Tungsten nanoparticles influence on radiation protection properties of polymers

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Abstract. In the presented article the results of the study of metal-polymer composites based on the ultra-high molecular weight polyethylene GUR 4122 with the addition of superdispersed tungsten nanopowders with 5, 10, 20, 40, and 50 mass percent content levels are given, their thermophysical, radiation-shielding, and mechanical properties are shown, and the influence of content levels of tungsten superdispersed nanopowders on these properties is analyzed. The conducted studies have shown the increase in the listed properties depending on the content level of tungsten superdispersed and nanopowders in the ultra-high molecular weight polyethylene GUR 4122. Owing to their properties, the obtained materials may be used in various fields, such as aviation, space technologies, mechanical engineering, etc.

1. Introduction

In recent years, in almost every field of industry, there has been a tendency to substitute products made of metal for parts, structures, and coatings made of polymers [1]. As a result, stricter operational requirements are imposed to polymers. One way to improve the quality of polymeric materials is to use various micron and submicron-sized fillers, such as aluminum oxide (Al$_2$O$_3$) [2], copper (Cu) [3], alumina [4], titanium dioxide (TiO$_2$) [5], graphite, molybdenum disulfide (MoS$_2$) [6], etc. Modification of polymers is accompanied by an increase in their physical and mechanical properties which permit to largely control the structure and properties of materials due to nucleation and orientation effects, a change in conformation of macromolecules, their chemical binding with the surface of nanosized particles, and the healing of structural defects [7].

The most promising polymer binder for creating composites is ultra-high molecular weight polyethylene (UHMW PE), which is the cheapest most affordable binder with a unique set of physical and mechanical properties, such as a strong wear resistance, stability in the corrosive environment, high impact elasticity, etc. [8]. Nevertheless, for the time being, polymer composites have not been widely adopted as radiation-resistant and radio-protective materials.

Traditionally, lead and barium are used to solve radiation shielding tasks. These materials are toxic and subject to quick ageing, that is why the problem of search for alternative radio-protective materials is of topical interest. Global trends in practical solution of the tasks of radiation shielding are focused on the development of effective, light, and economically rational materials. Therefore, UHMW PE represents an attractive material intended for an effective attenuation of particle radiation [2]. Besides, its use as a filler in heavy metal composites or their compounds lends it radio-protective (RP)

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properties [9]. To impart radio-protective properties, papers [10, 11] suggest the use of tungsten, boron carbide, and tungsten carbide nanopowders as a UHMW PE. However, a widespread use of these nanofillers is restrained by a rather high cost of nanopowders.

2. Objects and Methods of Research

The object of research was the following: a metal-polymer composite, based on ultra-high molecular weight polyethylene with the addition of the tungsten powder obtained as a result of processing hard-alloy production wastes employing the biodegradation method, based on the destruction of the alloy matrix with specially prepared solutions using the adapted association of microorganisms [12]. During the microbiological processing, binding components of the tungsten-nickel-iron alloy (Fe, Ni) oxidize and go to a liquid phase; the alloy matrix is destroyed; as a result, mechanical properties of tungsten change, it becomes cold-short, which leads to a faster crushing of raw materials. Tungsten represents the major elemental composition of the powder, over 96.7 % (table 1); its appearance is shown in figure 1.

| Table 1. The elemental composition of the tungsten powder. |
|------------------------------------------------------------|
| Element | Concentration, % |
|---------|-----------------|
| W       | 96.943          |
| Fe      | 1.297           |
| Co      | 1.016           |
| Ti      | 0.525           |
| Cr      | 0.219           |

**Figure 1.** A picture of the tungsten powder obtained through processing hard-alloy wastes using the biodegradation method.

It is established that the size of particles of the powder W lie within the range of 0.19 ... 2.344 microns, while 90% of them are smaller than 0.9 microns. The bulk density is 19.2 g/cm³. The specific surface is 4.2 m²/g.

The study of the influence of the tungsten powder on thermo-physical, mechanical, and radio-protective properties of the composite was conducted based on ultra-high molecular weight polyethylene GUR 4122 (Ticona GmbH); its main characteristics are given in Table 2 [13].

| Table 2. Properties of ultra-high molecular weight polyethylene. |
|---------------------------------------------------------------|
| Parameters | Density, (g/cm³) | Thermal linear expansion coefficient at 296...353 K | Thermal conductivity at 296 K (W/ (m·K)) | Specific heat capacity at 296 K, (kJ/kg·K) | Tensile yield stress, (MPa) | Tensile modulus, (MPa) |
| Standard   | ISO 1183 | ISO 11359, part 1-2 | - | Adiabatic calorimeter | ISO 527 | ISO 3167 |
|------------|---------|---------------------|-----|----------------------|--------|--------|
|            | 0.93    | ≈ 2·10⁻⁴            | 0.41 | 1.84                 | ≥ 17   | 790    |


The uniform filler distribution was done in the rotating electromagnetic field by means of non-equilibrium ferromagnetic particles. The resulting compositions were processed into samples using the method of compression molding ($T = 433 \text{ K}$, $p = 20 \text{ MPa}$). As a result, six samples of the same size ($d = 50 \text{ mm}$, $h = 10 \text{ mm}$), containing 0%, 5%, 10%, 20%, 40%, and 50% of tungsten powder respectively, were obtained.

The heat conductivity coefficient ($\lambda$, W/m·K) was determined using devices ИТ-400 in accordance with State Standard 25630.2 at temperatures 173 … 473 K.

The heat diffusivity coefficient of the materials was calculated using the equation (1):

$$\alpha = \frac{\lambda}{C_p \cdot \rho}$$

where  $\alpha$ is the heat diffusivity coefficient, m$^2$/s; $\lambda$ – heat conductivity coefficient, W/(m·K); $C_p$ – specific heat capacity, kJ/Kg·K; $\rho$ – density of the sample, kg/m$^3$.

The compressive yield stress was determined in accordance with State Standard 4651-78 using the testing machine FP – 100. To determine the tensile modulus ($E$), a diagram was used to estimate the values of loads, which correspond to the values of relative deformation of 0.1% and 0.3% (State Standard 9550-81). Calculations were carried out using the equation (2):

$$E = \frac{(F_2 - F_1)}{A_0(\Delta h_2 - \Delta h_1)}$$

where $F_1$ and $F_2$ are loads corresponding to the relative deformation of 0.1% and 0.3 % respectively, Н; $h_0$ is the initial height of the sample, mm; $A_0$ – area of the transverse sample, mm; $\Delta h_1$ and $\Delta h_2$ – changes in the height, corresponding to loads $F_1$ and $F_2$.

To investigate radiation-shielding properties of the metal-polymer composite, based on UHMW PE with the addition of the tungsten powder, the resulting samples were exposed to gamma radiation; the installation flow chart is shown in figure 2.

![Figure 2. The installation flow chart:](image)

1 – the source of gamma radiation $^{60}\text{Co}$ ($E = 1252 \text{ keV}$); 2 – dosimeter-radiometer DKC-96; 3 – the collimator; 4 – the sample; 5 – lead housing.

Passing through the collimator (3), $\gamma$-radiation from the cobalt source (1)$^{60}\text{Co}$ ($E = 1252 \text{ keV}$) forms a narrow directed beam of $\gamma$-quanta (figure 1). The samples of ultra-high molecular weight polyethylene are placed in turn after the collimator (4). The dosimeter-radiometer DKC-96 was used as a detector of the $\gamma$-quanta dose rate. The $\gamma$-quanta dose rate (without the samples) equalled 701.3 mSv/h.
3. Results and Discussion
The modification of the ultra-high molecular weight polyethylene using the tungsten powder results in the change of its thermo-physical properties (the coefficient of heat diffusivity, thermal conductivity) figure 3.

![Figure 3. A change of thermo-physical properties of the metal-polymer composite depending on the tungsten powder content.](image)

It has been established that, as a result of the modification of the polymer, as the tungsten powder content increases, so do the thermophysical properties of the polymer. Besides, a surge of rates is seen at 10% modifier content level; in particular, the coefficient of heat conductivity increases by more than 71%, heat diffusivity – by more than 35%.

The study of mechanical properties (yield stress and tensile modulus) of the investigated metal-polymer composites is shown in figure 5.

![Figure 4. A change of mechanical properties of the metal-polymer composite depending on the tungsten nanopowder content.](image)

With the addition of 5% of tungsten powder to the metal-polymer composite, a leap in the yield stress coefficient by more than 12% is observed; then, as the content level is increased two times, the coefficient is also increasing by 2% on average, with the exception of 50% concentration, where, on
the contrary, a decrease in the investigated coefficient by 0.12% is observed. As to the tensile modulus, it is steadily rising over the whole investigated range, reaching its maximum value of 1053.5 MPa at 50% filler content level, which is by more than 35% higher than the value of the initial polymer.

It has been established that the composites based on the ultra-high molecular weight polyethylene, modified with the tungsten powder, excel the base polymer in thermophysical (by more than 11…100%) and mechanical (by more than 5…35%) properties respectively.

When passing gamma quanta through metal-polymer composite samples under study it is obvious that as the tungsten powder content increases up to 10%, the attenuation factor of γ-quanta remains virtually unchanged (figure 5). With further increase in the tungsten powder content, the attenuation factor rises according to the non-linear dependence. The increase in the tungsten content in the sample by 50% results in the growth of the attenuation factor by 5%.

![Figure 5. A change of attenuation factor of γ-quanta depending on the tungsten powder content in the metal-polymer composite samples](image)

It is known that γ-quanta, passing through the samples under study, are exposed to three types of interaction, whose probability depends on the material of samples and γ-quanta energy: these are a photoelectric effect, Compton scattering, and the formation of electron-positron pairs.

In case of a photoelectric effect and the formation of electron-positron pairs, primary γ-quanta are absorbed by the protection matter. The formation of pairs is accompanied by the appearance of an electron and a positron; a photoelectric effect results in the emergence of a photoelectron. Thus, during these types of interaction the primary γ-quantum is dropped out of the beam. In case of a Compton effect, γ-quanta are scattered, and their energy decreases, resulting in the appearance of a recoil electron.

In the proposed installation (figure 2) the scattered γ-quanta of the beam are absorbed by the collimator material, and, having experienced the act of scattering, are dropped out of the beam. In case of a narrow beam, these three types of interaction do not result in the emergence of scattered γ-quanta in the vicinity of the detector of the γ-quanta dose rate. Therefore, in order to investigate the dependence of changes in the attenuation factor of γ-quanta on the thickness of materials under study, future work will require that additional research of γ-quanta passing through metal-polymer composite samples of different thickness be conducted. As in practice one generally encounters scattered radiation of γ-quanta (“broad-beam geometry”), it is planned to conduct a series of studies of the attenuation factor of γ-quanta in a broad beam.

4. Conclusion

Thus, as a result of the work performed, new metal-polymer composites based on the ultra-high molecular weight polyethylene and the superdispersed tungsten powder have been created. It has been determined that metal-polymer composites excel the base polymer in thermophysical and mechanical properties 1.1-2 times and by 17-35% respectively. The presence of tungsten particles in the structure
of the ultra-high molecular weight polyethylene gives it a set of new properties enhancing its applicability in the parts of movable joints.

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