Study of the kinetics of gas evolution of a polymer composite under the influence of vacuum and VUV

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Abstract. The paper presents data on the effect of high vacuum and vacuum ultraviolet (VUV) on a polymer composite based on polyimide track membranes. Polyimide track membranes were filled with POSS structures. For comparison, we also used pure polyimide films without filler. Exposure in high vacuum and surface treatment of the developed VUV composite were carried out in the imitation chamber of near-Earth space, located in the Space Materials Science Laboratory of BSTU named after V.G. Shukhov (Russia, Belgorod). The high resistance of the composite to high vacuum and VUV has been established. The total weight loss of the composite by 24 hours was 0.26 wt. % (after holding in vacuum) and 0.28 wt. % (after VUV).

1. Introduction
Composite materials are used in many industries [1-3]. The use of composites usually makes it possible to reduce the weight of a structure while maintaining or improving its mechanical characteristics, which is especially important for the space and nuclear industries [4-9]. Many works are aimed at creating composite radiation-shielding materials, for example, concrete. But in recent decades, a large number of works have been devoted to the development of composite materials based on polymers. Using various fillers, it is possible to create polymer composite materials that will be an alternative replacement for metal alloys used in spacecraft [10-12].

Not all polymeric materials can be used in space. Materials used in space have special requirements for resistance to sudden temperature changes (from -150 to +150 °C), resistance to vacuum ultraviolet (VUV), electrons and protons of the Earth's radiation belts, micrometeorite particles (in particular to atomic oxygen) and others [13]. It is also very important for the space sphere that gas does not escape from the material. In space, gas can get on the sensitive elements of the spacecraft: lenses, mirrors, electronic devices. This can damage the operation of the machine. Therefore, when developing new polymer composites, it is very important to study their resistance to gas evolution under conditions that simulate space.

In this work, we investigated the kinetics of gas evolution of a polymer composite based on polyimide track (nuclear) membranes filled with polyhedral oligomeric silsesquioxane (POSS) under the influence of high vacuum and VUV.

Polyimide is one of the few polymers that can withstand prolonged exposure to outer space without significant deterioration in physical and mechanical characteristics. Therefore, it is polyimide that is used to create composite materials for space purposes. It is known that the functional properties depend on the uniformity of the distribution of the introduced filler into the polymer matrix [14]. One of the
ways to create a uniform distribution of components is the modification of the filler [15-19]. In this work, we use a method for creating a polyimide composite, in which the polyimide is used in the form of polyimide track (nuclear) membranes. The pore holes are filled with POSS filler. In this way, polyimide composites with a nanofiller are obtained, the particles of which are not subject to aggregation.

2. Materials and methods
A polyimide in the form of polyimide track (nuclear) membranes (manufactured by ION TRACK TECHNOLOGY FOR INNOVATIVE PRODUCT (it4ip), Belgium) was used as a polymer matrix. The pore diameter was 200 nm, the pore density was 5·10^8 cm^−1, and the polyimide membrane was 25 µm thick.

The tracks of the polyimide membrane were filled with organosilicon structures — POSS particles. The tracks of the nuclear polyimide membrane were filled with organosiloxane structures by synthesizing the filler in a GSA-0.3 high-pressure reactor in the presence of polyimide membranes (autoclaving temperature 250 °C, holding time 4 hours).

Cyclohexyl trichlorosilane C₆H₁₁SiCl₃ (manufactured by PJSC Khimprom, Novocheboksarsk, Russia) and silicon tetrachloride SiCl₄ (KhORST, Moscow, Russia) were used as reagents for the synthesis of POSS. POSS was synthesized in a 99.75 % purity acetone solution (OOO Komponent-Reaktiv, Moscow, Russia). The synthesis of organosiloxane structures (POSS) under hydrothermal conditions in a high-pressure reactor is described in more detail in [20].

To assess the effect of introducing a filler into a polyimide matrix (track membrane), a pure polyimide film 25 µm thick (manufactured by Izoteks, Russia, Moscow) was used for comparison.

The kinetics of gas evolution of the developed composite was studied under the influence of vacuum and vacuum ultraviolet (VUV). Exposure in high vacuum and surface treatment of the developed VUV composite were carried out in the imitation chamber of near-Earth space, located in the Space Materials Science Laboratory of BSTU named after V.G. Shukhov (Russia, Belgorod). Simulation chamber parameters: pressure no more than 10⁻⁵ Pa, VUV radiation intensity 0.5 W/m², wavelength from 90 to 115 nm. A detailed description of the setup parameters and irradiation technology is described in [21]. Vacuum treatment and VUV irradiation were carried out at a temperature of 125 °C for 24 hours.

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

Weighing of all samples before and after evacuation (or VUV treatment) was carried out outside the chamber on a VLTE-210S laboratory balance (discreteness 0.001 g, accuracy class II High, self-calibration). Based on the weighing results for each of the samples, the specific weight loss Δm was calculated:

\[ Δm = m_0 - m_1 \]  (1)

where \( m_0 \) is the initial weight loss of the sample, \( m_1 \) is the weight of the sample after evacuation or VUV treatment.

3. Results and discussion

3.1. Surface Morphology Analysis
Figure 1 shows SEM images of the surface of a polyimide film and a polyimide composite based on a polyimide track membrane before and after various types of processing.
The initial surface of the film is smooth, without inclusions and defects (figure 1a). The strip in the center of the surface of the initial polyimide film is probably obtained by mechanical action as a result of film transportation, and not as a result of the synthesis of the film itself, and cannot affect the purity of the experiment (figure 1a).

**Figure 1.** SEM images of polyimide film (a, c, e) and polyimide composite (b, d, f) with the following processing: a, b – original; c, d – after evacuation, e, f – after VUV treatment.
After holding in vacuum (pressure no more than $10^{-5}$ Pa) at a temperature of 125 °C for 24 hours, the film surface did not change (figure 1c). A similar situation is observed upon irradiation of a polyimide film with VUV (intensity 0.5 W/m²) at a temperature of 125 °C for 24 hours – the surface does not change (figure 1e). It is known that VUV acts on surface layers in the nanoscale, while smoothing of the surface roughness can be observed [21]. Since the initial polyimide film is already sufficiently smooth and has a low roughness, VUV irradiation practically does not affect its surface, which is observed in figure 1e.

Figure 1b shows a SEM image of the initial polyimide composite based on polyimide track membranes filled with POSS particles. It can be noted that almost all the pores of the track membrane are filled. It is noticeable that after filling the internal pores with POSS particles, they grow on the membrane surface. Bumps are formed (figure 1b). After evacuation of the polyimide composite, its surface is smoothed and the «bumps» disappear (figure 1d). This effect is explained by the small force of interaction between POSS structures emerging on the membrane surface. Under the influence of a deep vacuum, excess particles («bumps») are carried away from the surface. Friction occurs between the POSS particles that were in the pores of the track membrane and the polyimide membrane, resulting in a triboelectric effect. Therefore, the attractive force of POSS structures located in the tracks of the polyimide membrane and the membrane itself is high, in contrast to POSS structures on the surface. A similar situation is observed after the treatment of the polyimide composite with VUV — all protrusions («bumps») on the membrane surface have disappeared (figure 1f).

### 3.2. Weight loss analysis

Figure 2 shows the kinetics of weight loss for a polyimide film (a) and a polyimide composite with POSS structures (b) as a result of exposure to vacuum and VUV treatment.

![Figure 2. Kinetics of weight loss of a polyimide film (a) and a polyimide composite with POSS-structures (b) as a result of exposure to vacuum and VUV treatment.](image)

Data analysis figure 2a showed that the polyimide film loses its mass under the action of high vacuum and VUV. The total weight loss of the polyimide film by 24 hours was 0.40 wt. % (after holding in vacuum) and 0.46 wt. % (after VUV). It can be noted that, under the influence of VUV, the film loses more weight than after exposure to vacuum. The mass loss is gaining at a smooth pace, and the mass loss kinetics curve itself is similar to a linear function graph. For space technology products, polymers are used that lose weight no more than 1%, the polyimide film meets this criterion.

A polyimide composite based on track membranes and POSS structures also loses mass under the influence of high vacuum and VUV (figure 2b). However, it can be noted that the weight loss of the composite is less than that of the polyimide film, all other things being equal. The total weight loss of the considered composite by 24 hours was 0.26 wt. % (after holding in vacuum) and 0.28 wt. % (after VUV). The greatest weight loss is observed in the first hours (figure 2b). This is most likely due to the
removal of structures protruding above the membrane surface from the POSS composite surface (figure 1b). Further, the mass loss proceeds at a smooth pace.

4. Summary
The work established the high resistance of a polyimide composite based on track membranes and POSS-structures to the effects of high vacuum and VUV. The possibility of removing excess filler protruding above the membrane surface by evacuation is shown. Under the influence of VUV, a pure polyimide film loses more weight than after exposure to vacuum. The mass loss is gaining at a smooth pace, and the film mass loss kinetics itself is similar to a linear function graph.

The total weight loss of the considered composite by 24 hours was 0.26 wt. % (after holding in vacuum) and 0.28 wt. % (after VUV treatment). The greatest weight loss is observed in the first 3 hours. This is most likely associated with the removal of POSS structures on the surface of the composite that protrude above the membrane surface. Further, the mass loss proceeds at a smooth pace.

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