AFM and SEM investigation of polymers irradiated in cosmic space

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Abstract

Polymer films (poliimide and fluoropolymer) were exposed in space at the Russian satellite "Mir" during 28 and 42 months. The appearance of macroscopic anisotropy was detected after this exposure. The microscopic structure of these samples was investigated by AFM and SEM methods and longitudinal surface structures oriented along the spacecraft flight direction were found. The specific features and origin of these structures are discussed.

Introduction

Exposure of polymer films in the space environment is rather specific among other types of irradiation due to complex character of irradiation. The energy of incident particles (of different nature and origin) is rather low – tens of eV, at the same time, the total irradiation fluence of incident particle during the long flight are rather high - so individual tracks could not be detected, and we see totally destructed surface. The behavior of polymer samples in open space, radiation resistance and macroscopic properties of such exposed samples, as well as their microscopic structure are of great interest [1].

Combination of different microscopic methods is often needed for investigation of polymer after radiation treatment. It is known that SEM and AFM are almost similar in lateral resolution, but there are situations in which one technique can provide a more complete information . The main advantage of the SEM is its large depth of field, which makes it possible to image very rough surfaces, structures with high aspect ratio. On the other hand, AFM can measure vertical surface variations below 0.5 Å, but its ability to measure tall and deep structures is limited. Therefore, two techniques together have a complementary capabilities and give a more complete picture of the sample [2,3].

Experiments

Polymer films were exposed at the Russian space station "Mir", which moved in the low earth orbit. Two series of polymeric films have been investigated: polyimides (PM-1E and Kapton 100 HN – PI) and fluoropropolymers (tetrafluoroethylene-hexafluoropropylene copolymers F4-MB and FEP –100A - FP). Special holders (cassettes) with polymers were put on the panel of the space station spacecraft and fixed at a certain angle to the flight direction because of panel incline. All samples were divided into two groups with different exposure time: for 28 months and 42 months. The total fluence for these cases can be estimated as 10^{22} – 10^{23} incoming particles per sq.cm.

Macroscopic parameters- surface tension and luminosity circle diagrams - were measured using standard technique (shape of drop of water at the surface and dependence of intensity of light reflection on orientation).

SEM investigations were made using TESLA BS-340 microscope (accelerating voltage 30 kV and magnification 2000- 10000) . The surface of samples was covered by thin copper layer for electrical conductivity.

The atomic-force microscope (AFM) Solver P-47 (NT-MDT, Russia) operated in resonance regime ("tapping" with frequencies 200-250 kHz. , in air, at room temperature) was used for investigation of samples surface. The unit was completed with NT-MDT silicon cantilevers with conical tips with high aspect ratio (cone angle is less than 22^{O}), typical curvature radius of tip – 10 nm and tip height 10-20 mcm. Using AFM not only topography was measured, but adhesion properties were also estimated and compared with macroscopic adhesion (obtained using drop of water shape measuring).

Results

The investigation of macroscopic parameters showed that all these polymers became anisotropic after exposure in cosmic space. The surface tension was studied: a drop of water at the surface has an elongated shape (for example - anisotropy factor was found to be ~1.8 on the surface of 28-month exposed PI film). The axis of drop orientation coincides with the direction of space vehicle flight. The same drop has an isotropic spherical shape on the control, non-exposed film surface .The luminosity was also investigated. The obtained circle diagrams proved the anisotropy of surface optical parameters. Moreover, the changing of sample orientation during flight leads to corresponding changing of direction of optical anisotropy axis. It must be mentioned that both effects (tension and luminosity) increased with increasing the exposure time.

Microscopic investigation were carried out and cause of macroscopic anisotropy was examined. The surface of polymer found to be greatly changed after cosmic exposure.

Figure 1 presents the SEM-image of the PI-film surface after 28-month exposure (a), and after 42-month exposure (b), and of the FP-film surface (respectively -after 28-month exposure (c), and after 42-month exposure (d)) .

It is easy to see that oriented space-organized structures are formed and their direction coincide with the direction of macroscopic anisotropy and, therefore, to the direction of spacecraft flight. The longitudinal size of formed structures vary from tens of nanometers to several microns. For example, according to Figure 1, after 28-month exposure the PI sample have structures with the longitudinal and transverse size of 5 – 20 μm and 0.5 - 2 μm, respectively. The size and shape of the structures depend significantly on exposure time. For both types of polymer the effect increased with the increasing of exposure time.

Figure 2 shows corresponding AFM pictures of the PI and FP film in the nanometer scale. (The directions of all the pictures are arbitrary and not coincide to each other). It is easy to see the oriented structure parameters at this scale too - for example, the surface waves with transverse size 0.1 – 0.3 μm are visible.

SEM and AFM data together often gave additional information [2,3] – in this case it enable us to estimate the relief parameters – the height of the surface ridges varying in a wide range, i.e. from tens to thousands of nanometers. Fine structure was detected at the large longtidual waves. A computer analysis of the structure slice showed organization at different scale levels. The main conclusion here is that "large" waves were modulated by "small" waves.

The conclusion about polymer stability can also be made: the PI was more damaged than FP. It is interesting that during other types of irradiation- heavy ions, fission fragments, or synchrotron – this polymer is one of the most stable and radiation resistant.

The obtained structures preserve their shape and size for a long time after in-flight exposure. This polymer structure is quiet stable in Earth conditions, which is probably explained by decreasing relaxation kinetics in the hard polymers.

It must be mentioned, that effect of surface structure formation was observed only on the open, "outer" film surface. No significant changes of surface shape were detected on the "inner" film surface (as well as on all other samples covered by the external protect film). At the same time, the adhesive properties were changed not only for "outer" surface, but for "inner" film surfaces too.

Discussions

The explanation of this effect is of great interest. It is known that at low earth orbits spacecraft materials are affected simultaneously by deep vacuum, solar radiation, molecular flux of residual atmosphere particles, thermal cycling, cold plasma, electrons, protons and other space environment factors. Besides, the materials can interact with intrinsic spacecraft atmosphere. This complex energetic impact can cause a substance transition into high-nonequilibrium state. Thus, during space exposure the materials are open nonequilibrium thermodynamic systems, where self-organization and formation of dissipated structures are possible [4-5].

The obtained results enable us to confirm this prediction and conclude that during space exposition films are under open system conditions, where space-organized structures are formed only because the system is far from equilibrium due to external conditions. Self-organization in the polymers determines the formation of the structure, which is more complex than the initial one. It is interesting that direction of dissipated structure orientation coincides with that of the space vehicle flight. This coincidence proves that continuous collision of particles of residual atmosphere molecule flux with open polymeric surfaces (energy from 0.3 to 10-25 eV) is the main environment factor of cosmic space which initiates and maintains self-organization and formation of the space-organized oriented structures. This might be also possible due to directed impulse transfer from space particles to the film surface during exposure. In our mind the direction of this pulse determines the direction of surface anisotropy. It is obviously that mechanism of polymer destruction in this case is quite different than that during heavy ions or synchrotron irradiation (see, for example, the behavior of PI samples).

The changes of adhesive properties of “inner” films could be explained by presence of residual atmosphere, which affect on all the polymer sheets.

So, it may be concluded that different cosmic factors changed different surface parameter of polymer film in space- surface topography and surface adhesive properties.

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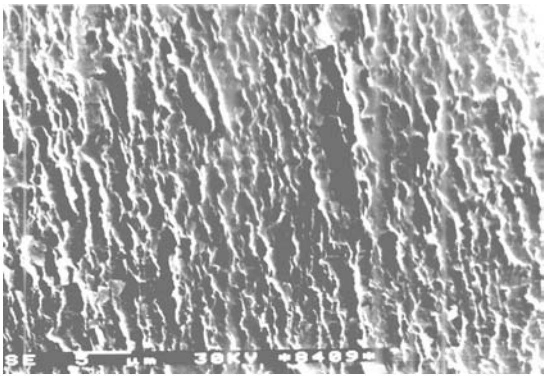

Fig.1a

Fig.1b

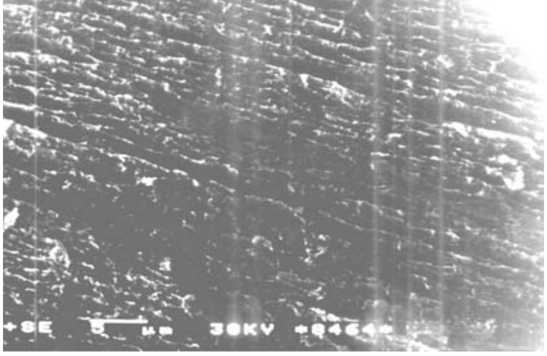

Fig.1c

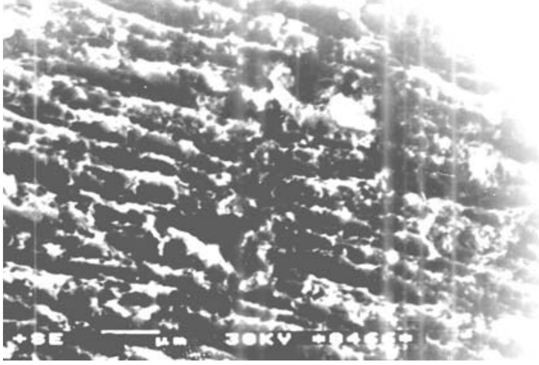

Fig.1d

Fig 2 a – c (Corresponding AFM pictures)