

Modification of Optical Characteristics of a Polymer Composite Material under Irradiation

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Abstract—Polymer composites based on polystyrene and modified SiO₂ are synthesized. Effect of the SiO₂ concentration on the surface (thermostatic) properties of the composites is analyzed. Surfaces of composites with different SiO₂ concentrations are microscopically studied. Minor amounts of spherical agglomerates are obtained at relatively high SiO₂ concentrations, and the size of the agglomerates may amount to 80 μm at a SiO₂ concentration of 30 wt %. Variations in the integral absorbance of solar radiation are studied for the polymer composites irradiated with vacuum-UV radiation at a temperature of 125°C.

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INTRODUCTION

Long-term reliable functioning of spacecrafts substantially depends on stability of construction materials and elements of on-board equipment against environmental effects in space. Estimations show that more than one half of malfunctioning events of the spacecraft equipment result from effects of open space. Several effects (in particular, solar UV radiation) lead to changes of near-surface layers of materials, especially, thermal control coatings (TCCs) deposited on the surfaces of spacecrafts for thermal stabilization [1, 2].

With respect to damages caused by solar irradiation in space, it is expedient to consider the effect of UV radiation with wavelengths of less than 200 nm (vacuum-UV (VUV) radiation) and photon energies of greater than 6 eV, which are sufficient for molecular bond breaking in polymer materials [3]. The physical difference of the UV and X-ray radiation lies in the fact that the former excites external electron shells and the latter excites internal electron shells. It is known that chemical and physical properties of materials are determined by the external electron shells. Thus, the UV absorption determines modifications of materials in open space.

VUV irradiation is known to cause changes of optical characteristics of TCCs, in particular, integral absorption coefficient of solar radiation α_s and emissivity, which lead to perturbations of the thermal regime of spacecrafts [4]. There has been considerable recent interest in the development of TCCs with improved working and technical parameters (adhesion to materials of spacecraft body, optical and electrophysical characteristics, and stability against effects

of open space) [5–7]. Note development of TCCs based on polymers and polymer composites, since application of heavy metals in space leads to high-intensity bremsstrahlung the intensity of which increases with an increase in the energy of incident electrons. Thus, relatively light polymer composites may serve as alternatives for existing materials [8].

Production technology of polymer composites is aimed at fabrication of materials with predetermined properties using variations in components (polymer matrix and various fillers). Such an approach makes it possible to fabricate new materials with improved working, mechanical, and optical characteristics and specific properties [9–12].

The purpose of this work is the development of polymer composites based on polystyrene filled with modified SiO₂ nanoparticles and study of the effect of filler on the surface properties of the materials under VUV irradiation.

MATERIALS AND METHODS

UPS-803E polystyrene (PS) serves as the polymer matrix for composites. The chemical formula of the material is written as $[-CH_2-C(C_6H_5)H-]_n$. Table 1 presents the main properties of the original PS.

Silicon-dioxide (SiO₂) nanoparticles serve as the filler. The nanoparticles are obtained with the aid of hydrolysis of ethyl orthosilicate (tetraethoxysilane (TEOS)) using the sol-gel technology. Note simplified technology of the sol-gel method in comparison with the conventional methods for synthesis. The method makes it possible to obtain high-purity products with minimum efforts [13, 14].

Table 1. PS properties

| No. | Parameter | Value |
|-----|---|------------------|
| 1 | Density, kg/m ³ | 1050 |
| 2 | Molecular mass, g/mol | 10 ⁵ |
| 3 | Glass-transition temperature, °C | 93 |
| 4 | Brinell hardness, MPa | 158 |
| 5 | Breaking elongation, % | 1.5 |
| 6 | Resistivity at a temperature of 20°C, Ω m | 10 ¹⁴ |
| 7 | Water absorption, % | 0 |
| 8 | Tensile strength, MPa | 40 |
| 9 | Vicat softening point, °C | 100 |
| 10 | Radiation index | 8.0 (50 Gy/s) |

Adhesive interaction of filler and binding agent and uniform dispersion of filler in the polymer matrix are important factors that determine physico-mechanical properties of polymer composites [15–17]. The interaction of filler particles with polymer can be implemented using various methods, in particular, surface chemical modification of filler [18–21].

The synthesized silicon dioxide is a hydrophilic substance. The filler is chemically modified to obtain hydrophobic properties and more uniform distribution in the PS matrix. The 136-41 water-repelling agent is used to modify the filler particles. The agent represents colorless oily liquid that is easily soluble in most organic solvents but insoluble in water. The chemical formula is written as [C₂H₅SiHO]_n (*n* = 10–15), and the content of active hydrogen is 1.3–1.45%.

The melt technology is used to fabricate polymer composites based on PS and modified silicon dioxide. It is known that efficient polymer composites based on thermoplastic materials can be produced using several methods, in particular, extrusion method of the introduction of filler into the polymer volume in melt. An advantage of such a method in comparison with solvent technology and in situ polymerization is related to the absence of multistage processes and solvents [22–24].

First, we mix dry components in a ball mill with a minimum amount of balls of no greater than 15%. Then, the composites are stored in a press mold at a temperature of 180°C over 1 h and pressed. The concentration of filler in the polymer composite ranges from 0 to 30%.

The dispersion of particles of modified silicon dioxide in the polymer matrix is estimated using SEM images of the surface of composites obtained with the aid of a TESCAN MIRA 3 LMU microscope.

The polymer composites are irradiated using a setup for technological and specific tests of samples made of polymer composites at the Center for Radia-

tion Monitoring, Shukhov State Technological University (Belgorod). The Center is certified by VNIIFTRI (Moscow) (certificate no. SARK RU.0001.443195).

The VUV intensity in the experiments is 0.5 W/m², the spectral interval is $\lambda = 90\text{--}115$ nm, and the pressure in the chamber is no greater than 10⁻⁵ Pa. The stability of the polymer materials against VUV irradiation is tested using a standard procedure in accordance with GOST R 25645.338-96.

The composites are placed in a chamber and degassed at a pressure of 10⁻⁵ Pa. The VUV-irradiation time is 24 h. The reflection spectra of the composites are measured using a UV-3600 spectrophotometer at the Center for Analysis of Composition of Substances (St. Petersburg). Spectra r_λ are measured in a spectral interval of 0.24–2.02 μm with a step of 0.5 nm.

RESULTS AND DISCUSSION

Figure 1 shows SEM images of the surface of polymer composites based on the PS matrix and modified silicon dioxide. It is seen that silicon dioxide is uniformly dispersed in the PS matrix at a filler concentration of 10 wt %. Note presence of spherical agglomerates with diameters of no greater than 20 μm (Fig. 1b). An increase in the concentration of silicon dioxide leads to an increase in the size of aggregates (Figs. 1c and 1d): the sizes amount to 40–60 and 80 μm at SiO₂ concentrations of 20 and 30 wt %, respectively.

The samples of the polymer composites are VUV irradiated at an irradiation time of 24 h. Then, we study the surface characteristics of the original and irradiated composites. Integral absorption coefficient α_s that serves as the main parameter of TCCs is calculated using reflection coefficients as

$$\alpha_s = 1 - R_s = 1 - \frac{\int_{\lambda_1}^{\lambda_2} J_\lambda \rho_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} J_\lambda d\lambda} = 1 - \frac{\sum_{i=1}^n \rho_{\lambda_i}}{n}, \quad (1)$$

where R_s is the integral reflection coefficient of solar radiation, r_λ is the reflection coefficient of the composite at wavelength λ , and n is the number of equal-energy fragments of the solar spectrum ($n = 24$). Table 2 presents wavelengths that correspond to the equal-energy fragments of the solar spectrum.

Table 3 presents integral absorption coefficients of solar radiation α_s for original and VUV-irradiated polymer composites at a temperature of 125°C.

The analysis of the results of Table 1 shows that an increase in the filler concentration from 10 to 30 wt % leads to a significant (almost two-fold) decrease in the integral absorption coefficient of solar radiation. The integral absorption coefficient of solar radiation

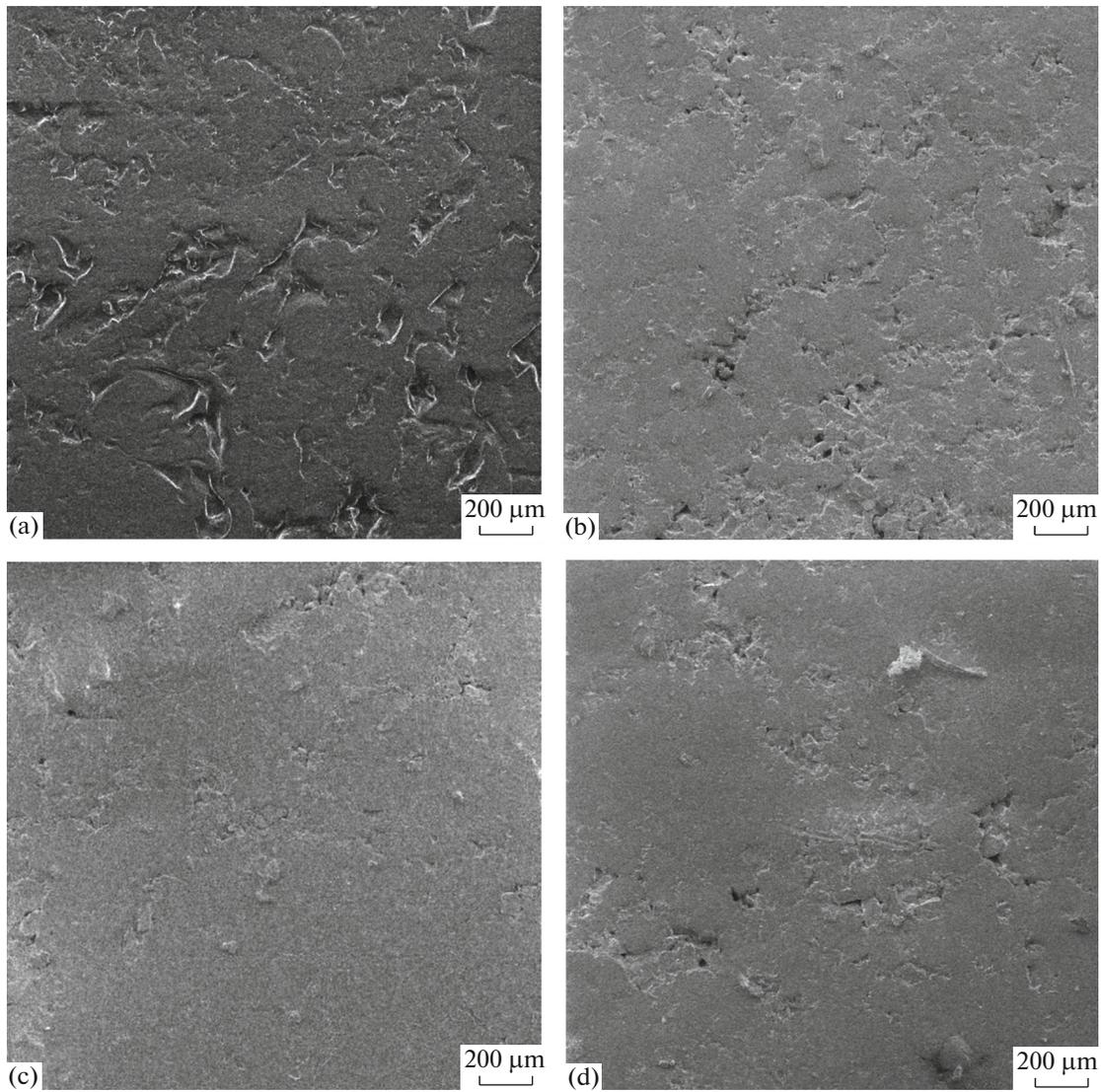


Fig. 1. SEM images of the surface of composites with SiO₂ concentrations of (a) 0, (b) 10, (c) 20, and (d) 30 wt %.

increases by 34, 27, and 19% at SiO₂ concentrations of 10, 20, and 30 wt %, respectively.

In accordance with the arbitration criterion on stability against VUV irradiation (GOST R 25645.338-96), an increase in the integral absorption coefficient must be no greater than 25%. The results of Table 3 show that the composites with a SiO₂ concentration of 30 wt % satisfy such a criterion.

Figure 2 shows the difference of absorption coefficients prior to and after irradiation ($r_{\lambda 0}$ and $r_{\lambda 1}$, respec-

tively) $\Delta r_{\lambda} = r_{\lambda 0} - r_{\lambda 1}$. We present the difference for the composition with a SiO₂ concentration of 30 wt %.

The analysis of the results of Fig. 2 shows that the most developed changes of the reflection coefficient caused by the VUV irradiation are observed in a wavelength interval of 240–500 nm. A maximum decrease in the reflection coefficient by 5.1% in comparison with the original level is observed at a wavelength of 280 nm. The difference of the spectra of the diffuse reflection decreases at wavelengths of greater than

Table 2. Wavelengths that correspond to the equal-energy fragments of the solar spectrum

| | | | | | | | | | | | | |
|----------------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|
| Point number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Wavelength, nm | 315 | 366 | 408 | 437 | 463 | 490 | 518 | 547 | 576 | 607 | 639 | 673 |
| Point number | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
| Wavelength, nm | 712 | 754 | 801 | 855 | 915 | 984 | 1060 | 1160 | 1270 | 1420 | 1640 | 2020 |

Table 3. Optical characteristics of the synthesized composites prior to and after VUV processing at a temperature of 125°C

| Filler concentration, wt % | α_s | |
|----------------------------|-------------------------|----------------------|
| | prior to VUV processing | after VUV processing |
| 10 | 0.378 | 0.506 |
| 20 | 0.215 | 0.273 |
| 30 | 0.191 | 0.225 |

490 nm (UV and visible spectral ranges). Thus, the VUV processing weakly affects the reflectance of the composite under study in such spectral intervals. The difference is no greater than 1.5% in the near-IR spectral range.

Surface changes of the composites due to VUV irradiation lead to changes of microhardness. Figure 3 presents the dependence of the Vickers microhardness on the content of modified SiO₂.

It is seen that the VUV processing of the synthesized composite leads to a minor increase in the

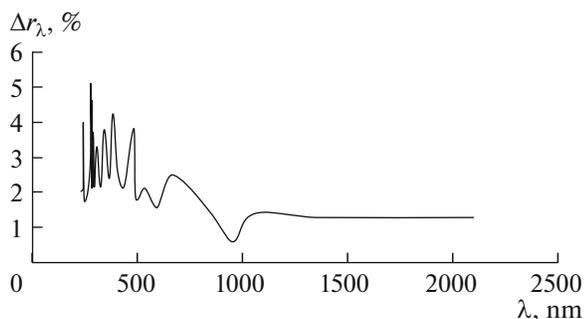


Fig. 2. Difference spectrum of the diffusion reflection of the composite with a SiO₂ concentration of 30 wt %.

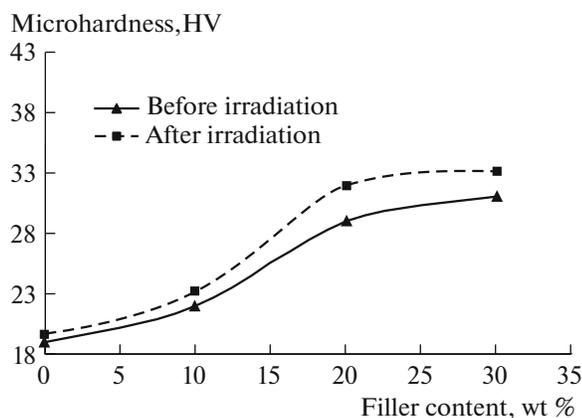


Fig. 3. Plots of the Vickers microhardness vs. SiO₂ concentration.

microhardness of composites with different concentrations of filler.

Evidently, an increase in the microhardness results from the intermolecular linking in the composite under VUV irradiation. Such linking leads to the formation of a barrier layer that provides suppression of the diffusion of low-molecular products of the matrix destruction and radicalization to the inner space and, hence, an increase in the microhardness and surface wear-resistance of the polymer [25]. The rate of linking and the ultimate concentrations of links in the surface layer depend on the processing conditions and structure of materials [25].

CONCLUSIONS

We have considered development of polymer composites based on polystyrene matrix and nanodispersed filler. Silicon-dioxide (SiO₂) nanoparticles that are modified using water-repelling silicon-organic liquid serve as a filler.

At a filler concentration of 10 wt %, silicon dioxide is uniformly dispersed in the PS matrix. The sample contains insignificant amount of spherical agglomerates with diameters of no greater than 20 μm. An increase in the content of silicon-dioxide particles leads to an increase in the size of aggregates.

An increase in the filler content from 10 to 30 wt % leads to a significant (almost two-fold) decrease in the integral absorption coefficient of solar radiation. VUV irradiation of the composites with SiO₂ concentrations of 10, 20, and 30 wt % results in an increase in the integral absorption coefficient of solar radiation by 34, 27, and 19%, respectively. The arbitration criterion of the stability of polymer materials against VUV irradiation allows an increase in the integral absorption coefficient by no greater than 25%. Composites with a SiO₂ content of 30% satisfy such a criterion.

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