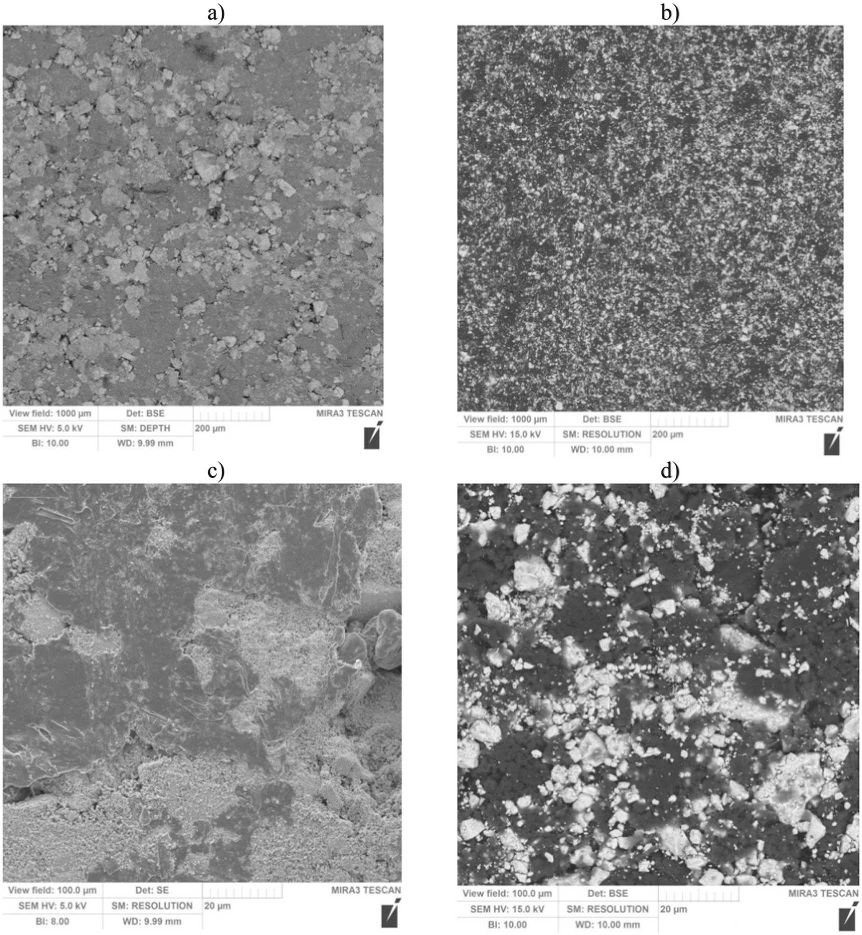

Fig. 1. SEM images of polymer composites obtained by mixing components manually in an agate mortar (a, c) and using cryogenic grinding (b, d).

Data analysis Fig. 1 shows that when the components are manually mixed in an agate mortar, an uneven distribution of titanium hydride (light area) occurs in the fluoroplastic matrix (dark area). Particles of titanium with this method are combined into large conglomerates. When using cryogenic grinding of components, a much more uniform distribution is observed (Fig. 1 b, d). This method will prevent the agglomeration of highly dispersed titanium hydride particles obtained during grinding, ensuring high homogeneity of the polymer composite. In addition, the use of joint cryogenic grinding will significantly improve the physicomechanical and radiation-protective characteristics of finished composites due to the introduction of the maximum amount of filler.

Table 1 shows the data on Vickers microhardness of composites and fluoroplastic (PTFE) after molding and subsequent annealing. The load in all measurements was the same –200 g. The measurements were carried out at 5 different points. Table 1 shows the arithmetic mean values of the microhardness, taking into account the standard deviation. Figure 2 shows the obtained prints of a tetrahedral pyramid on the samples under study.

Table 1. Microhardness of composites after molding and subsequent annealing.

Sample	Mixing type	Vickers microhardness (HV)	
		Molded	Annealed
PTFE	–	4.2 ± 0.32	5.7 ± 0.41
PTFE+ $TiH_{1,7}$ (60 wt%)	In a mortar	4.5 ± 0.28	6.1 ± 0.36
	Cryogenic grinding	5.2 ± 0.29	6.8 ± 0.35

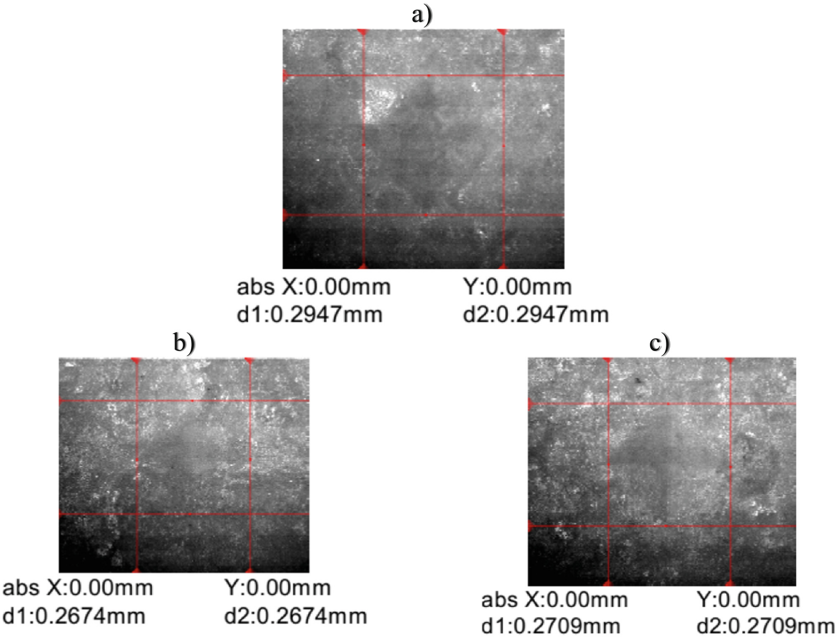

Fig. 2. Image of the imprint of the indenter of a microhardness tester when measuring the microhardness of fluoroplastic (a), composites with 60 wt% titanium hydride obtained by mixing in a mortar (b) and mixing using cryogenic grinding (c).

Analysis of the data presented in Table 1 showed that annealing at a temperature of 350°C significantly increased the microhardness of all the samples under study. For pure fluoroplastic, this value increased by 35.7%, and for composites by 35.5% and 30.7% when using grinding in a mortar and cryogenic grinding, respectively. It is noticeable that the introduction of the proposed filler in both cases increases the microhardness in comparison with unfilled fluoroplastic. However, when using cryogenic grinding, the hardness is much higher.

4 Conclusion

The possibility of using cryogenic grinding for the synthesis of composites based on fluoroplastic and finely ground titanium hydride has been established. This method made it possible to prevent the agglomeration of highly dispersed titanium hydride particles obtained during grinding, ensuring high homogeneity of the polymer composite. In addition, the use of joint cryogenic grinding made it possible to significantly increase the physicomechanical characteristics of the finished composites, which were evaluated by the Vickers microhardness. For annealed samples without cryogenic breakage, the microhardness was 6.1 ± 0.36 HV, and for samples obtained by cryogenic grinding –6.8 ± 0.35.

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