

Peculiarity of polymeric materials destruction on the low Earth orbits

V.K. Milinchuk¹, M. Marchetti², E.R. Klinshpont¹, I.P. Shelukhov¹,
T.N. Smirnova³, G. Allegri²

¹Institute of Nuclear Power Engineering, Studgorodok, 1, 249020 Obninsk, Kaluga Region, Russian Federation

²Universita degli Studi di Roma “La Sapienza”, Via Eudossiana, 16, 00184 Roma, Italy

³Khrunichev State Space Research Industrial Centre, Novozavodskaya, 18, 121087 Moscow, Russian Federation

Abstract

The paper reports on the research of two polymer film sets after in-flight exposure on the orbital space station “Mir” for 28 and 42 months. The investigated films include the samples of polyimide (grades PM-1E, Kapton 100 HN, polyimide coated with fluoroplast, one-side aluminised film PM-1UE-OA), copolymers of tetrafluoroethylene with hexafluoropropylene (grades F4-MB, FEP-100A). During exposure a part of the polymeric films was open to the space environment, while the other part was protected by polymeric films or quartz plates. The investigations showed a drastic change of physico-chemical, optical and strength characteristics in all open-to-the-space-environment films. The properties of the protected polymeric materials varied insignificantly. The method of scanning electron microscopy enabled to observe oriented space-organized structures with the longitudinal size varying from tens of nanometers to several microns on the surface of 28-month exposed polyimide films. The size and shape of these structures depend significantly on exposure time. The studies of the 42-month exposed samples showed larger structures with the longitudinal and transverse size of more than 50 μm and 1 – 5 μm , respectively. The direction of structure orientation coincides with that of the space vehicle motion. According to the data of the force atomic microscopy, the structure thickness varies in a very wide range, i.e. from tens to thousand nanometers. The investigation results can prove the occurrence of self-organization processes and dissipative structure formation in solid bodies in space.

Key-words: orbital space station “Mir”, in-flight exposure, low Earth orbits, polymers, self-organization processes, dissipative structure.

1. Introduction

The polymers used in different spacecraft components at low Earth orbits (LEO) are affected by deep vacuum, solar radiation, cold plasma, thermal cycling, atomic oxygen and other neutral and charged particles. The interaction of materials with the hazardous factors of the space environment decreases the initial physico-chemical, mechanical, optical, thermo-physical and other critical performance characteristics, and finally results in complete degradation of the polymers [1]. Since numerous space environment factors (SEF) simultaneously impact the materials of different chemical composition and structure, the character of this interaction is complicated. Therefore, it is hardly possible to expect that ground tests can ensure a reliable and substantiated prediction of the operation resource for the spacecraft materials used in LEO-missions. The data on the material behaviour in such space missions was obtained under simultaneous effect of multiple SEF factors [2,3]. It is an important problem of the space materials science to obtain the data on the material behaviour during spacecraft missions through controlled reduction of the affecting factors, changing their intensity and varying material location on the spacecraft surface. Another crucial issue relates to the information about changing property-changing, structure and mechanisms depending on the time of material exposure.

The purpose of this paper is to attract attention to the research of properties and structures of the polymeric films exposed to the space environment. The investigation results present particular interest to the researchers in the field of space materials technology, open thermodynamic systems, synergistics, physics and chemistry of solids, polymeric chemistry and etc.

2. Experimental

2.1. In-flight exposure procedure

Two sets of polymeric films were tested on the orbital space station ‘Mir’. Exposure time for the first and second sample sets was 28 and 42 months.

The tests were made on fluoropolymers and polyimide samples:

- fluoroplasts F4-MB (thickness 86 μ m) and FEP-100A (copolymers of tetrafluoroethylene with hexafluoropropylene (thickness 25 μ m);
- polyimide films PM-1E (thickness 40 μ m) and ??pton 100 ?N (thickness 26 μ m);
- polyimide coated with fluoroplast films (thickness 43 μ m);
- one-side aluminised polyimide films PI-1UE-OA (thickness 21 μ m).

The films intended for 28- and 42-month exposure were fixed on the panels of the “Komplast” cassette, where the panels were right-angle oriented to each other. The panels were made of metallic plates, which served as substrates for film samples mounting with twine arimide threads.

2.2. Methods of polymeric film investigation after in-flight exposure

Investigation of the surface morphology

Combination of different microscopic methods were used for investigation of surface morphology of polymers. Scanning electron microscope (SEM) TESLA BS-340 was used at accelerating voltage 15-30 kV. The investigation by means atomic force microscope (AFM) Solver P-47 (NT-MDT) were carried out in vibration mode at resonance frequency 150-250 kHz. This mode was used to reduce a load on the polymer surface. Many working parameters of SEM and AFM are quiet different: for example, the vertical resolution of AFM method is much higher, which made it possible to investigate small differences in height. On the other hand, SEM, due to high depth resolution, gave possibility to investigate deep cavities and “high” fragments of surface structure, which is impossible in the case of AFM.

The changes of the surface and bulk properties of the films were investigated using an optical microscope P? L?? L-213 (LOMO Company) and a vertical projection optical instrument I? V - 3 type ? VE - 1. A sample thickness was measured with an accuracy $\pm 1 \mu\text{m}$.

The studies of physico-chemical surface properties were made using the method of edge wet angle for a drop of bidistilled water on the film surface. The measurements were made with cathetometer ?? -8 at room temperature in the air; a measurement accuracy for vertical intercepts was $\pm 15 \mu\text{m}$.

Optical properties of polymeric films.

Luminosity coefficient β was determined on light dissipating samples in the spectral range 400 – 750 nm using F? U photometer and a selective absorber to correct the spectral sensitivity of the multialkaline photoelement F -15 to visibility curve. The value β was determined as the luminosity ratio of the surface dissipating light in a certain direction to the “ideal” light dissipating surface in the same luminosity conditions. An “ideal” dissipater is a surface reflecting 100% of the incident light flux at the same luminosity in all dissipation directions. Circle diagram β was measured in the normal-to-sample direction at 45° illumination angle to the film surface. The main error of β measurements at 45° light

incidence and observation angle 0° did not exceed $\pm 1\%$. A circle diagram β was measured separately for the inner and outer surface of each film taking into account a sample orientation in the arrangement.

Mass measurements. A mass of films was weighed on the laboratory balances VLR – 200 with an accuracy ± 0.05 mg.

3. Results and discussion

The change of initial polymer properties significantly depends on the way the films contact with a spacecraft environment at LOW. The films were fixed on the panel in stacks so that a part of them was protected by the same polymeric films or quartz plates or fixing threads. All protected films changed insignificantly in contrast to unprotected samples. It indicates that hazardous factors at LEO mainly affect outer surfaces of the outside films and do not leave any damage signs on the samples inside the stack [2,3]. Thus, degradation of polymers occurs strictly on the surface. Table represents the variation of thickness and specific mass loss of polymers exposed on the orbital space station ‘Mir’.

Table

Variation of thickness and specific mass loss of polymers exposed on the orbital space station ‘Mir’

Polymer	Thickness variation, μm (%)		Specific mass loss, mg/cm^2	
	After 28 month	After 42 month	After 28 month	After 42 month
F4-MB	+4(+ 10)	+14 (+28)	+4	+7,5
FEP-100A	- 2(- 8)	-5 (- 20)	-0.09	-0.3
PM-1E	- 6 (- 15)	-12 (- 30)	-1.25	-2.3
??pton 100 ?N	-7(- 27)	-16(- 61)	-1.0	-2.3
Polyimide coated with fluoroplast film	-11(- 26)	-	- 0.5	-
One-side aluminised polyimide film	-8(- 38)	-17(- 81)	- 2.0	- 4.5

Figure 1 (a) presents SEM image of the open polyimide film PM-1E surface after 28 month exposure. It is evident that oriented space-organized structures are formed with the longitudinal size varying from tens of nanometers to several microns. The size and shape of

the structures depend significantly on exposure time. According to Figure 1 (b), after 42 month exposure the sample have larger structure with the longitudinal and transverse size of 5-100 μm and 0.5 - 5 μm , respectively. The effect of the surface structure formation was observed only on the outer film surface. No significant changes were noticed on the inner film surface (as well as on all other samples covered by the external film). A computer analysis of the structure slice showed organization at different scale levels. The direction of structure orientation coincides with that of the space vehicle flight.

Figure 2 shows AFM image of the polyimide film PM-1E surface obtained. The film surface is a nonhomogeneous layer with the thickness varying in a wide range, i.e. from tens to thousand of nanometers. This morphology of the surface layer gives evidence in favor of the complex oriented organized structures generated in amorphous polymers.

Investigations of the circle luminosity diagrams proved the formation of such oriented structures on the surface of exposed polyimide films. Figure 3 shows an expressed anisotropy of the circle luminosity diagrams on the surface of exposed polyimide film PM-1E. After 28 and 42 month exposure, the films from two series were oriented on the panel at a right angle to each other. If the film orientation on the panel varies at 90^0 angle to the vehicle direction motion, the direction of anisotropy axis changes at the same angle in the circle luminosity diagrams. The axis of the circular luminosity diagrams is perpendicular to the structure orientation direction.

As follows from investigations, the formation of oriented space-organized structures causes the change of value and direction of the polymer surface tension. According to Fig, 4, a liquid drop has an elongated shape and anisotropy factor of ~ 1.8 on the surface of unprotected 28 month exposed film. The same drop has an isotropic spherical shape on the protected film surface. The axis of drop orientation coincides with the direction of both structure orientation and space vehicle flight.

At LEO spacecraft materials are affected simultaneously by deep vacuum, solar radiation, atomic oxygen, molecular flux of residual atmosphere particles, thermal cycling, cold plasma, electrons, protons and other SPF [1]. This complex energetic impact can cause a substance transition into high- nonequilibrium state. Besides, the materials can exchange substance with intrinsic spacecraft atmosphere. Thus, during space exposure the materials are open nonequilibrium thermodynamic systems, where self-organization and formation of dissipated structures are possible [4-8].

The obtained results enable to conclude that space exposed 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 high energy heavy particles (from 0.3 to 20 eV) of residual atmosphere molecule flux with open polymeric surfaces is the main space environment factor that 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. The structures preserve shape and size for a long time after in-flight exposure, which is probably explained by decreasing relaxation kinetics in the hard polymers.

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Captions

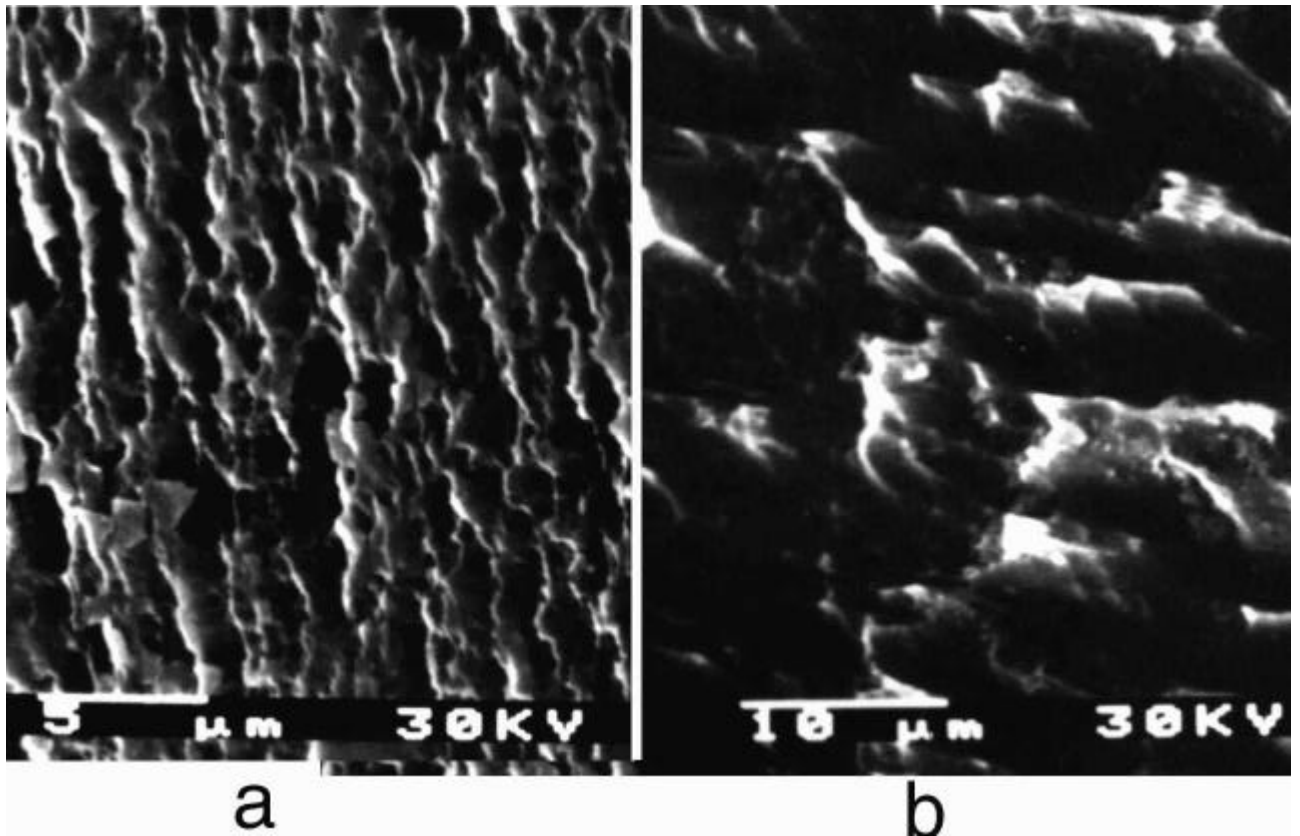


Fig.1. SEM images of a polyimide film P? -1E surface after 28 (a) and 42 (b) months exposure on the orbital space station “Mir”.

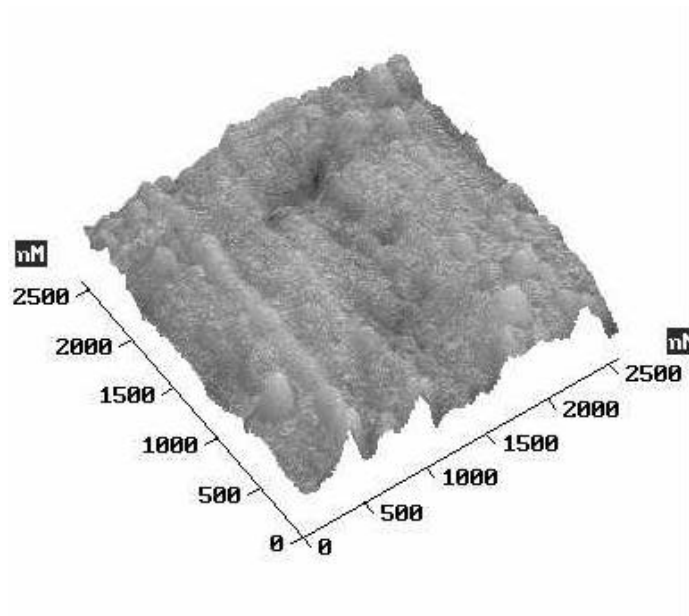


Fig.2. AFM image of polyimide a film P? -1E surface after 42 months exposure on the orbital space station “Mir”.

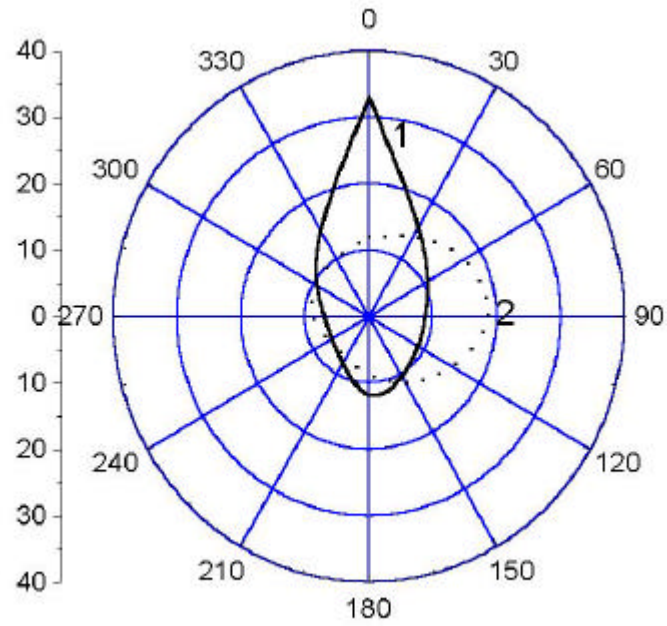


Fig.3. Circle luminosity diagram of a polyimide film P? -1E surface after 28 (1) and 42 (2) months exposure on the orbital space station "Mir".



Fig. 4. Photograph of distilled water drop on polyimide film surface P? -1E after 28 month exposure on the orbital space station "Mir".