Conference Paper

Radiation and Protective Polymeric Dielectric Aggregates with Effect of the Active Protection

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Abstract

In case of electrical breakdown of dielectrics electromagnetic interferences can destabilize operation of the electronic equipment and instruments of aerospace complexes. In the conditions of space flight the initiated electrobit phenomena as a result of high-energy ionizing radiation, solar flashouts and radiation belts of Earth, finally, lead to corrupting of dielectric materials, especially polymeric materials and aggregates. In operation the possibility of receiving constructional dielectric polymeric aggregates capable to remove the accumulated excess electrical charge, for protection of jackets of the electronic equipment of space aircraft is shown. Materials are received in the way joint dispersion of a polymeric matrix and reactive hydrophobic metallooligomer in the form of nanodispersible powders in a polymer melt with the subsequent solid-phase compaction under pressure. As the active fillers of polymeric aggregates high-dispersible radiation-hardened metallooligomer on the basis of bismuth polietilsilikonat, capable to be sewed chemically with polymeric matrixes as a result of radiation solid-phase polymerization are used.

Keywords: polymer matrix, bismuth polyethylsilicone, dielectric composites, active protection, mechanoactivation, solid-phase compaction.

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1. INTRODUCTION

Dielectric materials, when irradiated with charged particles and photon radiation with an energy of 1-50 MeV, can accumulate an excess electric charge and create high electrical potentials in the volume of the irradiated material with a current density of 100 A/cm^2. The ability of a dielectric to effectively accumulate an electric charge is determined by its high resistivity, the heterogeneity of its structure, and the presence of deep energy traps in its forbidden zone. If the intensity of the electric field in the volume of the irradiated dielectric from the internal charge exceeds its electrical strength (1-2 MV/cm), then an electrical breakdown of the dielectric occurs on its surface. Physics of this type of electric breakdown has not been sufficiently studied. With

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an electrical breakdown in the bulk of the dielectric, discharge channels are formed that disrupt the structure of the initial material. The discharge channel with electrical dielectric dielectric goes to the free outer surface of the dielectric and a wide spectrum of electromagnetic interference is injected into the surrounding space.

In the electric breakdown of dielectrics, electromagnetic interference can destabilize the operation of electronic equipment and instruments of aerospace complexes. In conditions of space flight, initiated electric discharge phenomena under the influence of high-energy ionizing radiation, solar flares and radiation belts of the Earth ultimately lead to the destruction of dielectric materials, especially polymeric materials and composites. The intensity of anomalies for a year on operating satellites from electric discharge phenomena in the volume of dielectric elements of equipment reaches several hundred. At the same time, radiation anomalies make up almost half of all the anomalies.

The creation of new types of highly effective polymer composites of this functional purpose necessitates the improvement of the theory and practice of their design. Until now, general approaches to the creation of active radiation protection against charged cosmic particles (electrons, protons), capable of reducing the density of particles on the dielectric surface, have not been solved to date, at least up to 10^3 - 10^5 el /cm^2× s (in the electron beam) with an energy higher 1 MeV.

In Russia, until 1994, Neurostop was produced (B/O Isotope), which was made from a mixture of high-purity polyethylene with powdered lead and was designed to protect against γ-radiation. To protect against slow neutrons, polymer composites containing boron were used. An analogue of the domestic protective material ”Neutrostop” is the material ”Neutronstop” (”Kovo”, Czech Republic). In the US, the material is ”Light-Lead”, which is a mixture of lead in an inert polymer. A material with a density of 3030 kg/m^3 has a multiplicity of attenuation of γ-radiation at a thickness of 51 mm (equivalent thickness of lead 6.25 mm) $1{,}3 \cdot 10^3$ (E = 0.2 MeV); 3.2 (E = 0.5 MeV) and 1.7 (E = 1.0 MeV). To protect the devices use flexible lead windings ”Lead Blanket” (USA). This material is a γ-protective elastomer with a high content of lead. The lead equivalent in this material is 0.5 from metallic lead. The multiplicity of attenuation of γ -radiation with a protective screen thickness of 12.5 mm (equivalent thickness of lead 6.25 mm) is: at E = 0.2 MeV 1300; at E = 0.5 MeV 3.2; at E = 1.0 MeV, K = 1.7. The polymer composites Marlex (Nukem, Germany), Piercan le Latex (France), etc., which are a mixture of high-density polyethylene with highly disperse additions of compounds of heavy elements (mainly lead or tungsten), possess similar properties.

Thus, in domestic and world practice, when creating radiation-protective polymeric composites, the main attention was directed to the study of heterogeneous systems obtained by mechanical melt mixing of thermoplastics, mainly polyethylene with metallic lead. As a result, similar systems with a set of positive properties had a number of technical drawbacks. These materials, due to their heterogeneity, have relatively low mechanical characteristics, and in real operating conditions, the insulation of the superconducting system is in a radiation-charged state under strong mechanical stresses, which can act as a synergistic factor that reduces the dielectric strength. In addition, the known materials noticeably reduce their mechanical characteristics under cryogenic temperatures (below -50 °C), which does not allow their use for spacecraft, and with the subsequent heating of radiation-charged dielectrics, numerous electrical breakdowns are observed both on the surface and in the volume of the dielectric.

An important task in the creation of filled polymers is the possibility of regulating the adhesion interaction in order to improve the properties of composite materials. One of the most effective methods of enhancing interfacial adhesion in filled polymers is the creation of a chemical bond between the polymer-filler by using polyfunctional low-molecular compounds-compounds capable of chemical interaction with both the active centers of the filler surface and with the reactive groups of the polymer matrix. This tendency, which has been outlined in recent years, has hardly been reflected to date in the development of polymer dielectric radiation protection systems. The oligomers introduced into the polymer compositions also play the role of sensitizers, allowing to significantly reduce the radiation dose with the resulting positive effects. Typically, the oligomer introduced into the polymer reduces the softening point, and the polymer on its part increases the polymerization rate of the oligomer. Thus, in the basis of polymer-oligomeric technology, a principal possibility is posed to simultaneously accelerate the processing and improve the quality of polymer compositions.

In the known materials ”Light Lead”, ”Lead Blanket”, ”Marlex”, etc. as a result of electrical breakdown in the volume of the dielectric, discharge structures are formed in the form of Lichtenberg figures. In the discharge channels, fractal cluster particles are formed due to the evaporated substance and much more. As a result, even with insignificant mechanical loads, the dielectric collapses.

Modern radiation protection from polymeric composites should be constructed from the calculation of the use as active highly dispersed radiation-resistant fillers - metal oligomers, capable of chemically cross-linking with polymer matrices under the influence of radiation solid-phase polymerization.

2. MATERIALS AND METHODS

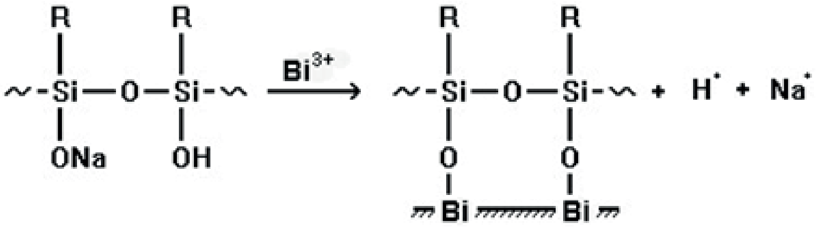
When creating radiation-protective polymeric composites, the work used a variant of manufacturing a composite material in two stages: the joint dispersion of the polymer matrix and the reactive hydrophobic metal oligomer in the form of nanodispersed powders or in the polymer melt (solution), followed by solid-phase compaction at a pressure of 1 GPa. As active fillers of polymeric composites, highly dispersed radiation-resistant metal oligomers based on bismuth polyethyl siliconates (PESB), which are chemically crosslinkable with polymer matrices under the influence of radiation solid-phase polymerization, are used.

The technology of obtaining a composite material based on powdered polymer binders proposed by us makes it possible to perform electrostatic interaction of the components, which ensures high stability of the polymer binder in filled polymer matrices. Such an approach makes it possible to avoid the formation of discharge channels and to obtain polymer dielectric materials that retain their high mechanical characteristics at temperatures below -190 °C.

Synthesis of the metallo-oligomer filler was carried out by heterophasic interaction by treatment of a water-alcohol solution of sodium ethylsiliconate ($RSi(OH)_2ONa$, where $R = C_2H_5$) with a solution of five-channel bismuth nitrate in an aprotic solvent (acetone).

3. RESULTS AND DISCUSSION

The flow of chemical transformations during the synthesis of PESB can be represented as follows:

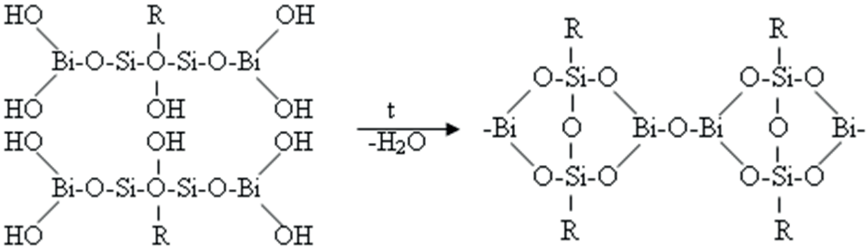


$$\sim\text{-}\underset{\text{ONa}}{\overset{\text{R}}{\text{Si}}}\text{—O—}\underset{\text{OH}}{\overset{\text{R}}{\text{Si}}}\text{-}\sim \xrightarrow{\text{Bi}^{3+}} \sim\text{-}\underset{\text{O—Bi}}{\overset{\text{R}}{\text{Si}}}\text{—O—}\underset{\text{O—Bi}}{\overset{\text{R}}{\text{Si}}}\text{-}\sim + \text{H}^{+} + \text{Na}^{+}$$

(1)

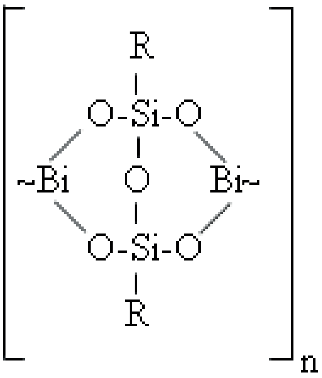
The presence of water molecules in GKZh-10 hydrolyzes a bismuth ion to form a dibasic bismuth cation:

$$Bi^{3+} + 2OH^{-} \rightarrow Bi(OH)_2{}^{+} \qquad (2)$$



(3)

According to IR spectroscopy, the cryoscopic analysis method and mass spectroscopy, the approximate scheme of the elementary link of the oligomeric chain of the formed PESB is presented as follows:



(4)

where n = 12. The molecular weight of the elementary link of the oligomer is about 612 a.m.u. The oligomer has a chain structure, in which a silanol group content (≡Si-OH) is possible in the siloxane chain.

The elementary composition and the molecular weight of the synthesized metallo-oligomer are given in Table 1. The bulk density of the PESB is 2150 kg/m^3, and the maximum density at compaction reaches 5750 kg/m^3.

Table 1: Elementary composition and molecular weight ($\overline{M}$) of oligomeric powder PESB.

Oligomer	Atomic composition,% mass.					$\overline{M}$
	Si	Bi	O	H	C	
PESB	9,15	70,70	13,07	1,23	5,84	7344

A rigid amorphous impact-resistant polystyrene with a molecular weight M = 300000 and an elementary composition of % mass C- 92.31 was used as the polymer matrix; H - 7.69 (GOST 28250-89).

Composite materials were obtained by mixing powdered or granular polystyrene and metallo-oligomer filler in a mixer, mechanically activating them in a jet mill, then mixing the composition with a plasticizing additive with synthetic fatty acid-SFA, C_{17}-C_{21} fractions on rollers at a temperature of 468-473 K for 10 minutes. The mechanical mixtures of polystyrene with a filler content of 40 to 95% by weight were subjected to mechanical activation, followed by granulation in an extruder and loading of the pellets into a heated (373-393 K) mold. The hot pressing mode is set as follows: pre-pressing of the material to R_{sp}. = 10 MPa, raising the temperature to 423 K (exposure τ = 10 min), raising the temperature to 473-493 K and pressure to 80-90 MPa (τ = 1 - 2 min), cooling the mold under pressure to 343-353 K, release of pressure.

Quality control of highly filled polymeric dielectric composites was performed by ultrasonic pulse method and its longitudinal elasticity modulus (E) was determined from the velocity (V) of longitudinal ultrasonic waves in the material [1]:

$$V = (E/\rho)^{1/2} \tag{5}$$

where: ρ - is the density of the material

The results of acoustic tests are shown in Figure 1.

Thus, an ultrasonic method was used to determine the optimum degree of filling of the composite with bismuth polyethyl siliconate, which was 85% by weight.

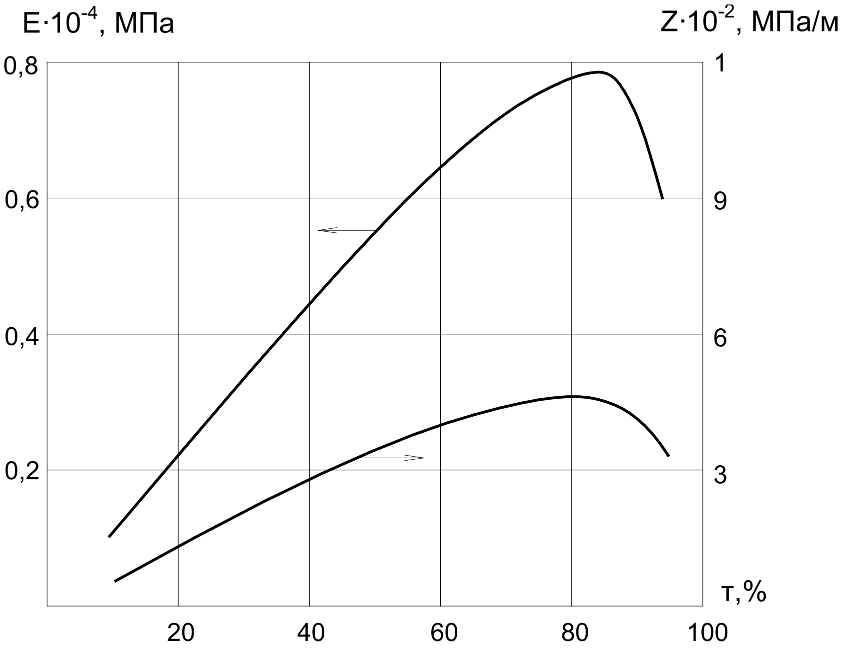


Figure 1: Modification of the longitudinal elastic modulus (E) and specific acoustic resistance (Z) of the polymer composite from the content of bismuth polyethyl siliconate.

The effect of active protection is realized by introducing a layer of chemically precipitated lead sulfide with a semiconductor effect into the volume of the polymer composite. Precipitation was carried out from a mixture of solutions of acetic acid lead $Pb(CH_3COO)_2$ and thiourea $(NH_2)_2CS$ on a substrate of filled polymer composites in an alkaline medium [2, 3]:

$$(NH_2)_2CS = S^{2-} + CN^{2-}{}_2 + 4H^+ \tag{6}$$

The equilibrium of this reaction is strongly shifted to the left, and its active flow becomes possible only as the S^{2-} ions are bound to a sparingly soluble sulfide. The formation of PbS can be described by the reaction:

$$Pb^{2+} + (NH_2)_2CS + 2OH^- = PbS + H_{2+}CN_2 + 2H_2O \tag{7}$$

The use of hydrazine hydrate as a strong reducing agent to create an alkaline medium allows for a higher degree of compensation of impurity levels in the volume of PbS crystals.

The results of physico-mechanical tests of a polymer dielectric composite with 85% content of bismuth polyethyl siliconate are shown in Table 2.

According to [4], the long-term strength of amorphous polymeric materials depends on the type of their stressed state. Tests on the effect of tension, torsion (samples in the form of a cylindrical dumbbell), bending (samples in the form of a flat plate) on the durability of compositions based on polystyrene with 85% filling of bismuth polyethyl siliconate were performed.

Table 2: Physicomechanical properties of a polymer composite based on polystyrene and bismuth polyethyl siliconate obtained by hot pressing.

Index	Parameter PK
Density, ρ, kg / m^3	4400
Breaking stress on bending, δ, MPa	30
Breaking stress torsion, δ, MPa	25
Breaking tensile stress, δ_c, MPa	18
Breaking stress of compression, δ_c, MПa	85
Elastic modulus, E, MPa	$0{,}92 \cdot 10^{-4}$
Relative extension, ε, %	0,25
Microhardness, HV, kgf / mm^2	18
Softening temperature, T$_{soft}$, K	403

The form of the stress state determines the short-term strength (δ_{kp}) and the durability of the polymer composite. For δ_{kp}, the strength corresponding to the time (τ) of the load action lgτ = 0 was assumed.

The curves of the durability of a polymer composite under isothermal conditions are shown in Fig. 2 and have the form of isotherms. The maximum strength of the composite is observed with bending, and the minimum value with stretching. At temperatures below 353 K, the composite collapses in a quasi-brittle mechanism. In the interval 0<lgτ <6, the function lgτ = $f(\delta)$ is linear. At a temperature above 353 K the mechanism of destruction of the composite has a transitional plastic character and the value of δ_0 for any kind of stress state is slightly different from each other and is 6-8 MPa.

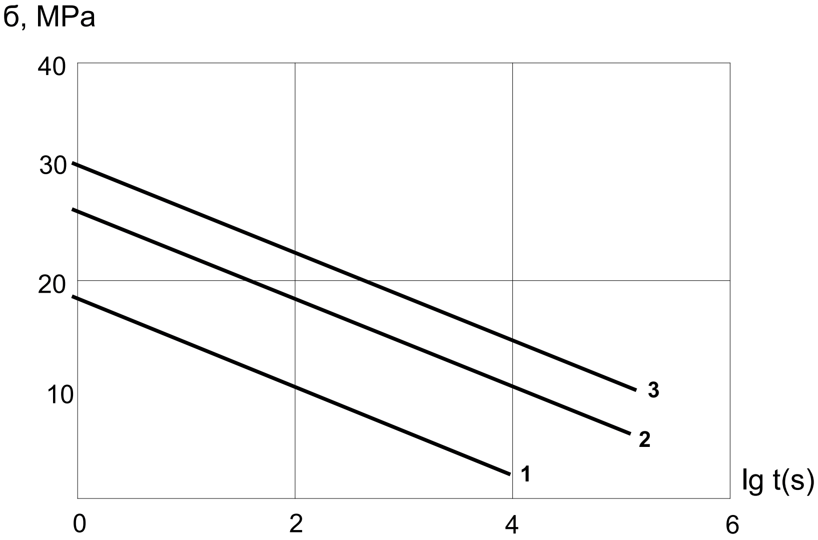


Figure 2: Dependence of the long-term strength of a composite based on polystyrene with 85% filling of bismuth polyethyl siliconate on time and type of stress state at 298 K: 1 - stretching; 2 - torsion; 3 – bending.

On the basis of the research, high-design dielectric radiation protection polymeric composites with high specific resistivity and mechanical compressive strength (above 120 MPa) have been developed. The material is heat-stable up to 300 °C, withstands thermal cycling from -196 °C to +25 °C, is capable of effectively retaining the introduced radiation charge, is resistant to vacuum ultraviolet with a wavelength of 5-200 nm and exposure to solar electromagnetic radiation in the wavelength range 200-25000 nm and radiation intensity up to 108 W /m^2. In addition, the effect of active protection is realized in the material, consisting in the fact that the accumulated excess electric charge is derived from the dielectric through the embedded semiconductor zones. In this case, the remote charge can be used to recharge the batteries of the aerospace complexes.

4. CONCLUSIONS

1. The possibility of synthesis of highly disperse hydrophobic organometalloxane powders is achieved, in the siloxane chain of which there is chemically bound bismuth with a high concentration of bismuth atoms in the oligomeric volume.
2. The possibility of using as active excipients active highly dispersive radiation-resistant metal oligomers - bismuth polyethyl silicones, capable of chemically

cross-linking with polymer matrices under the influence of radiation solid-phase polymerization is shown.

3. It is possible to create in the bulk of the dielectric semiconductor zones from the chemically precipitated lead sulphide, which allows the accumulated excess electric charge to be output.
4. The form of the stressed state of a polymer dielectric composite has a significant effect on its short-term and long-term strength, and, consequently, on the operability of the structural material.
5. The obtained results testify to sufficiently high physicomechanical parameters of a highly filled polymeric dielectric composite based on impact-resistant polystyrene. The resulting composites can be used as structural dielectric materials in the design on their basis of the protective shells of the electronic equipment of spacecraft.

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