
MATERIALS FOR ENERGY AND RADIATION-RESISTANT MATERIALS

Polymer Composite Material for Radiation Protection of Electron Linear Accelerators

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Abstract—The results of the synthesis of a polymer composite material based on a fluoroplastic mold powder filled with tungsten(VI) oxide are reported. Data on the modification of tungsten(VI) oxide with K-9 organosilicon resin are presented. It has been established that the creation of a silicon shell on the surface of oxide particles changes the hydrophilic nature of the surface to a hydrophobic one, which is evaluated by a change in the contact angle. Fluoroplastic and modified WO₃ powders were mixed by cryogenic grinding for 30 min at a temperature below –60°C. Next, the homogenized powder mixture was loaded into a mold, heated to a temperature of 280°C, kept for 1 h, and then pressed at a specific pressure of 80 MPa. The flexural strength is 21.17 MPa at the filling of 30 wt % and 18.86 MPa at the filling of 60 wt %. The passage of electron radiation with energies from 1 to 10 MeV through the proposed composites has been simulated in the CASINO V2 software. Trajectories of electron motion have been plotted and the electron effective range in the specified composite material has been calculated.

Keywords: fluoroplastic, radiation protection, linear electron accelerator, composite, effective electron range

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INTRODUCTION

Linear accelerators have many applications, including X-ray generation in medicine, radiation treatment of food and agricultural products, study of the properties of subatomic particles, etc. [1]. The linear accelerator design depends on the type of accelerated particle: electrons, protons, or ions. In addition to the X-ray imaging machines conventionally used in medicine, linear electron accelerators are becoming increasingly popular in the treatment of oncological diseases. In this case, ionizing radiation acts by damaging the DNA of cells, including cancer ones [2]. As is well known, electron accelerators can be successfully used to combat infectious plant diseases, reducing the number of phytopathogens on seeds [3]. Pulsed linear accelerators are widely used abroad for cold electron pasteurization of food products [4], so the shelf life of the latter can be increased by a factor of 2–4 [5].

The widespread use of electron irradiation in industry requires ensuring the safety of service personnel. The requirements for radiation protection of electron accelerators must meet SanPiN 2.6.1.2573-19. The materials that can be used for radiation protection of linear electron accelerators are heavy concrete, ceramic composites, metal-matrix composites, and

polymer composites. Concrete is a relatively cheap material acceptable for manufacture of structures of various shapes. Its good protective properties against the effects of neutrons and X-rays are due to the high water content and relatively high density. To improve the radiation-protective properties, concretes can be additionally supplemented with special fillers. For example, in [6, 7], the high efficiency of concretes with titanium hydride shot was demonstrated. However, concrete products as protectors against electron radiation have certain drawbacks. In concretes exposed to ionizing radiation, intense dehydration of calcium hydrosilicates occurs, as well as radiolysis of free and chemically bound water, which leads to radiation embrittlement [8].

In [9], it was shown that MgO-based ceramic materials with small CaO, ZrO₂, and SiO₂ additives can be effectively used for protection against electron irradiation. The possibility of using alumina ceramics as a vacuum beam channel in a fast-cycling synchrotron was investigated in [10]. It was established that alumina ceramics have a fairly high flexural strength (over 300 MPa before electron beam irradiation), and the experimental results did not show deterioration of the flexural strength after irradiation with an electron beam with an energy of 2.5 MeV at a dose of 1000 MGy.

A metal composite material is known that ensures the efficient biological protection against fast electrons with an energy of up to 6.2 MeV at an absorbed dose of up to 2 MGy and against γ radiation in the energy range of 0.06–1.2 MeV at an absorbed dose of up to 10 MGy [11].

Currently, special attention is paid to the radiation-protective materials based on polymer binders. Despite the high strength and performance characteristics of metal alloys, in substances with a high atomic number, high-energy electrons more effectively generate bremsstrahlung X-rays and γ radiation, the harm of which to biological objects is much more serious [12]. Therefore, a promising area for radiation protection of linear electron accelerators is the use of polymer-based materials, for which this problem is less significant. Many studies were devoted to the creation of radiation-protective polymer composites [13–15]. To synthesize them, a polymer binder is mixed with an appropriate filler and then the finished product is formed. The main difficulty in creating polymer composites is to introduce the maximum possible amount of a filler while maintaining the high mechanical properties. The complexity lies in the uniform distribution of a filler over the entire composite volume. To solve this problem, a filler can be modified to create a shell around its particles, which significantly reduces aggregation of the latter [13].

The aim of this work was to study the synthesis of polymer composites based on a fluoroplastic matrix and tungsten(VI) oxide. To introduce a larger amount of filler, it was pre-modified to create a hydrophobic shell. The process of modeling the effect of electron irradiation with an energy of 1–10 MeV on the developed polymer composites is considered.

EXPERIMENTAL

Polytetrafluoroethylene (F-4 PN-20 fluoroplastic) was used as a polymer binder. The fluoroplastic mold powder was manufactured at the OOO Fluoroplastic Products (Belgorod, Russia).

Tungsten oxide WO_3 (99.9% pure, TU 48-4205-122-2019) was chosen as a filler. Its bulk density is 2.8 g/cm³ and loss on ignition is 0.2%.

A hydrophobic shell was created on the tungsten oxide surface from a grade-A K-9 resin (OOO Superplast, Moscow, Russia). K-9 organosilicon resin is a product of condensation of methylsilanetriol and phenylsilanetriol obtained from the corresponding silane chlorides. To create a modifying solution, 20 g of a grade-A K-9 resin and 30 g of toluene were mixed. Dissolution occurred for 60 min in an ultrasonic bath without heating at an ultrasound frequency of 40 kHz. This yielded a slightly viscous transparent solution. After the dissolution time had elapsed, the solution temperature was monitored with a laboratory ther-

mometer; no increase in the solution temperature was detected.

The resulting viscous solution was supplemented with 15 g of WO_3 and kept in an ultrasonic bath for 90 min until a homogeneous yellow emulsion was obtained. No increase in the solution temperature after the ultrasonic treatment was detected either.

Toluene was evaporated for 24 h under a hood under natural conditions. Then, the adhered powder was ground in a ball mill for 5 min.

The fluoroplastic and modified WO_3 powders were mixed using cryogenic milling for 30 min at a temperature maintained below -60°C . Next, the homogenized powder mixture was loaded into a mold, heated to a temperature of 280°C , held for 1 h, and then pressed at a specific pressure of 80 MPa. After pressing, the polymer composites were cooled down to room temperature and then sintered at a temperature of 350°C for 3 h. Sintering of the fluoroplastic composites leads to an increase in density, a decrease in thermal expansion, and an increase in thermal conductivity, which is related to structural changes accompanied by intensification of the adhesive interphase interaction [16].

The composites were pressed on a REM-100-A-1-1 testing machine (OOO Metrotest, Bashkortostan, Russia).

SEM images of the filler particle surface were obtained on a TESCAN MIRA 3 LMU high-resolution scanning electron microscope at the High Technology Center of the Belgorod State Technological University.

The contact angles were measured at room temperature using a Kruss DSA30 drop shape analysis system (Kruss GmbH, Germany).

The flexural strength of the composites was determined by standard methods in accordance with GOST ISO 17138:2014. Loads were applied for three-point bending tests.

The passage of an electron beam with an energy of 1–10 MeV was simulated by the Monte Carlo method in the CASINO V2.481 program [17]. The program uses tabulated elastic interaction (Mott) cross sections and experimental braking forces for calculating the trajectories of electron motion in matter [18]. This allows one to plot the trajectory of electron motion and calculate the electron effective range in a specified composite. The initial data for the program are the density and atomic composition of a material. The specified energy range (from 1 to 10 MeV) is related to the fact that most of the applied linear electron accelerators have an electron beam energy of up to 10 MeV [1, 3].

RESULTS AND DISCUSSION

Figure 1 illustrates the granulometric analysis of the powder of the filler used. The analysis of the WO_3

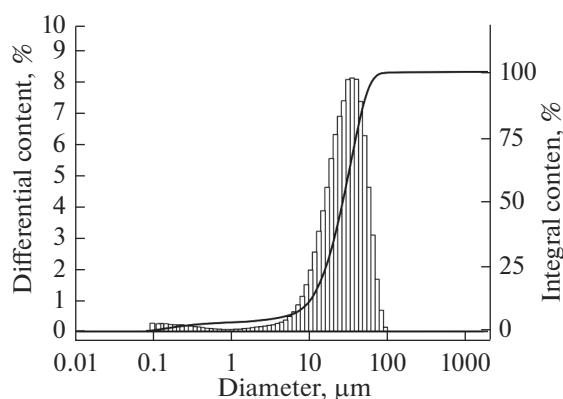


Fig. 1. Fractional composition of the tungsten(VI) oxide filler powder.

particle size distribution showed that particles range from 0.01 to 100 μm in size with the majority of particles (60%) being 30 μm in size (Fig. 1). The modal particle diameter is 35.41 μm and the specific surface area is 15279 cm^2/cm^3 .

Figure 2 presents the SEM image of WO_3 particles. Particles have different shapes, from round to cubic, and sizes from 100 to 250 nm. However, particles are highly susceptible to aggregation and the aggregated particle sizes vary from 2 to 30 μm .

Owing to the significant aggregation of tungsten oxide particles, they were modified in order to create a hydrophobic shell on the particle surface. The creation of the shell will allow the uniform distribution of tungsten oxide particles over the entire composite volume and significant reduction of their aggregation [13]. Figure 3 shows an image of a water droplet on the ini-

tial tungsten oxide powder (Fig. 3a) and the powder modified with K-9 organosilicon resin (Fig. 3b). The initial powder has a pronounced hydrophilic surface: the contact angle is 23.2°. After modification, the hydrophobic–hydrophilic balance of the powder particle surface changes: the powder becomes hydrophobic and the contact angle increases to 131.1°.

Composite samples containing 30 and 60 wt % of the modified tungsten oxide powder were synthesized. To evaluate the introduction of the filler into the composites, reference pure fluoroplastic samples were made. The density of pure fluoroplastic was 2.15 g/cm^3 , which is consistent with the data on the density of F-4 fluoroplastic. The density of the composite containing 30 wt % of the modified filler is 2.65 g/cm^3 and the density of the composite with 60 wt % of the modified filler is 3.15 g/cm^3 . The introduction of the filler significantly increases the density of the composites, since tungsten oxide has a density of 7.16 g/cm^3 .

Figure 4 shows the dependence of the flexural strength of the investigated composites on the degree of filling. To plot the curve, three samples of each composition were tested. On the basis of the data obtained, a regression curve was plotted taking into account the confidence interval of 95%. The highest flexural strength belongs to the samples without filler. As the content of the modified filler grows, the strength characteristics noticeably degrade (Fig. 4). However, even with a modified tungsten oxide filling of 60 wt %, the composite exhibits structural properties ($\sigma = 18.86 \text{ MPa}$).

To evaluate the protective properties of the composites against irradiation with electrons with an energy from 1 to 10 MeV, the passage of an electron

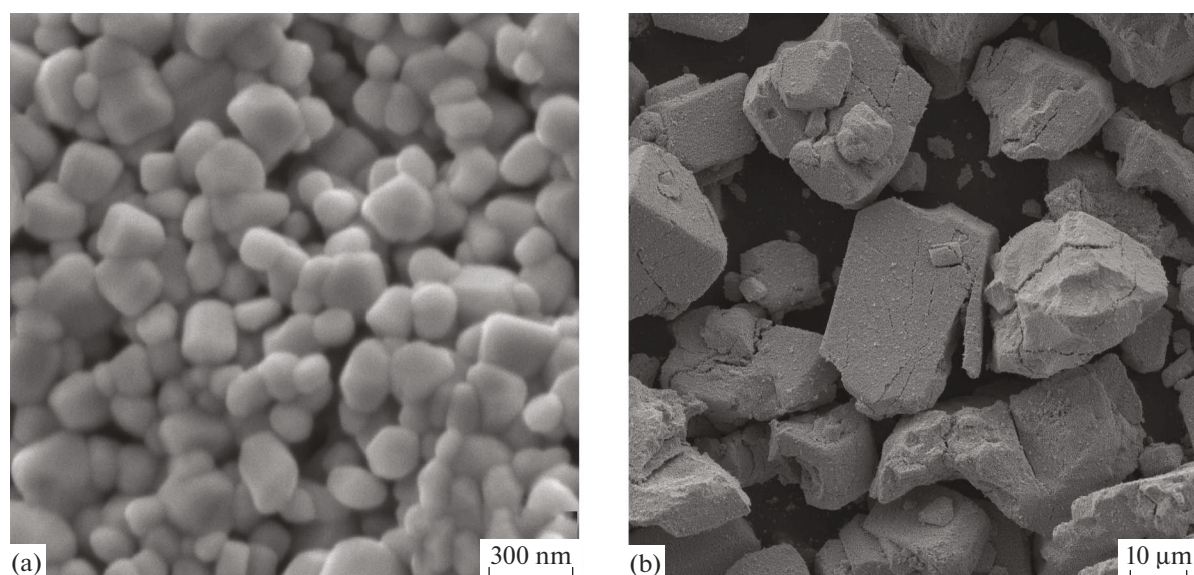


Fig. 2. SEM image of tungsten(VI) oxide filler particles.



Fig. 3. Image of a water droplet on (a) the initial and (b) modified tungsten oxide powder.

beam through the materials of the proposed compositions and, for comparison, through the pure fluoroplastic sample without filling was simulated. The simulation was carried out in the CASINO V2.481 software.

Data on the chemical composition of the investigated materials are given in Table 1.

In the calculation program, the total number of emitted electrons was 1000. All electrons began their motion at one point located close to the material. In Fig. 5, the trajectories of electron motion in the investigated materials and the change in their kinetic energy during motion are plotted.

When colliding with atoms and nuclei, electrons deviate significantly from the initial direction of motion and move along a tortuous trajectory. An effective range is introduced for electrons, which is determined by the minimum thickness of the substance measured in the direction of the initial velocity of the beam and corresponding to the complete absorption of electrons.

Table 2 gives the effective range of electrons in the studied compositions calculated in the program.

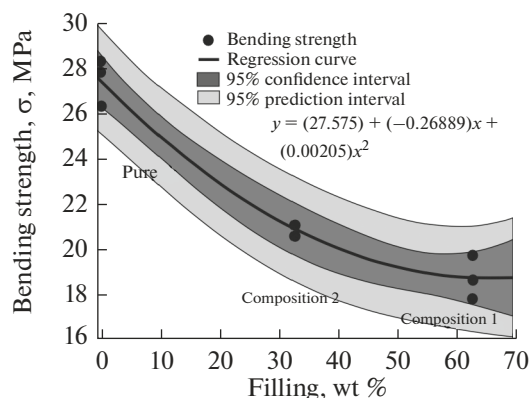


Fig. 4. Dependence of the flexural strength of the investigated composites on the degree of filling.

Analysis of the data on the effective range of electrons showed that, with an increase in the electron energy, the effective range increases significantly. For pure fluoroplastic without filling, with an increase in the initial kinetic energy of electrons from 1 to 5 MeV, their effective range increases by a factor of 4.56, and with an increase in the initial kinetic energy of electrons from 1 to 10 MeV, it increases by a factor of 12.73. For the composite filled by 30 wt %, with an increase in the initial kinetic energy of electrons from 1 to 5 MeV, the electron effective range increases by a factor of 12.39 and, with an increase in the initial kinetic energy of electrons from 1 to 10 MeV, by a factor of 25.9. For the composite with filling of 60 wt %, with an increase in the initial kinetic energy of electrons from 1 to 5 MeV, the effective range of electrons increases by a factor of 9.33, and with an increase in the initial kinetic energy of electrons from 1 to 10 MeV, it increases by a factor of 21.16.

It is noticeable that filling with tungsten oxide significantly reduces the effective range of electrons in the composites as compared with pure fluoroplastic under the initial simulation conditions. In particular, when simulating the passage of electrons with an initial kinetic energy of 1 MeV, a decrease in the effective range of electrons by 68.65% is observed at the modified tungsten oxide filling of 30 wt %, and a decrease by 69% is observed at the filling of 60 wt % as compared with pure fluoroplastic. The simulation of the passage of electrons with an initial kinetic energy of 5 MeV showed a decrease in the effective range of electrons by 26.41% at the modified tungsten oxide filling of 30 wt % and a decrease by 45.25% at the filling of 60 wt % as compared with pure fluoroplastic. The simulation of the passage of electrons with an initial kinetic energy of 10 MeV showed a decrease in the effective range of electrons by 36.24% at the modified tungsten oxide filling of 30 wt % and a decrease by 48.57% at the filling of 60 wt % as compared with pure fluoroplastic.

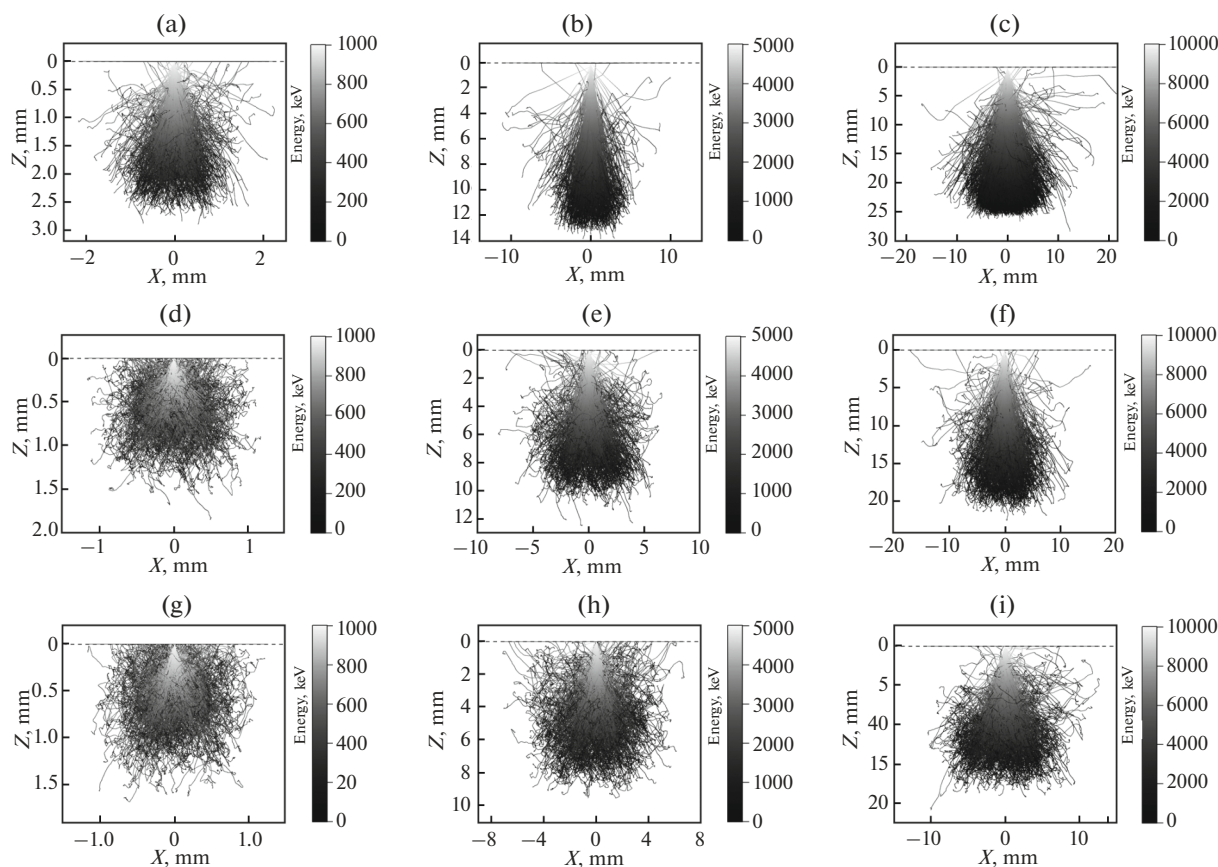
The introduction of the proposed filler significantly shortens the effective range of electrons over the

Table 1. Chemical composition of the investigated materials for the simulation

Material	Content of atoms in the material, wt %			
	W	O	C	F
Pure fluoroplastic without filling	0	0	24	76
Composite with filling of 30 wt %	23.79	6.21	19.08	50.92
Composite with filling of 60 wt %	47.58	12.41	11.89	28.12

Table 2. Effective range of electrons in the investigated materials

Material	Effective range (mm) of electrons with energy		
	1 MeV	5 MeV	10 MeV
Pure fluoroplastic without filling	2.262	11.939	28.804
Composite with filling of 30 wt %	0.709	8.785	18.366
Composite with filling of 60 wt %	0.700	6.536	14.815

**Fig. 5.** Electron trajectories simulated in the CASINO V2.481 software in (a, b, c) fluoroplastic, (d, e, f) the composite with a filling of 30 wt %, and (g, h, i) the composite with a filling of 60 wt % at initial electron energies of (a, d, g) 1, (b, e, h) 5, and (c, f, i) 10 MeV.

entire energy range under study. Shortening of the effective range will allow for a significant reduction in the thickness of radiation protection for linear electron accelerators, which is of special importance for upgrading the available operating electron accelerators.

CONCLUSIONS

The compositions and technology for synthesizing polymer composite materials based on the fluoroplastic molding powder and tungsten(VI) oxide were developed. A method for modifying tungsten(VI) oxide with K-9 organosilicon resin was proposed, which made it possible to create a hydrophobic shell on the oxide surface. After the modification, the hydrophobic–hydrophilic balance of the tungsten oxide powder particle surface changes significantly: the hydrophilic powder (23.2°) becomes hydrophobic; the contact angle increases to 131.1°.

Although the introduction of the modified filler reduces the strength of the samples, the developed composites have sufficiently high strength characteristics and can be used as structural materials. The flexural strength of the composite with the modified tungsten oxide filling of 60 wt % is $\sigma = 18.86$ MPa.

The simulation showed that, when the filler is introduced, the effective range of electrons is significantly reduced at an energy from 1 to 10 MeV as compared with the pure polymer without filling. The use of the developed composites will reduce the thickness of radiation protection of linear electron accelerators. Further research will be aimed at studying the generation of bremsstrahlung X-rays and γ radiation under the interaction of electron radiation with the developed materials and evaluating the protection against this radiation.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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