Influence of tungsten nanopowders W, tungsten oxide WO₃, tungsten carbide WC on changing radio protective properties of polymers

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Abstract. The paper considers the possibility of improving radio protective properties of polymers by modifying with nanopowders: tungsten W, tungsten oxide WO₃, tungsten carbide WC, obtained from hard-alloy waste. The study determined the coefficients of linear attenuation of gamma radiation in the energy range of 59.93 keV...1408 keV at various concentrations of nanopowders 20...80% of the mass of the material, with a step of 20%. The comparative characteristic of the obtained data is given. The developed composite materials can be used in the systems of passive protection, dosimetry, space technology, as well as greatly facilitate the weight of various structural products.

1. Introduction

At present, the main materials used in the construction of protection against ionizing radiation are lead and reinforced concrete structures, which have a number of disadvantages: a large mass, high cost of construction, etc. As an alternative to traditional materials can be considered more functional, flexible and lightweight materials - polymers (polyurethane, rubber, polypropylene, etc.) [1-4]. Among polymers polyurethane has the greatest number of advantages in evaluating physical and mechanical characteristics: high mechanical strength, elasticity, shape preservation at multiple deformations, wear resistance and durability, resistance to acids and various solvents, a wide range of operating temperatures, good resistance to any kind of mechanical processing [5]. Application of polymers as the basic material of protection allows to make protective compositions of any geometrical forms, which is quite problematic to perform for standard materials of protection, such as reinforced concrete [6]. However, despite a number of advantages, pure polyurethane transmits a flow of gamma quanta [7]. Therefore, improving the radiation-protective properties of the polymer is a very urgent task today. In this paper, the authors suggested using modifying additives in the form of tungsten nanopowder and its compounds.

2. Experimental part
As a matrix of nanocomposite we used plastic based on polyurethane ARTCAST70 with the following characteristics: density 1.03 g·cm$^{-3}$, average viscosity 150 mPas at 25 °C; tensile strength 27 kgf·cm$^{-2}$. Nanopowders of tungsten W, tungsten oxide WO$_3$ and tungsten carbide WC, obtained by [8] technology from tungsten carbide cobalt waste, were used as a filler increasing radio protective properties of the studied plastic [8]. Microstructure of particles of investigated modifiers obtained from hard alloy scrap is presented on electronic microscopes (fig. 1).

As shown in previous studies [9-10], tungsten powders and tungsten carbide are mainly nanoplates with an average size of 40-200 nm, tungsten oxide up to 100 nm. Larger particles are represented as agglomerates of irregularly shaped particles, especially in tungsten oxide powder. For the study, samples were made in the form of plates 50×50×2 mm in size with different nanopowder content of 20, 40, 60, 80 wt.% of the plastic mass. As sources of gamma rays we used sample spectrometric gamma emitters: $^{241}$Am and $^{152}$Eu. Therefore experimental samples were exposed to gamma rays of energy range 59.93...1408 keV.

3. Experimental data analysis

To estimate radiation-protective properties of nanomodified plastic samples, the coefficients of linear attenuation of gamma radiation of material at different content of nanopowders 20, 40, 60, 80 wt.% were determined experimentally by analytical means (Fig. 2).

Based on the presented results of the study (Fig. 2) of changes in the linear attenuation coefficient of plastic from the content of nanopowders in the energy range of 59.93...1408 keV, it can be seen that the nature of the distribution, in spite of the amount of added nanopowder, remains the same. At low energies of 59.93 keV and 122.7 keV the value of attenuation coefficient is the highest, and at energies of 244.79 keV and more there is a sharp decline. At that this pattern is characteristic for all samples with different content of additives:

- the addition of 20 wt % nanopowder in the composite matrix increases the linear attenuation coefficient in the energy range of 59.93 ... 122.7 keV on average: when adding tungsten carbide more than 16.3 times; when adding tungsten carbide more than 10.6 times and when adding tungsten oxide more than 6.9 times compared to the reference sample;

- when the additive is increased up to 40 wt%, the best protective properties are shown in tungsten - the attenuation coefficient is 1.682 cm$^{-1}$ at 59.93 keV and 1.451 cm$^{-1}$ at 122.7 keV;

- composites with the addition of 60 wt% nanopowder have almost the same protective properties regardless of the type of nanopowder - the value of the linear coefficient of attenuation of gamma radiation increases by 18...20 times compared to pure polyurethane;

- the greatest protective properties have composites with 80 wt % of nanopowders introduced into the matrix, while tungsten additive increases the value of the linear attenuation coefficient to 8.3 cm$^{-1}$ (0.1 cm$^{-1}$ for pure polymer) at 59.93 keV quantum energy. However, when the energy is doubled, the value of the attenuation factor sharply decreases to 1.3 cm$^{-1}$.

Thus, analyzing the experimental data (Fig. 2), we can see that the linear coefficient of attenuation of gamma radiation has a direct dependence on the radiation energy, and the nature of the distribution
is the same in all cases. Protection from quanta with energies of 59.93 and 122.17 keV is most effective when the processes of Compton scattering (Compton effect) and photo effect are most probable. That is, the gamma quantum, undergoing a series of collisions with electrons of the atom (scattering) eventually ceases to exist.

Protection from quanta with energies of greater than 244.7 keV changes - the probability of Kompton scattering interaction is unlikely, and for the process of pair formation the energy must reach 3 MeV. But despite this, the protective properties in the presence of nano additives (tungsten carbide, tungsten oxide and tungsten) are more than 6 times higher than the protective properties of pure polyurethane.

In the case of protection from gamma quanta with energies greater than 244.7 keV, the picture changes - the probability of the Kompton scattering interaction is unlikely, and for the process of pair formation the energy must reach 3 MeV. But despite this, the protective properties in the presence of nano additives (tungsten carbide, tungsten oxide and tungsten) are more than 6 times higher than the protective properties of pure polyurethane.

Taking into account that μ represents a fraction of decrease in flux density of falling gamma quanta when they pass a 1 cm thick protective layer, the density of protective material is an important parameter, as gamma quanta interact with electrons of atoms, the presence of which in a unit of volume is directly proportional to the probability of interaction, and, consequently, to the multiplicity of attenuation of the flow of ionizing particles. As can be seen from the presented values (Table 1) of density of investigated samples, nano additives essentially increase the value of density of a material in comparison with a control sample.

Table 1. Density of polyurethane-based plastic with the addition of nanoprops

| nano additive,% | ρ, g·cm⁻³ | nano additive,% | ρ, g·cm⁻³ | nano additive,% | ρ, g·cm⁻³ |
|----------------|-----------|----------------|-----------|----------------|-----------|
| 0%             | 1,03      | 0%             | 1,03      | 0%             | 1,03      |

Figure 2. Change of linear coefficient of gamma radiation attenuation by protective screen of reference sample (without modifier) and modified by W, WC , WO₃ nanopowders of plastic samples at different concentrations a) 20% wt % b) 40 wt % c) 60 wt % d) 80 wt %.
4. Conclusions

A study of the effect of the content of tungsten oxide, tungsten carbide and tungsten nanopowders obtained from carbide scrap on the radiation protective properties of a composite material based on a matrix of polyurethane has shown that:

- The most effective plastic filler for radiation protection purposes is the addition of tungsten nanopowder, which even at 20 mas. % allows to increase the value of gamma radiation attenuation coefficient from 0.1 cm\(^{-1}\) for pure polyurethane to 1.067 cm\(^{-1}\) at energies of quanta in 59.93 keV;
- in addition, the dynamics of gamma radiation absorption is preserved with increasing energy: the most effective way is to attenuate the flow of low-energy gamma of quanta (59.93 keV), with increasing energy up to 244.79 keV there is a sharp decline in absorption. Starting from 343.79 keV, the values of the linear attenuation coefficient are almost the same;
- according to the data of the experiment, the base composite matrix can be represented by almost any material depending on the necessary properties taking into account the operating conditions, since the addition of tungsten-based nanopowder and its compounds (tungsten oxide, tungsten carbide) increases the density of the material more than 3 times, thus improving its radiation protective properties.

In the future, taking into account the linear coefficient of attenuation of the gamma of radiation by the protective medium and the energy spectrum of quanta, it is possible to choose the optimal thickness of the protective screen, which allows reducing the flow of quanta to values that ensure compliance with radiation safety requirements.

The use of a composite material based on a matrix of polyurethane with the addition of nanopowders based on tungsten, all other things being equal, will allow the use of the proposed material in dosimetry, space technology, as well as significantly reduce the weight of various structural products.

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