Experimental results concerning effect of electron radiation on mass loss of a polymeric composite in subsequent thermostimulated outgassing process are presented. To analyze and interpret experimental data the mathematical model describing the outgassing process of polymeric composites is used.

1. INTRODUCTION

In service conditions, spacecraft external coatings are subjected to various factors of space environment, including solar and ionizing radiations, residual Earth atmosphere (for low orbits), etc. Among the most negative effects of space environment is the mass loss of polymeric composites (PC) being the spacecraft thermal control coatings, due to the outgassing and sublimation processes. Rates of the processes are mainly defined by solar and low-energy ionizing radiations that produce principal contribution to near-surface absorbed doses.

Generation of volatile products (VP) and their emergence from PC is a complex physical-chemical process depending on its chemical composition, physical state, temperature, and external factors. Therefore, chemical transformations in PC being the result of irradiations define in general generation of VP, except for emergences of adsorbed and absorbed gases, monomeric remnants and impurities. This radiation-substance interaction makes the molecular system to become ionized or excited. Thus, generation of active centers (excited molecules, ions and radicals) in material precedes to chemical reactions. It is known that concentration of radiation-induced electron excitations is defined by absorbed dose rate and weakly dependent on radiation type [1-2].

To confirm resistance of spacecraft materials to space environment accelerated tests are carried on. Prior to testing the radiation resistance of spacecraft materials, distribution of the radiation exposure doses that they would be subjected to in service conditions are calculated (for example, by the Monte-Carlo method). These absorbed energy depth profiles are simulated in laboratory by electron and proton radiations. Meanwhile ionizing radiation intensities in simulating plants are 10^4 to 10^5 times greater than those in service conditions. Whether the choice of acceleration factor is reasonable or not – the issue remains open. Therefore, the aim of the present research is the study of mass loss of PC in dependence on electron radiation intensity.

2. EXPERIMENTAL RESULTS

To study mass loss rates on radiation intensities, a PC was applied on 30-mm aluminum disks. Each was weighed before and after experiments. The first stage consisted in irradiating five sample parties by electrons with $\Phi_e \approx 1.22 \times 10^{16}$ cm$^{-2}$ with different differential flux densities ($\Phi_e$, cm$^{-2}$s$^{-1}$). Initial electron energy was 40 keV. Irradiation modes are given in Table 1.

<table>
<thead>
<tr>
<th>Sample party</th>
<th>$\phi_e$, 10$^{-11}$ cm$^{-2}$s$^{-1}$</th>
<th>$\Phi_e$, 10$^{16}$ cm$^{-2}$</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>1.22</td>
</tr>
<tr>
<td>2</td>
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<td>1.22</td>
</tr>
<tr>
<td>3</td>
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<td>1.22</td>
</tr>
<tr>
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<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>22.6</td>
<td>1.22</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Time dependences of mass loss $M_{total}(t)$ of irradiated PC samples for the temperature-induced outgassing process in vacuum have been found at the second stage of experiments. To find kinetics of mass loss of PC we used a quartz microbalance - measuring device that is meant for converting change of mass on surface of quartz piezoelectric resonator into accretion of output frequency. Output frequency in our case was changed due to deposition of outgassed products on a sensor surface of the microbalance.

The following conditions maintained in experiments concerning temperature-induced outgassing and deposition of VP: vacuum 2x10$^{-5}$ Pa, sample temperatures in isothermal outgassing process was 100±1°C, quartz piezoelectric resonator temperature was minus 187±0.5°C. Experimental results are given in
Fig. 1. Here is seen that mass loss rate of irradiated samples rises with increase of flux density from 0 to $1.123 \times 10^{12}$ cm$^{-2}$s$^{-1}$. But the opposite behavior is observed for $\phi \approx 2.0 \times 10^{12}$ cm$^{-2}$s$^{-1}$ where the outgassing rate of the irradiated sample become less than that of the non-irradiated one (from party No 6).

There are competitive processes in PC under electron irradiation in vacuum, first, VP generation due to radiolytic decomposition of organic components and, second, decrease of VP concentrations $C_i(x,t)$ at the cost of outgassing process, radiation-induced decomposition and chemical reactions. Therefore, numerical analysis of the experimental data gave solutions of corrected differential equation system describing the outgassing process:

$$\frac{\partial C_i(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( D_i(x) \frac{\partial C_i(x,t)}{\partial x} \right) - \sum_j \sigma_{ij} C_j(x,t) - \chi_i C_i(x,t) - S_i(x), \quad x \in [0,h], \quad 0 < t \leq T,$$

$$C_i(x,t)\big|_{t=0} = R_i = \text{const}, \quad x \in [0,h], \quad (2)$$

$$\left[ D_i \frac{\partial C_i(x,t)}{\partial x} + (a_i + k_i) C_i(x,t) \right]_{x=0} = 0, \quad 0 < t \leq T,$$

$$\frac{\partial C_i(x,t)}{\partial x} \big|_{x=h} = 0, \quad 0 < t \leq T,$$

where $\sigma_{ij}$ – weighting coefficient of the radiation-induced decomposition of $i$-component through $j$-channel, s$^{-1}$; $M$ – number of destruction channels of $i$-component; $\chi_i$ – chemical reaction rates with involvement of $i$-component, s$^{-1}$; $k_i$ and $D_i$ – effective desorption and diffusion coefficients of $i$-type VP respectively; $R_i$ – concentration of $i$-type VP in material at initial moment; $S_i'(x)$ – source function of $i$-type VP dependent on electron energy, composition and thickness of material; $a_i$ – parameter defining influence of radiation on desorption kinetics of $i$-type VP, $\mu m/s$; $T$ – radiation time, s.

The corrected function of $i$-type VP source was determined by calculating distribution of absorbed doses in material using the Monte-Carlo method. In the case of monochromatic electrons, if disregarding the breaking radiation, the source function is the following

$$S_i'(x) = A \exp[-B(x-C)^2], \quad (5)$$

where $A$ is defined by differential electron flux density, $B$ and $C$ depend on material composition, thickness and electron energy.

Fig. 2 demonstrates accumulation of radiolysis products in PC that is suppressed by outgassing process under irradiation in vacuum.

Fig. 4 shows space-time distributions of VP concentrations in PC samples that were obtained by solving (1)-(4) for different radiation intensities (b, d, f, h). It also demonstrates changes of VP concentrations in
reference samples (a, c, e, g) that were in vacuum chamber, but not under irradiation, during the exposure times of $T = 25, 12, 3$ and 1.5 hours respectively.

Fig. 3. Space-time distribution of VP concentrations in reference samples (a, c, e, g) and in samples that have been subjected to electron radiation of the same fluence ($\Phi_e \approx 1.22 \times 10^{16}$ cm$^{-2}$) but different differential electron flux densities ($\varphi_e$, cm$^{-2}$s$^{-1}$): b – $\varphi_e \approx 1.42 \times 10^{11}$; d – $\varphi_e \approx 2.8 \times 10^{11}$; f – $\varphi_e \approx 1.23 \times 10^{12}$; h – $\varphi_e \approx 2.26 \times 10^{12}$
One can see from Fig. 1 (b) that increase of $\varphi_e$ from $1.42 \times 10^{11}$ to $1.23 \times 10^{12}$ cm$^{-2}$s$^{-1}$ results in growth of mass loss of irradiated sample. Estimations of distribution of VP concentrations in PC under irradiation indicated that $C(x,t)$ grows along with the radiation intensity (See plots b, d, f). This can be explained as follows. The greater radiation intensity, the lesser time the samples are inside the vacuum chamber where simultaneously take place accumulation of radiolysis products in samples and the outgassing process (See plots of reference samples a, c, e, g) restricting growth of VP concentrations.

Further increase of differential flux density leads to acceleration both the chemical reactions in samples under irradiation and their outgassing. Therefore, as soon as $\varphi_e \approx 2.26 \times 10^{12}$ cm$^{-2}$s$^{-1}$ is achieved, VP concentration in irradiated sample (Fig. 3, h) became less than in corresponding reference samples (Fig. 3, g). As a result, mass loss of irradiated sample under temperature-induced outgassing became less than that for initial one (See Fig.1 b). Obtained results can be explained by the fact that in addition to radiolysis products, extra vibrational excitations appear in PC under irradiation. Their generation is due to nonradiative transitions of electron excitations into thermal vibrations. Because number of electron excitations is proportional to radiation intensity, concentration of vibrational excitations should also be proportional to it. So, appearance of additional excitations with increase of $\varphi_e$ accelerates diffusion (including the surface diffusion) and desorption of VP that is the outgassing process. Local warming of VP source is also the reason of growth of outgassing rate under great intensities [4].

Having obtained enough detailed information concerning effect of the radiation intensity on space-time distribution of VP concentrations in PC, our next step was studying influence of model parameters on outgassing kinetics through the material-vacuum boundary. To find the outgassing rate one should know VP concentrations in the near-surface layer at any moment that is the function $C(h,t)$. It can be found by solving (1)-(4). Using these solutions and boundary conditions (3) of proper differential equations (1) one may find functions of outgassing rates of individual components from VP source surface unit

$$\frac{dF_i(t)}{dt} = k_i C_i(h,t).$$

Its time integration give values of VP fluxes $F_i(t)$ through the material-vacuum boundary within the time interval $t$

$$F_i(t) = \int_0^t k_i C_i(h,\tau) d\tau.$$  

When making analysis of experimental data, another feature of outgassing process was revealed. In fact, samples of PC in each party had various thickness ($h \approx 80; 90; 100; 120 \mu m$). It was found that when all other things being equal the process rate depends on sample thickness and molecular composition of outgassed products. Fig. 4 shows results of numerical analysis of two types of VP fluxes from surface unit of a sample in dependence on its thickness.

To analyze influence of kinetics parameters of a mathematical model on behavior of $C(x,t)$ and $M_{total}(t)$, the non-dimensional parameter $Nu = k \cdot h / D$ (analog of the Nusselt number) was used. Fig. 5 (a) shows dependence of VP concentration profile after 250 hours of vacuum outgassing on $Nu$ and (b) mass loss from unit surface on the material-vacuum boundary in dependence on $Nu$ and time. Here is seen that restriction of the outgassing process is desorptive for $Nu \leq 0.01$ and diffusive for $Nu \geq 50$. 

![Fig. 4. Dependence of i-type (a) and j-type (b) outgassed product fluxes on thickness of PC sample at $k_i \approx k_j$, $D_i \approx 5D_j$.](image-url)
To find time dependence of mass loss of a PC we used (7) that defined the function $F_i(t)$. Thus, total mass loss of a PC within the period $t$ can be calculated as follows

$$M_{\text{total}}(t) = \sum_i m_i F_i(t) = \sum_i m_i k_i \int C_i(h, \tau) d\tau,$$

(8)

where $m_i$ – mass of $i$-type molecule, $S_0$ – surface area of a sample.

Again Fig. 5 confirms validity of such numerical analysis of the function $C(x, t)$ because desorptive and diffusive restrictions of the outgassing process are obviously seen on the plot (a).

4. CONCLUSIONS

Results of this work are essential to understand the physics of radiation-induced processes in PC and find intensity of irradiation in tests of spacecraft materials and coatings. When carrying on radiation resistance tests of PC the differential electron flux density should be limited by value of $\phi_e \leq 10^{12} \text{cm}^{-2} \cdot \text{s}^{-1}$.

It is seen from the outgassing kinetics of PC irradiated by electrons $\Phi_e=1.22 \cdot 10^{16} \text{cm}^{-2}$ that increase of differential flux density from $10^{11}$ to $10^{12} \text{cm}^{-2} \cdot \text{s}^{-1}$ results in subsequent growth of mass loss for temperature-induced outgassing in vacuum. But if $\phi_e > 2 \cdot 10^{12} \text{cm}^{-2} \cdot \text{s}^{-1}$ mass loss of irradiated sample became less that that of original one. This can be explained by the following:

1. Starting from a threshold value of differential flux density decrease of VP concentration in PC due to the outgassing process under irradiation compared with their accumulation in radiolysis became prevalent;
2. If part of electron excitation energy proportional to radiation intensity transfers to thermal vibration energy, additional vibrational excitations appear in material. Therefore, increase of $\phi_e$ accelerates kinetic processes like diffusion and desorption of VP that is accelerates the outgassing process under irradiation;
3. Behavior of intramolecular reactions changes under high radiation intensities when possibility of multiple excitations increases. Therefore, character and aggregate yield of outgassed products are proportional to absorbed energy and may change under great absorbed dose.

5. ACKNOWLEDGEMENTS

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6. REFERENCES