Changes in the surface structure of melamine-formaldehyde particles in complex plasma

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Abstract. The surface modification of polymer microspheres by complex plasma was studied. Melamine-formaldehyde spherical microparticles, falling into neon dc glow discharge, acquired an electric charge on their surface and hung in a dust trap, where the electric field strength was strong enough. They were long trapped, forming three-dimensional ordered structures. Depending on the exposure time, the particle sizes and surface properties changed. Scanning electron microscopy provided insight in the particle morphology changing. The dependence of the particle size on the exposure in plasma was measured; the modification of the surface structure was investigated. The results of the statistical processing of the surface structure are presented.

1. Introduction
An analysis and modification of the surface layers of various materials are of virtual importance in connection with the development of nanotechnologies [1, 2]. The first results on the action of a dusty plasma on polymer particles were reported in paper [3]; it was found that, under the experimental conditions, the microparticles were heated to a temperature that exceeds that of the plasma. In this communication, we continue the investigation of melamine-formaldehyde particles that decrease in size under the action of the plasma and exhibit uniform modification of the surface [4].

2. Experiment
The gas-discharge chamber of especial design for collecting and extracting dust particles is presented in figure 1. A stratified glow discharge was initiated in the Ne filled tube (10 cm in length, \( R = 0.7 \) cm, \( p = 0.4 \) Torr, \( i = 2.5 \) mA). Monodisperse spherical melamine-formaldehyde (MF-R) particles injected into the plasma had a diameter of 7.3 ± 0.4 µm and a density of 1.5 g/cm³. Microparticles that have passed through the plasma discharge acquire an electric charge. They hang in the area of traps where the electrical field strength is strong enough. MF-R particles are kept in traps for a long time, forming a three-dimensional ordered structure (complex plasma). When the discharge was turned off, the particle collector was at the bottom of the chamber (movable platform \( D = 10 \) mm, \( h = 3 \) mm). The plasma exposure time ranged from 5 to 25 min. An analysis of the modification of microspheres was carried out using the
Figure 1. Discharge chamber: 1—electrodes; 2—vacuum valves; 3—container with the filling powder; 4—stratas; 5—platform for collecting microspheres; and 6—magnet for position control of the platform 5.

Figure 2. Scanning electron microscopy images of melamine-formaldehyde microspheres (a) before and (b) after exposure in plasma.

Merlin Zeiss scanning electron microscope. When processing the microphotographs, we used the Gwyddion software for analyzing the height fields and images. Gwyddion enables the processing of original (raw) images obtained in grayscale from a Merlin scanning electron microscope. Further processing of the fragments of these images in Gwyddion using statistical functions yielded information on the distribution of irregularities over the surface of particles.

3. Results and discussion
Images of the initial microsphere MF-R and the microsphere extracted from discharge are represented in figure 2. It can be seen from the figure that the texture of the microsphere surface changes under the action of the plasma. Figure 3 shows a fragment of the scanning
Figure 3. Fragment of the scanning electron microscopy images of the microspheres edge after exposure in plasma for 25 min (Gwyddion visualization).

Figure 4. Changing the diameter of melamine-formaldehyde microspheres during the exposure in plasma.

electron microscopy image of the microsphere edge (after exposure in plasma for 25 min), which allows us to estimate the size of the irregularities (up to 100 nm). The particles that have spent 5 min or more in the dust-plasma traps become smaller in diameter (figure 4). Over time intervals exceeding 30 min, melamine-formaldehyde particles melt, become degraded, and lost their spherical shape.

Images recorded using the Merlin scanning electron microscope are stored in a TIFF format, in the grayscale values from 0 to 255. A value of zero corresponds to absolute black, and value of 255 is for white. To analyze the roughness of the surface, the zero position was shifted to the average value using an integrated module.
The measured distributions of roughness (heights) of the surface on the plasma exposure time can be described as follows. The initial distribution of heights were close to the Gaussian distribution (figure 5, curve $a$). The distribution was random, which is likely to reflect the technology of manufacturing of calibrated melamine-formaldehyde particles.

At relatively short times (5 min), the most probable height (in grayscale) was shifted to the value of −25 (figure 5, curve $b$); that is, a large proportion of new relatively small irregularities are developed on the surface, while the right wing of the distribution builds up. The heights increase from 25 to 100. At long times (20–25 min, curve $c$), new irregularities continue to emerge, and those existing increase (values of −50 and +50 in curve $c$, respectively). As a result (at 25 min), the distribution approached constant and became a trapezoidal shape.

4. Conclusion
Discussing the presented results, we note the following. First, we found a modification of the polymer microspheres in a dusty plasma and quantitatively measured this modification. Secondly, we tried to understand how ions that have a thermal energy equal to several hundredths of an electron volt in a low-temperature plasma cause such a significant modification of the polymer particles? One possible explanation for the reported results could be following. Under our experimental conditions, the energy of ions in the low-temperature plasma was 0.03 eV; the charge of particles constituted about $1 \times 10^5$ elementary charges ($e$); the number of ions incident on the particle surface per unit time was $1 \times 10^9$. Ions accelerated by the field of the charged particle acquire energies on the order of 10 eV. This energy is sufficient to heat MF-R microspheres to the melting point.

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