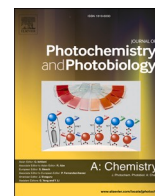




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Changes in surface properties of PI/WO₂ coatings after vacuum ultraviolet irradiation

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ABSTRACT

This paper presents the results of a study on the effects of deep vacuum and vacuum ultraviolet (VUV) irradiation on polymer coatings based on thermoplastic polyimide (PI) and tungsten oxide (WO₂). Samples from pure PI (without filling) and polymer coatings with 65 wt% WO₂ (PI/WO₂) were studied. The VUV irradiation occurred at 125 °C for 24 h, with no more than 10⁻⁵ Pa pressure. The VUV radiation intensity was 0.5 W/m², and the wavelength was 90–115 nm. The total mass loss after VUV treatment for PI was 1.29 wt%, and for PI/WO₂ coating it was 0.63 wt%. The changes in the structure of PI and PI/WO₂, established by IR spectroscopy, lead to loosening of the structure of the materials' surface layers. A decrease in surface microhardness was measured after 24 VUV treatments for PI (12.17 %) and for PI/WO₂ coating (3.68 %), compared to the initial microhardness. It was found that VUV treatment of PI/WO₂ coating lead to an increase in surface roughness, while smoothing (decrease in roughness) of the surface was observed for pure PI.

1. Introduction

The development of astronautics is continuously associated with the development of new technologies for the creation of rocket and space technology. Particular attention is paid to the creation of a radiation-resistant electronic component base for space technology. To eliminate failures of electronic equipment on spacecraft, a radiation-resistant element base and protective shielding are used, which ensure the maximum active life and reliability, with minimum dimensional and mass characteristics [1,2]. Therefore, the problem of protecting the element base from radiation is reduced to choosing the most effective protective screen.

As a protective shield, polymer composite coatings filled with radiation-protective mineral fillers, for example, PbO [3], Bi₂O₃ [4,5], Bi₁₂SiO₂₀ [6], WO₃ [7], WO₂ [8], etc., can be used. Most of the works on the development of polymer composite coatings for space purposes is devoted to the analysis of their stability under the influence of ionizing radiation, mainly from gamma and neutron radiation [9–12]. However, in conditions of orbital flight, elements of the spacecraft located on its outer side, in particular materials based on polymers, are exposed to the

negative influence of several factors of outer space at once. The main ones are deep vacuum (pressure no more than 10⁻⁵ Pa), atomic oxygen, electron and proton radiation, thermal cycling, and vacuum ultraviolet (VUV) [13–16]. One of the negative consequences of the effect of VUV on polymers is the loss of their mass (gas evolution). As a rule, polymers have relatively high gas evolution [17–19].

For most polymers, VUV radiation is absorbed in a thin surface layer, because VUV has a short length and higher photon energy [20–26]. However, this energy is enough to cause the breakdown of some organic bonds. Experiments on the effect of VUV on PI materials show that VUV does not lead to a significant loss in polymer mass, but leads to a decrease in reflectance in the ultraviolet (UV) and visible wavelength regions [27,28].

In a previous study, the influence of VUV on PI materials of various grades, such as Kapton HN (DuPont, USA) and Upilex S (UBE Industries, Japan), was considered [29]. VUV degradation experiments showed that PIs decompose much faster than silicones of various grades, such as DC 93–500 (Dow Corning, USA) and Elastosil S 690 (Wacker, Germany).

Inorganic substances are also subject to the negative effects of VUV. UV in high vacuum can create oxygen vacancies in oxides [30], which

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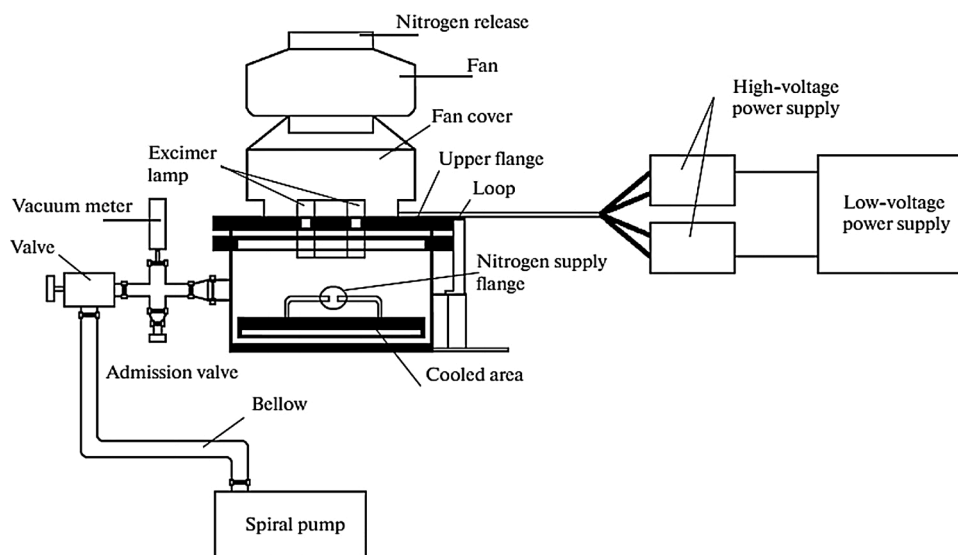


Fig. 1. Schematic diagram of plant for testing samples of polymer composites in conditions imitating those of near-Earth space environment.

leads to significant color changes (especially darkening), which is especially important for white reflective fillers for temperature-controlled paints.

Due to changes in the physicochemical properties of the surface of the polymers under the influence of VUV, there is a change not only in the optical properties of the material, but also in the structure of the relief. In the works of R.V. Lapshin et al. [31], it was established that during VUV treatment of a polymethyl methacrylate film with a wavelength of $\lambda = 123.6$ nm, surface nano roughness was smoothed. S Tanaka et al. found that photophysical and chemical changes in vinyl polymers (polyethylene, polystyrene, and polyvinyl alcohol) under the influence of VUV with wavelength $\lambda = 172$ nm lead to a change in surface wettability [32]. G.K. Belmontea et al., upon VUV treatment of polypropylene and vinyl alcohol, obtained superhydrophilic surfaces (contact angle $< 10^\circ$) 30 min after irradiation [33].

Recently, many studies have been devoted to the influence of UV and VUV not only on pure polymers, but also on polymer composites with various mineral and synthetic fillers [34–39]. In [40], the authors found that Comparing with epoxy resin, the epoxy composite with nano-TiO₂ particles brings significantly less mass loss, slighter flexural strength variation and decreasing gas extraction with less gas component varieties after VUV. Peng D. et al. found that the introduction of even 5.0 wt % POSS – TiO₂ into epoxy (EP) resin practically does not change the value of bend strength after UV. Meanwhile, a typical tough feature was observed from the SEM photo for POSS – TiO₂ / EP nanocomposite after UV exposure [41].

This paper presents data on the effects of VUV irradiation on polymer coatings based on thermoplastic PI and WO₂. The mass loss of polymer coatings in a deep vacuum and after VUV irradiation was studied. Changes in the surface layer after VUV irradiation are also shown.

2. Materials and methods

2.1. Synthesis

The binder used was a PI-PR-20 polyimide pressed material (Institute of Plastics OJSC, Moscow, Russia) in the form of a fine powder with a particle size not exceeding 250 μm . The proportion of volatiles did not exceed 0.5 wt%.

Tungsten oxide (WO₂) was used as a filler (Yugreaktiv Chemical Products Base LLC, Rostov-on-Don, Russia). Mass fraction of the main substance was 99.5 %. The particle size was 0.1–95 μm , the specific

surface of the particles was 4489 cm^2/cm^3 , and the modal diameter was 29.14 μm .

PI/WO₂ coatings were prepared by direct compression at a temperature of 380–400 $^\circ\text{C}$ and specific pressure of 100 MPa. Samples of pure PI without filling and polymer coatings with 65 wt% WO₂ were made. It was previously found that 65 wt% WO₂ is the optimal content for the PI/WO₂ coating. At high 65 wt% WO₂ values, the physicochemical characteristics of PI /WO₂ coatings are significantly reduced [42]. A detailed synthesis scheme for PI/WO₂ coatings is described by Cherkashina N.I. et al. [42].

2.2. VUV irradiation

The exposure to high vacuum and the surface treatment of the coatings with VUV were carried out in a near-Earth space simulation chamber located in the Laboratory of Space Materials Science at BSTU, named after VG Shoukhov (Russia, Belgorod). Schematic diagram of plant for testing samples of polymer composites in conditions imitating those of near-Earth space environment is shown in Fig. 1. The installation includes 12 vacuum ultraviolet emitting excimer lamps, each on a separate flange with an intensity of 0.5 W/m^2 in the range 90–115 nm.

Before exposure to vacuum and VUV treatment, the samples were subjected to conditioning: vacuum degassing at a temperature of 80 $^\circ\text{C}$ for 1 h. Exposure to high vacuum was carried out at a pressure no more than 10^{-5} Pa and at a temperature of 125 $^\circ\text{C}$ for 24 h. VUV irradiation was at a pressure of no more than 10^{-5} Pa and at a temperature of 125 $^\circ\text{C}$ for 24 h.

After every 3 h of the experiment, the samples were taken out, weighed, and reloaded into the simulation chamber. The mass of volatile condensing substances was determined using quartz microbalances, which are based on a piezoresonance sensor. The sensor is a high-frequency quartz resonator containing an AT-cut crystalline element. The use of resonators of this type will allow, with the smallest error, to record the mass of volatile condensing substances in a vacuum.

2.3. Research methods

The mass loss of PI/WO₂ coatings after every 3 h of testing was determined on an analytical balance CAUW-220D (CAS) with an accuracy of 10^{-5} g.

IR spectra of samples were recorded before and after irradiation with VUV with a Fourier IR spectrometer VERTEX 70.

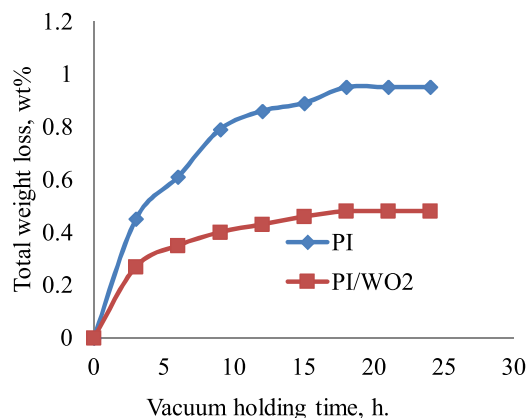


Fig. 2. Curves of the dependence of the mass loss of the test samples on the exposure time in high vacuum.

For scanning electron microscopy, a TESCAN MIRA 3 LMU field emission electron microscope (TESCAN, Czech Republic) was used.

Probe scanning microscopy was carried out on an Ntegra-Aura scanning probe microscope. The studies were performed in continuous or intermittent contact modes on an Ntegra-Aura instrument (NT-MDT Company, Zelenograd, Russia) using commercial Si or SiN cantilevers (NSG01, NT-MDT, Russia) under atmospheric conditions and low vacuum. As substrates, mica (muscovite) or highly oriented pyrolytic graphite (pyrographite) was used to study the surface of fresh chips. Processing and construction of atomic force microscopy (AFM) images was performed using the software NOVA (NT-MDT, Russia) and ImageAnalysis (NT-MDT, Russia).

Vickers surface microhardness was measured using a NEXUS 4504 hardness tester. The indenter was a Vickers tetrahedral diamond pyramid with a square base and an angle at the apex between the opposite faces of 136°. The load in all dimensions was the same (200 g).

3. Results and discussion

3.1. Mass loss of PI/WO₂ coatings after exposure to vacuum

Fig. 2 shows the mass loss curves of pure PI samples without filler and PI/WO₂ coatings with 65 wt% filler after exposure to high vacuum. Analysis of the data showed that the kinetics of the mass loss of pure PI without filler upon exposure to vacuum become gentle, and the curve of mass loss vs. processing time begins to slow down. By 18 h of the experiment, the loss of PI mass ceases and its maximum value is 0.95 wt %. When holding the PI/WO₂ coating in a vacuum, it is noticeable that the mass loss is much less than the mass loss of PI. By 18 h of evacuation, the curve of the PI/WO₂ mass loss vs. time reaches a plateau, and the total coating mass loss is 0.48 wt%. Analysis of the curves in Fig. 2 showed that introduction of the proposed WO₂ filler into PI significantly increases (almost 2 times) its resistance to evacuation.

The loss of mass by materials used in the construction of spacecraft, especially polymer coatings, is associated with their ability to trap tiny gas bubbles under atmospheric pressure. The effect of a deep vacuum on polymeric materials in outer space contributes to the release of trapped gases, which leads to the release of volatile substances from materials. Then, the isolated molecules are most likely to settle on the cold surfaces of the spacecraft (SC) [43]. This molecular contamination can affect the optical properties of the surfaces of space vehicles, especially for sensitive optical partitions such as lenses or arcs of electronic components. Ultimately, contamination of the surface of devices can lead to a violation of their functional responsibilities and the failure of the entire spacecraft. Therefore, it is recommended to use polymer materials for space technology products in which the total mass loss under vacuum-thermal exposure does not exceed 1 %, and the content of volatile condensing

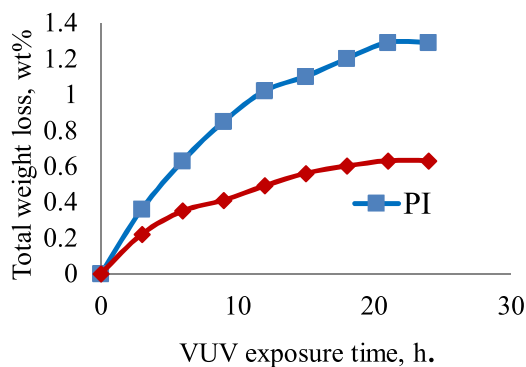


Fig. 3. Curves of the dependence of the mass loss of the studied samples on the time of VUV treatment.

substances does not exceed 0.1 % [44,45]. In the present study, the content of volatile condensing substances after 24 h exposure was 0.07 wt % for PI and 0.03 wt% for PI/WO₂, which is much lower than the limiting values according to ASTM E1559-09 (2016) [44].

3.2. Mass loss of PI/WO₂ coatings after VUV

Fig. 3 shows the mass loss curves of pure PI samples without filler and PI/WO₂ coatings with 65 wt% filler after VUV exposure. Analysis of the data obtained showed that the curves of the mass loss of the studied samples after VUV irradiation were similar to the mass loss curves of the samples under high vacuum (Fig. 2). The weight loss for both pure PI and the PI/WO₂ coating increased with increasing VUV treatment time. Both curves reached a plateau at 21 h of VUV irradiation. Total weight loss after VUV treatment was 1.29 wt% for PI and 0.63 wt% for PI/WO₂ coating. A comparative analysis of the data on the total weight loss of samples after exposure to vacuum (Fig. 2) and after VUV irradiation (Fig. 3) showed that VUV irradiation has a more significant negative effect on weight loss than exposure to vacuum.

3.3. IR spectroscopy

The increase in mass loss of samples after VUV treatment with respect to the weight loss after exposure to vacuum is associated with photodestruction. It is known that the effect of VUV can lead to bond breaking, especially in polymers, which can ultimately lead to a number of chemical and physical processes: the breaking of macromolecules, their crosslinking, chain repacking, crystallization, dicyclization, etc. [28–32]. To assess the contribution of the binder and filler to the photodestruction of the surface of the entire composite under the influence of VUV, Fourier transform IR spectroscopy of the binder (PI) and filler (WO₂) samples was carried out separately before and after VUV processing. Powdered WO₂ was VUV irradiated using the same irradiation parameters as for PI.

Fig. 4 shows the IR spectra of the original PI sample and the VUV treated sample. The spectrum of the initial PI contains absorption bands with the following maxima: 484, 535, 544, 568, 613, 647, 670, 738, 837, 887, 960, 992, 1128, 1146, 1255, 1350, 1404, 1461, 1512, 1730, 1786 cm⁻¹, and wide absorption bands in the region of 2850–3000 cm⁻¹ and 3100–3650 cm⁻¹. The configurations of these peaks refer to —CH bonds (RCH = CHR, R₂C = CH₂, R—CH = CH₂), to —CO bonds (secondary alcohol groups), to C—N and >N—H bonds (amino acids and associated groups >N—H, —NH₂), to >C=C< bonds (aromatic groups), to —C≡C— bonds (alkynes), and to —OH bonds (carboxyl groups).

Changes in the IR spectrum of PI after VUV irradiation indicate the occurrence of photolytic destruction on the surface of the PI with the formation of carboxyl and amide groups. In the IR spectrum of PI after VUV treatment, an absorption band appears in the 1700–1720 cm⁻¹ region corresponding to the formation of carboxyl groups (C=O). There

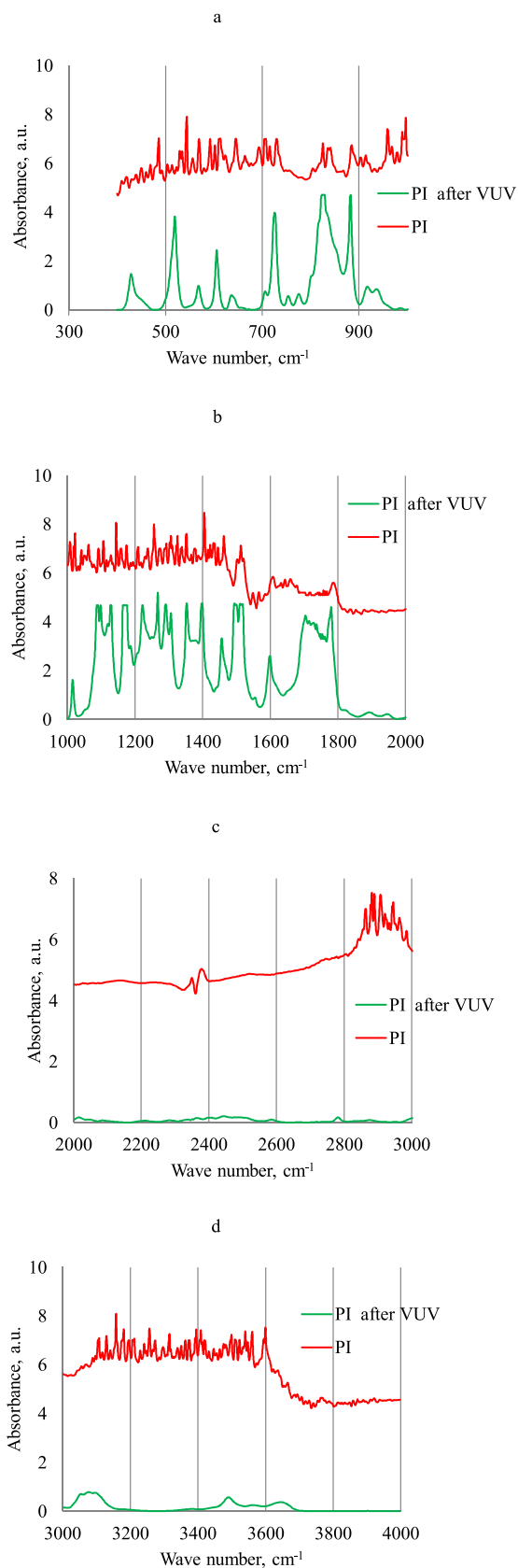


Fig. 4. IR spectra of the original PI and treated VUV at different wave number range: a) 400–1000 cm⁻¹, b) 1000–2000 cm⁻¹, c) 2000–3000 cm⁻¹, d) 3000–4000 cm⁻¹.

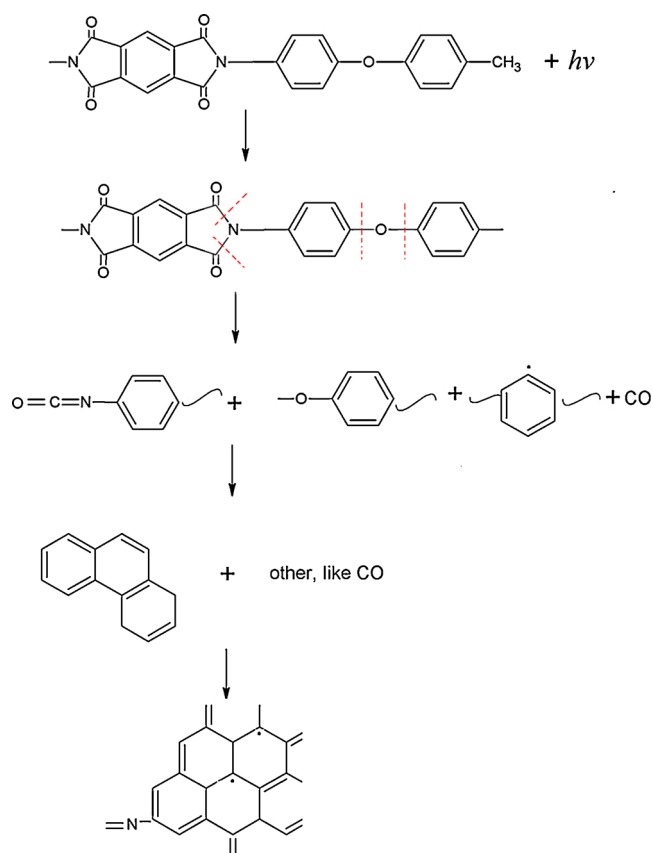


Fig. 5. The possible change in PI molecule structure under VUV irradiation [46] (Reprinted with permission from John Wiley & Sons, Inc.)

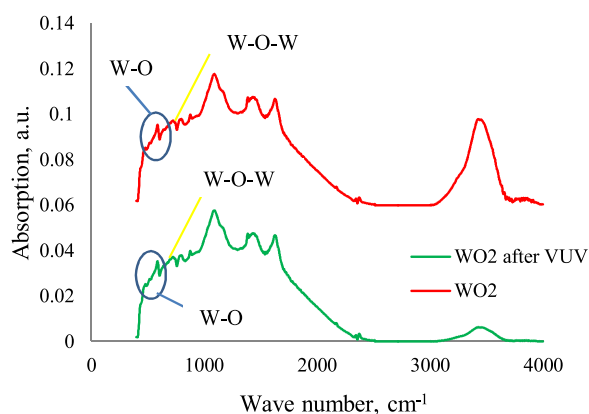


Fig. 6. IR spectra of the original WO₂ and treated VUV.

is an increase in the concentration of C–C, C=O bonds (1780 cm⁻¹ in the cycle), C–N (1380 cm⁻¹), which indicate the destruction of aliphatic groups. Cyanates ($-\text{N}=\text{C}=\text{O}$), imines ($\text{C}=\text{C}=\text{N}$), amides ($\text{C}-\text{O}-\text{N}$) can be formed in this case. Further destruction can also be expected to form a free amino group, i.e., break of a macrochain. The decrease in the band intensity of the IR spectrum of PI after VUV irradiation in the region of 3400–3650 cm⁻¹ can be explained by a decrease in the number of groups ($-\text{OH}$) as a result of the removal of chemically bound water under the influence of VUV and an elevated temperature of 125 °C. Fig. 5 shows the possible change in PI molecule structure under VUV irradiation using data [46].

Fig. 5 shows the rupture of the C=O, C–N bonds in red, as determined from the IR spectroscopy of the polyimide after VUV treatment (Fig. 4).

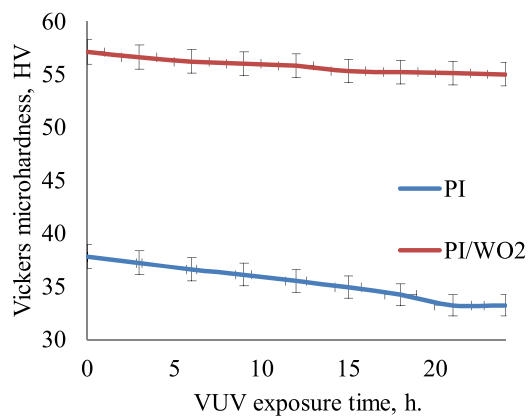


Fig. 7. Curve of the microhardness of samples according to Vickers from the time of VUV processing.

Fig. 6 shows the IR spectra of the starting WO₂ filler and the VUV treated WO₂ filler. The IR spectrum of the initial WO₂ filler contains an intense band in the region $\nu = 500\text{--}720\text{ cm}^{-1}$, which is attributed to the structural vibrations of W—O bonds [47,48]. The weak band at 788 cm^{-1} is attributed to the W—O—W bridge oscillations of WO₂ [47, 48]. The absorption bands at $871\text{ and }947\text{ cm}^{-1}$ are assigned to modes of bridging O—W—O vibrations, and those at 1465 cm^{-1} are assigned to the vibrational modes of Lewis centers. The band at 1640 cm^{-1} is associated with OH groups adsorbed by the surface. Also, the absorption of structural OH groups includes a wide absorption band in the region of $2900\text{--}3650\text{ cm}^{-1}$. After VUV irradiation, the IR spectrum of WO₂ shows a significant decrease in the band intensity in the region of $2900\text{--}3650\text{ cm}^{-1}$. This indicates a decrease in adsorbed water with simultaneous exposure to VUV and an elevated temperature of $125\text{ }^{\circ}\text{C}$. No other changes in the IR spectrum of WO₂ were detected. Analysis of the data in Fig. 6 showed that the VUV energy is insufficient to break the strong O—W—O bond in the WO₂ structure, so VUV only removes adsorbed water. The obtained data on IR Fourier transform spectroscopy of the PI sample (Fig. 4) and the filler (Fig. 6) separately before and after VUV treatment showed that VUV initiates PI photodestruction but does not affect the structure of WO₂.

3.4. Change in microhardness

The changes in the chemical structure of PI and PI/WO₂ coating, established by IR spectroscopy, should lead to loosening of the mechanical structure of the surface layers of the studied materials and to radiation destruction of their surface. To study this effect, an analysis of the microhardness of a VUV treated surface was carried out. Fig. 7 graphically shows the dependence of the Vickers microhardness of PI and PI/WO₂ coating on the VUV treatment time. Fig. 8 shows the obtained prints of a tetrahedral pyramid on the initial samples (200 g load), which were not subjected to VUV treatment. An analysis of these data showed a slight change in the microhardness of the surface of PI and PI/WO₂ coating during VUV treatment. The decrease in surface microhardness after 24 VUV treatments was 12.17 % for PI and 3.68 % for PI/WO₂ coating, compared to the initial microhardness.

3.5. Atomic force microscopy (AFM)

For a finer analysis of surface changes in PI and PI/WO₂ coating after VUV treatment, atomic force probe microscopy (AFM) was studied. Analysis of surface roughness parameters was carried out on a $10 \times 10\text{ }\mu\text{m}$ area. By the parameters presented in Figs. 9 and 10, one can judge the degree of surface roughness of the studied samples. An analysis of the statistical parameters of the surface shows that the initial surface of PI is quite smooth and even without any strong depressions or protrusions, and that the average roughness (Sa) is in the nanoscale (Fig. 9a).

A change in the surface roughness parameters of PI after VUV treatment (Sa, Sz, Sq) indicates a significant change in surface morphology (Fig. 9). The photon energy from $9.6\text{--}15\text{ eV}$ is high enough to excite electrons to high levels near the ionization threshold [49]. Therefore, treatment of PI with VUV led to the breaking of various chemical bonds in the polymer molecules, which was confirmed by the results of IR spectroscopy (Fig. 4).

Cleavage and recombination of radicals formed by VUV photolysis can lead to double bonds and transverse bonds. Therefore, VUV can modify polymer surfaces without damaging the bulk properties since the characteristic depth of penetration of VUV into polymers does not exceed several hundred nm, due to the high absorption ionization ($10^4\text{--}10^5\text{ cm}^{-1}$) [49]. Such a complex effect led to the effective functionalization of the surface layer of PI and smoothing of the surface. This is clearly seen from the data in Fig. 9, which shows that Sa decreased from 94 to 44 nm.

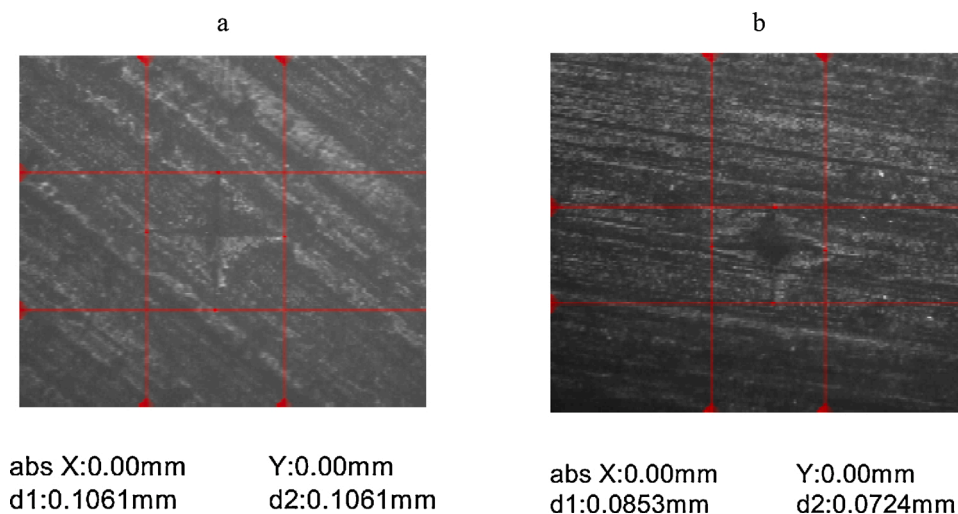


Fig. 8. Image of the indenter print of a microhardness meter when measuring the microhardness of the initial samples: a – PI, b – PI/WO₂.

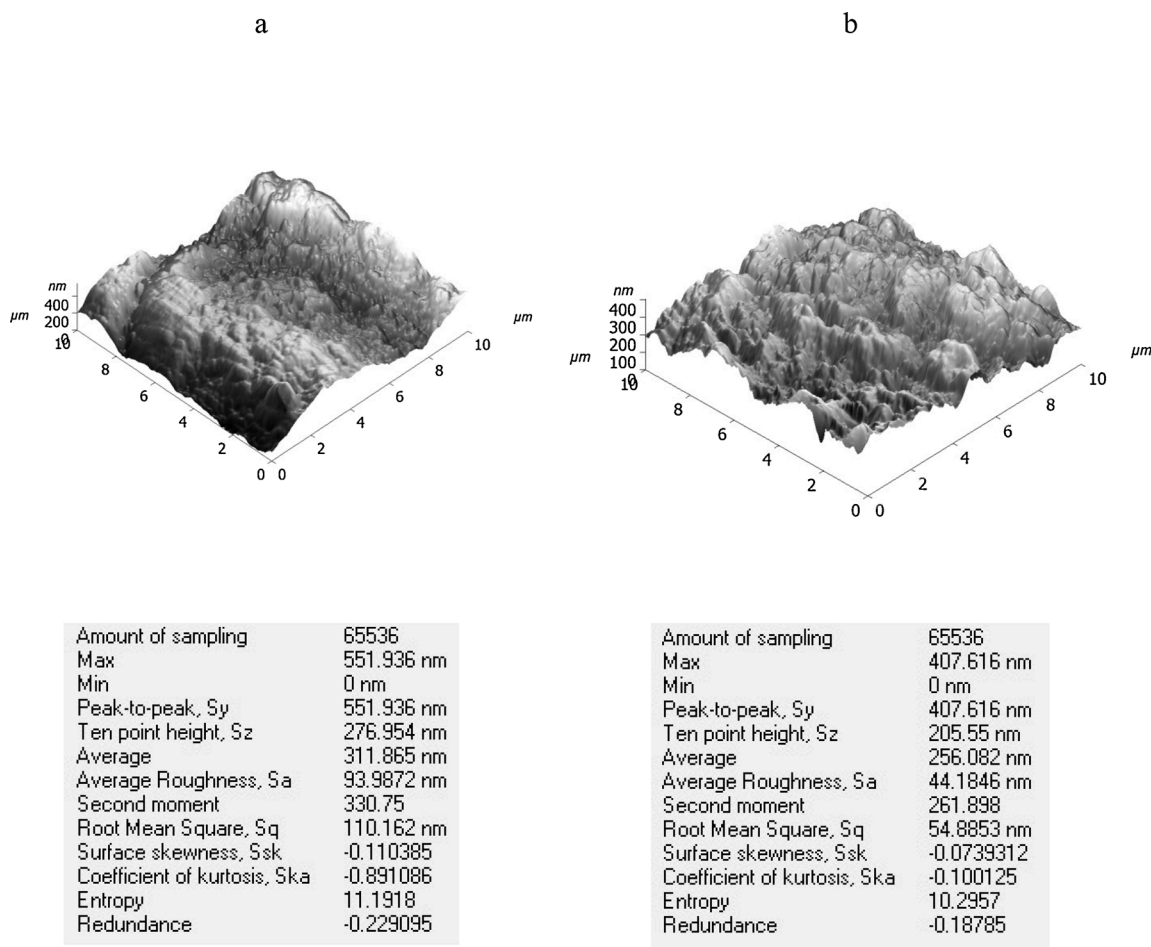


Fig. 9. AFM image and basic statistical parameters of surface roughness PI before (a) and after (b) VUV treatment.

An analysis of the statistical roughness parameters (Fig. 10a) of the initial surface of the PI/WO₂ coating shows that, compared with PI, the surface of the PI/WO₂ coating is rougher. The Sa for PI is 94 nm, compared with 125 nm for the PI/WO₂ coating. This is due to the high heterogeneity of the phases of the components of the composite: hard dispersed filler (WO₂) and soft thermoplastic matrix (PI). After VUV treatment of the PI/WO₂ coating, a significant increase in surface roughness parameters (Sa, Sz, Sq) occurred. After treatment with VUV, the PI/WO₂ roughness increases, while for pure PI it decreases. The increased surface roughness observed in PI/WO₂ after VUV treatment can be explained by the fact that the filler is not susceptible to photolysis under the influence of VUV. Therefore, WO₂ particles located on the surface of the PI/WO₂ coating itself do not undergo any transformations associated with the entrainment of material from the surface. Under the influence of VUV, only thermoplastic PI particles located on the surface of the composite are subject to changes. As a result of photolysis, partial destruction of PI molecules occurs and the further entrainment of gaseous products. This leads to the formation of deep depressions at the site of PI destruction, which is clearly seen in Fig. 10b.

4. Conclusions

Studies were carried out to study the effects of deep vacuum and VUV on PI and a PI/WO₂ coating with a WO₂ content of 65 wt%. It was found that the introduction of the proposed filler increased the resistance of the PI/WO₂ coating to gas evolution (mass loss) in a deep vacuum. The total mass loss in vacuum over 24 h was 0.95 wt% for PI and 0.48 wt% for the PI/WO₂ coating.

It was found that VUV had a more significant negative effect on weight loss compared with exposure to vacuum. Using Fourier transform IR spectroscopy, it was shown that VUV initiated PI photodestruction, but did not affect the structure of WO₂. The occurrence of photolytic destruction on the surface of PI was observed, with the formation of carboxyl and amide groups, and further destruction caused the formation of a free amino group.

The decrease in surface microhardness after 24 VUV treatments was 12.17% for PI and 3.68% for PI/WO₂ coating, compared with the initial microhardness. It was found that VUV treatment of PI/WO₂ coating led to an increase in the surface roughness, while smoothing (decrease in roughness) of the surface was observed for pure PI.

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CRediT authorship contribution statement

N.I. Cherkashina: Writing - original draft, Conceptualization. **V.I. Pavlenko:** Project administration, Funding acquisition. **A.V. Noskov:** Data curation. **A.N. Shkaplerov:** Methodology. **A.A. Kuritsyn:** Methodology. **A.I. Gorodov:** Investigation.

Declaration of Competing Interest

The authors report no declarations of interest.

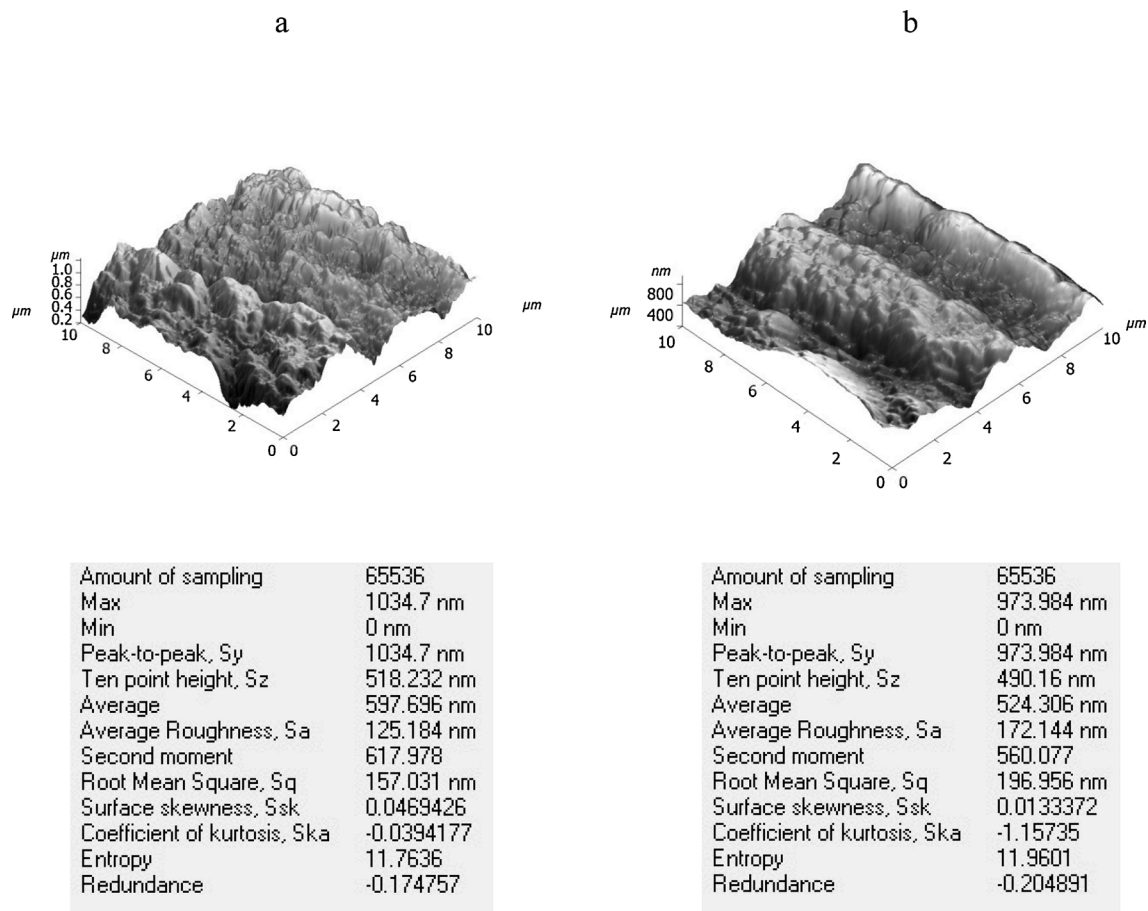


Fig. 10. AFM image and basic statistical parameters of the surface roughness of the PI/WO₂ coating before (a) and after (b) VUV treatment.

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