STRUCTURE AND PROPERTIES OF POLYMERIC COMPOSITE MATERIALS DURING 1501 DAYS OUTER SPACE EXPOSURE AT "SALYUT-7" ORBITAL STATION

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SUMMARY

Specimens of polymeric composite materials for aviation and space applications such as glass fiber reinforced plastics (GFRP), carbon fiber reinforced plastics (CFRP), organic fiber reinforced plastics (OFRP), hybrid plastics (HP) based on epoxy compounds were exposed to the space environment on the surface of "Salyut-7" orbital station. The space exposure lasted 1501 days as a maximum. The data relating to the change in mechanical properties, mass losses, glass transition temperature, linear thermal expansion coefficient, and microstructure after various periods of exposure are given. It has been found that the change in properties is caused by the processes of binder postcuring and microerosion of the exposed surface of plastics. The phenomenon of strengthening of the surface layer of hybrid composites, due to which the nature of destruction changes at bending loads, has been revealed.

INTRODUCTION

On the initiative of the "Salyut" Design Office and the All-Union Institute of Aviation Materials, a comprehensive study on the effectiveness of modern polymeric composite materials (PCM) after direct long duration exposure to the space environment at "Salyut" and "Mir" orbital stations has been conducted in Russia since 1978. A major goal of the study is to obtain data on the effective degree of space environment factors (SEF) on PCM.

Physical methods with a high resolution have been used along with the traditional techniques for measuring mechanical parameters. A selection of these experimental results has been reported in [1-6]. This review includes general regularities concerning the behaviour of PCM on the "Salyut-7" orbital station's surface, the results obtained, analysis and conclusions relating to the ageing mechanism, the effect of composition, production technology, and protective screens on the change in the properties of PCM during long term exposure to the space environment.
### Table 1. Characteristics of PCM Specimen

<table>
<thead>
<tr>
<th>No</th>
<th>Name and Composition of PCM (Epoxy Matrix+ Filler)</th>
<th>Type of PCM</th>
<th>Laying</th>
<th>Size of Specimens, mm</th>
<th>Exposure time, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Organite 7T (5-211BN + SVM cloth article 5303/74)</td>
<td>OFRP</td>
<td>laminated plastic</td>
<td>92x5x2</td>
<td>304, 382², 686</td>
</tr>
<tr>
<td>2</td>
<td>KMU-31 (5-211B + carbon thin ribbon LU-3)</td>
<td>CFRP</td>
<td>0⁰, 90⁰, layer ratio is 1:1</td>
<td>92x5x2</td>
<td>304, 382², 686</td>
</tr>
<tr>
<td>3</td>
<td>SK-5-211B (5-211B + glass fiber cloth T-10-80)</td>
<td>GFRP</td>
<td>laminated plastic</td>
<td>92x5x2</td>
<td>304, 382², 686</td>
</tr>
<tr>
<td>4</td>
<td>VPS-7 (EDT-10P + glass fiber cloth T-10)</td>
<td>GFRP</td>
<td>laminated plastic</td>
<td>92x5x2</td>
<td>304, 382², 686</td>
</tr>
<tr>
<td>5</td>
<td>KMU-2 with one-sided foil coating⁵ (SP-97 + carbon ribbon LU-3)</td>
<td>CFRP</td>
<td>0⁰, 90⁰ foil AD1MM 0.03 mm</td>
<td>66x25x0.46</td>
<td>456⁴, 1501</td>
</tr>
<tr>
<td>6</td>
<td>KMU-3ln⁵ (5-211B + carbon ribbon LU-3)</td>
<td>CFRP</td>
<td>0⁰, 90⁰ +0.01mm glass fiber cloth layer</td>
<td>66x50x0.46</td>
<td>456⁴, 1501</td>
</tr>
<tr>
<td>7</td>
<td>KMU-4l (ENFB + carbon ribbon LU-P)</td>
<td>CFRP</td>
<td>0⁰, 90⁰</td>
<td>66x8x1.75</td>
<td>456⁴, 1501</td>
</tr>
<tr>
<td>8</td>
<td>KMU-4l (ENFB + carbon ribbon LU-P)</td>
<td>CFRP</td>
<td>±45⁰, 0⁰, 90⁰</td>
<td>66x8x1.75</td>
<td>456⁴, 1501</td>
</tr>
<tr>
<td>9</td>
<td>KMU-3l/VK-9/ KMU-3l (5-211B + carbon thin film LU-3/adhesive VK-9/5-211B + carbon ribbon LU-3)</td>
<td>HC (CFRP + CFRP)</td>
<td>0⁰, 90⁰ ; layer ratio is 1:1</td>
<td>33x8x3</td>
<td>102, 456⁴, 1501</td>
</tr>
<tr>
<td>10</td>
<td>VPS-7/VK-9/KMU-3l(EDT-10P⁶ + ( glass-fiber cloth T-10/ adhesive VK-9/ 5-211B + carbon ribbon LU-3)</td>
<td>HC (GFRP + CFRP)</td>
<td>laminated VPS-7; 0⁰, 90⁰ in KMU-3l; layer ratio is 1:1</td>
<td>33x8x3</td>
<td>102, 456⁴, 1501</td>
</tr>
<tr>
<td>11</td>
<td>VPS-7/VK-9/ VPS-7 (EDT-10P + ( glass fiber cloth T-10/ adhesive VK-9/ EDT-10P + glass fiber cloth T-10)</td>
<td>HC (GFRP + GFRP)</td>
<td>laminated systems; layer ratio is 1:1</td>
<td>33x8x3</td>
<td>102, 456⁴, 1501</td>
</tr>
</tbody>
</table>

Notes: 1 - the type of PCM: OFRP - organic fiber reinforced plastic, CFRP - carbon fiber reinforced plastic, GFRP glass fiber reinforced plastic, HC - hybrid composite; 2 - specimens subjected to the test after 304 days of exposure; 3 - exposure with foil: in an inner and outer double layer; 4 - specimens subjected to the test after 102 days of exposure; 5 - exposure with glass fiber cloth on the inside in two ways: in a single layer and in a double layer; 6 - exposure with an outer VPS-7 layer.
Materials

Materials of various classes of PCM for aviation and space applications, including GFRP, OFRP, CFRP and hybrid composites, have been selected to conduct the study. The class of CFRP is presented to a much greater extent. Hybrid plastics representing homogeneous and heterogeneous adhesive systems have been first studied. Materials, their composition, exposure conditions and exposure times are listed in Table 1. Before and after the experiments the specimens were stored at a temperature of \( 293 \pm 3 \) K and at a relative humidity of \( 60 \pm 20\% \).

Exposure Conditions

During the space exposure, easy-to-remove holders with the samples of PCM were located at a distance of 50 mm from the orbital station's screen-vacuum-insulated body near the transfer module (Fig.1). Exposure conditions were characterized by the following parameters: the ambient pressure in proximity to the panels with samples was \( 1.3 \times 10^{-2} \) \( Pa \); the impact of extra-atmospheric Sun was cyclic with a cycle time of 90 min, of which, on the average, 20 min were in solar illumination; the maximum duration of experiments was 1501 days \( (2.4 \times 10^4 \) cycles, 334 equivalent solar days); the averaged concentration of atomic oxygen was estimated as \( 10^{10} N cm^{-3} \) \( (N\)-number of atoms). The concentration of \( O^+ \) and \( O_2^+ \) charged particles was 1-3 orders below. The kinetic energy of atoms was approximately 5
eV; the fluence of atomic oxygen was $7.7 \times 10^{18} \text{m}^{-2}\text{s}^{-1}$ at an altitude of 300 km and at a velocity of 7.7 km/s; the power of ionizing radiation dose was approximately 0.5 rad/day; the intensity of solar UV-radiation was $1.4kW/m^2$ in the wavelength range from 0.1 to 0.4$\mu$m; the proton flux with an energy from 0.1 to 4 MeV was $10^8 p^+/cm^2 s$; the electron flux with an energy from 0.1 to 4 MeV was $10^8 e^-/cm^2 s$.

Methods of Study

Two groups of methods were used to conduct the study [1-6]. Methods for which small samples are required were preferred.

The first group was composed of methods characterizing the operating parameters of PCM. The strain-stress characteristics were estimated following the recommendations given in the paper [7]. To determine the mechanical parameters at bending, a scheme of three-point bending of a right-angled bar was used. Loading of samples was performed on the rupture-test machine, a movable bearing velocity which was $13 \pm 1mm/min$. From the bending tests the four parameters were estimated: $E_c$ - modulus of compression, $E_{br}$ - flexural modulus, $\sigma_c$ - strength along the normal stresses, $\sigma_{br}$ - strength along the tangential stresses. The mass loss was measured using ADV-200M analytical balance with an accuracy of $10^{-7}kg$. The density was estimated by the method of hydrostatic weighing in distilled water at 295 K.

The second group was composed of methods for studying the structure and physical-chemical processes of ageing of PCM. The special requirements imposed upon these methods were the precision and the reproducibility of measurements.

When evaluating thermal expansion, a linear quartz dilatometer with optical reading system [4], the error of measurement of which didn't exceed $1\mu m$, was used. The linear thermal expansion coefficient $\alpha_T$ was calculated from the measurements of thermal expansion $\Delta l/l_0$ ($l_0$ is the initial length of a sample).

The microstructure of materials was studied using MBS-9 light microscope and JSM-35C scanning electron microscope designed by JEOL (Japan). The investigation techniques and the interpretation of epoxy matrices' microphotos have been reported in [8].

More comprehensive and precision measurements were taken by dynamic mechanical analysis (DMA). For this purpose, some further steps [9] were provided in the construction of an inverted torsion pendulum and in the measurement techniques to increase the precision of measurements of dynamic shear modulus $G'$ and mechanical loss tangent $\tan \delta$ in the temperature range from 77 to 573 K.

RESULTS AND DISCUSSION

Microscopy Data

Even in the first series of experiments [1] it was ascertained that for uncoated PCM under the impact of SEF the stripping of filler fibers occurs due to the destruction and removal of the epoxy matrix surface layer. Depending on the type and chemical composition of fibers, their structure and surface either remain unchanged (glass fiber) or are subjected to etching (which is characteristic of plasma etching in carbon fibers and organic fibers), or even a partial destruction and removal of fibers occur (carbon and organic fibers) on long duration exposure.
Microcracks disposed mainly along the fibers are detected on the surface of specimens (both a right side facing an incident particle flux and a rear side). It has been ascertained that these microcracks are caused by temperature cycling. The composition of epoxy binder, the character of fiber laying, the level of inner tensions, the difference between linear thermal coefficients of a binder and a filler, the exposure duration and other factors have an effect on the formation and the growth of microcracks.

The VPS-7 glass fiber reinforced plastic is the most stable material in the degree of surface conservation among all the studied PCM. However, the surface of GFRP in hybrid No. 10 is damaged to a much greater extent than that one in monoplastic or in hybrid No. 11. It is explained [6] by further temperature stresses in the layer of VPS-7 due to the distinction between values of hybrid layers (See below).

Stable microstructural changes of epoxy matrix on the surface, in the volume and at the fiber interface are observed under the effect of SEF, along with the erosion effects. With increase in exposure time \( \tau \), the following processes occur: the aggregation of microparticles (it was reported in [8] before), loosening of initially closely packed matrix in the surface layer, and the reduction in size of overmolecular formation with higher density of packing.

At the surface of binder thin film the boundaries between particle aggregates become more prominent.

Aluminium-foil coating of the KMU-2 surface practically retains the initial structure of the CFRP surface, thus supporting the applicability of such a protection of PCM from the effect of SEF.

### Mass Losses

Mass losses of the specimens under the effect of SEF are determined by two components

\[
\Delta M = \Delta M_1 + \Delta M_2, \tag{1}
\]

where \( \Delta M_1 \), mass losses due to moisture desorption and low molecular products residues are proportional to the volume of the specimen; \( \Delta M_2 = \frac{\Delta m}{S} \times S_{\text{exp}} \), mass losses due to microerosion effect and etching are proportional to the square of unexposed surface of the specimen \( S_{\text{exp}} \).

With increase of \( \tau \) to \( \tau_1 = 100 \div 300 \) days the rate of the change of \( \frac{\Delta m}{S} \) decreases [6], because the fibers of reinforcing filler with higher erosion stability are stripped as the surface layer of a binder moves farther and farther. Table 2 illustrates that the magnitude \( \frac{\Delta m}{S} \) correlates with the thickness of stripped surface layer \( \Delta h_{12} \) of composites in time \( \Delta \tau = \tau_2 - \tau_1 \), where \( \tau_1 \geq 102 \) days; \( \tau_2 \geq 1501 \) days [6].

### Table 2. Microerosion of Unprotected Surface of PCM

<table>
<thead>
<tr>
<th>PCM*</th>
<th>Exposure time, days</th>
<th>( \bar{V} = \frac{\Delta m}{S \Delta t} \times 10^3 ), g/m² day</th>
<th>( \Delta h_{12}, \mu m )</th>
<th>( \Delta h ) in 10 years, ( \mu m ) (Calculation by the formula(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial time</td>
<td>final time</td>
<td>duration</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>382</td>
<td>686</td>
<td>304</td>
<td>254</td>
</tr>
<tr>
<td>2</td>
<td>382</td>
<td>686</td>
<td>304</td>
<td>156</td>
</tr>
<tr>
<td>3</td>
<td>382</td>
<td>686</td>
<td>304</td>
<td>38</td>
</tr>
</tbody>
</table>

847
The last column of Table 2 represents the estimation of the stripped surface layer thickness $h$ after 10 years of exposure by the relationship

$$\Delta h = \Delta h_1 + K\bar{v} \times (\tau - \tau_2),$$

(2)

assuming that at $\tau_2 > 300 \div 1500$ days the rates of mass loss $\bar{v} = \frac{\Delta m}{3(\tau_2 - \tau_1)}$ are constant. The coefficient of proportionality - $K = 0.82 \mu m \ m^2/g$ [6].

From the data given in Table 2 conclusions about comparative erosion stability of tested PCM are evident.

Erosion stability increases in the following sequence: organic fiber reinforced plastics - carbon fiber reinforced plastics - glass fiber reinforced plastics. For CFRP erosion stability increases in the sequence No. 2 → No. 6 → No. 5 → No. 7 → No. 8. Erosion stability depends on the way of laying, showing an increase in the plastic with diagonal reinforcement (No. 7 and No. 8). Erosion stability of GFRP in hybrid No. 11 is higher than in hybrid No. 10. As will be show below, in a hybrid composed of heterogeneous materials the distinctions between $\alpha_T$ produce additional temperature stresses and strengthen the destruction of a binder on the surface. The screening either with aluminium foil or polytetrafluoroethylene thin film [1-3] protects the surface of PCM from the effect of erosion. An increase in volumetric content of a filler has a beneficial effect on erosion stability.
Density

The density of PCM remains stable during 1501 days of exposure, changing no more than 1-2% due to surface effects, which is in agreement with microscopy data.

Mechanical Properties

In a few series of experiments [1, 3, 6] it was shown that after exposure the strength parameters of PCM (with the exception of OFRP) don't decrease or even increase (Fig. 2a). The phenomenon of enhancement of strength measured at $T = 393$ K is more noticeable as compared to the initial magnitude at the same temperature (Fig. 2b). The dependences of elasticity modulus at strength, compression and shear are different. For example, $E_x$ and $G_{xy}$ shear modulus in plane of the sheet don't change or increase, but the $G_{xy}$ modulus of interlayer shear is reduced by 20-24% for the PCM studied in the paper [3] (Fig. 2c,d). The same characteristics measured at 393 K are generally higher than the initial values at this temperature. For instance, the increase in $E_{bx}$ by 1.5-2 times is recorded in hybrids No.9 and No.10 (Fig. 2e,f). By and large, it is a rather diversified and complicated situation due to a wide scatter (up to 20-30%) of parameters.

The investigations have established two main reasons for such an ambiguous dependence of the PCM mechanical properties parameters. The first reason is connected with the general regularities of mechanical measurements. As the specimens of PCM were of comparatively small size (Table 1), the nature of PCM destruction had a significant effect on the results of measuring [7]. For example, Table 3 shows the fact that for hybrids No.9 and No.10 as distinct from No.11, the nature of destruction at bending load changes after space exposure [6].

Table 3. The Nature of Fracture of Hybrid Composites

<table>
<thead>
<tr>
<th>PCM*</th>
<th>In the initial state</th>
<th>After 1501 days of exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.9</td>
<td>Cross fracture due to normal stresses or delamination flaws along the adhesive-bonded joint due to tangential stresses.</td>
<td>Cross fracture due to normal stresses in the exposed layer. Lack of any adhesive bonded joints fracture.</td>
</tr>
<tr>
<td>No.10</td>
<td>Cross fracture or delamination flaws of CRFP; delamination flaws along the adhesive bonded joints due to tangential stresses.</td>
<td>Dominant fracture of CRFP layer due to tangential stresses. Lack of any adhesive bonded joints fracture.</td>
</tr>
<tr>
<td>No.11</td>
<td>Cross fracture due to normal stresses or delamination flaws along the adhesive-bonded joint due to tangential stresses.</td>
<td>Similar to the initial state.</td>
</tr>
</tbody>
</table>

* Designations are given in Table 1.
Fig. 2. Exposure-time dependences of the mechanical properties parameters of PCM as compared to the initial magnitude:

a - bending strength (• - N1; ○ - N2; □ - N3; ○ - N4; □ - N7; □ - N8)
b - bending strength for hybrid No. 10 at various temperatures
c,d - strength (○ - $\sigma_x$, □ - $\sigma_y$) and modulus (□ - $E_x$, ○ - $G_{xy}$, □ - $G_{xz}$) of glass fiber reinforced plastic (c) and carbon fiber reinforced plastic (d) according to the data [3]
e,f - flex modulus at various temperatures for hybrids No.9 (e) and No.10 (f)

Taking into account the results obtained in [5, 10], such a change in the nature of fracture is a sign of increasing hardness and strength of carbon fiber reinforced plastic which is a component of hybrid. Strengthening as will be shown below is caused by binder postcuring.

The second reason responsible for a various character of the curves in Fig. 2 e,f derives, according to the data of [10-14], from the superposition of destruction and binder postcuring processes and it will be analysed below.
DMA Data

The investigations performed by DMA method have provided the most detailed body of information on physical and chemical transformations in PCM under the effect of SEF. In a number of papers it has been ascertained a direct relationship between the type of DMA-curves and the structure and the composition of PCM [11-13], chemical structure of a binder [10, 11] and the processes of plasticization [14], ageing [15-16], etc. It is general practice to examine the temperature-dependences of dynamic shear modulus $G'$, mechanical loss tangent $tg\,\delta$, sound velocity $c_s = \sqrt{G'/\rho}$, where $\rho$ - density of material [11].

Fig. 3 depicts an example of DMA-curves for PCM No.1, No.2, No.3 in the initial state and after two exposure periods. A comprehensive analysis of these curves is given in the paper [11]. It has been ascertained that the existence of two temperature regions of decreasing $G'$, to which the maximums in the curves $tg\,\delta(7)$ correspond, is a general regularity. One can obtain an amount of information on the local molecular mobility ($\beta$-peak $tg\,\delta$ at 200 K) and the segmental mobility of a binder ($\alpha$-peak at 400 $\pm$ 10 K) according to the change in $tg\,\delta$ peak height, their position on the temperature scale, as well as according to the interfaces of relaxation regions. The filler has an effect on the character of DMA-curves. For instance, for OFRP (Fig.3a), $\alpha'$-peak $tg\,\delta$ at 530 K reflecting segmental mobility process and glass transition region of SVM-fiber [11].

As the exposure time increases, $G'$ decreases for PCM No.1 and No.2 in glassy state. The temperature of $\alpha$-peak $tg\,\delta$ increases by 20-30 K, but $\alpha'$-peak height and position remain intact (Fig. 3a, b, c). These and other changes in DMA-curves are in good agreement with the general scheme of changes commonly observed on postcuring of PCM binder [2, 10, 15, 16]. In Table 4 are given [6] the changes in glass transition temperatures for disordered matrix of a binder ($T_{g1}$) and for more ordered domains ($T_{g2}$) of all PCM under maximum duration of SEF effect. Despite different exposure times, the comparison of temperature shifts is rather correct, because the main process of transformations in a binder finishes for 500-700 days (Fig. 4). On evidence from Table 4, for all PCM, one can observe no case of reducing $T_{g1}$ and $T_{g2}$, which could point to the destruction of a binder [6, 15, 16]. Thus, the process of postcuring dominates clearly over that of possible degradation of exposed surface layer.

The analysis of Table 4 and similar data allow a number of concrete practical conclusions. For instance, the glass transition temperatures of a binder 5-211B of various CFRP kinds (No.No. 2, 6, 9, 10) in the initial state fluctuate in the range from 0 to 40 K. It depends on the composition and production technology [10]. From Table 4 it is evident, that $328 \leq T_{g1} \leq 364 K$, $361 \leq T_{g2} \leq 401 K$. After 456-1501 days outer space exposure the scatters in magnitudes $T_{g1}$ and $T_{g2}$ decrease to 10-15 K. It is apparent, that, on postcuring, a binder keeps to its limiting value of cross-linking degree.

The minimum shifts of $T_{g1}$ and $T_{g2}$ occurred in those materials which were the least heated under solar radiation. The closer the temperature of the heating composite is to the glass transition region of binder, the greater the shift of glass transition temperatures is.

Using composites No. 1 and No. 2 (Fig. 3 a,b) as an example, a manifestation of "anomalous" reduction of $G'$ in glassy state with an increase in crosslinking degree is illustrated [17]. The graph inversion of $G'(T)$ occurs close to $T_{g1}$. Such an effect is clearly defined in KMU-31 (No.7) carbon fiber reinforced plastic (Fig. 5). Its phenomenological theory is given in the book [18]. Its mechanical mechanism is also known: with increasing cross-linking degree due to additional steric limitations in glassy state, molecular packing level is decreased while the increase of free volume is observed, so $G'$ decreases.
which is often treated by mistake in the literature as the result of microdamages buildup at ageing.

Fig. 3. DMA - curves of PCM No. 1(a), No. 2(b), No. 3(c) in the initial state (1) and after 304 (2) and 686 (3) days outer space exposure.
Fig. 4. Exposure - time dependences of glass transition temperatures $T_{g1}$ and $T_{g2}$ for KMU - 4I carbon fiber reinforced plastic: empty circles - No. 7. (laying $0^0, 90^0$), dark circles - No. 8. (laying $0^0, 90^0, \pm 45^0$)

Fig. 5. Exposure - time dependences of dynamic shear modulus for KMU - 4I carbon fiber reinforced plastic measured at various temperatures
Table 4. Effect of exposure to the space environment on glass transition temperatures of PCM binder [6]

<table>
<thead>
<tr>
<th>PCM, Exposure Conditions</th>
<th>$\tau$, days</th>
<th>$T_{g1}, K$</th>
<th>$T_{g2}, K$</th>
<th>$\Delta T_{g1}, K$</th>
<th>$\Delta T_{g2}, K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>initial state</td>
<td>after exposure</td>
<td>initial state</td>
<td>after exposure</td>
</tr>
<tr>
<td>1</td>
<td>686</td>
<td>328</td>
<td>345</td>
<td>399</td>
<td>418</td>
</tr>
<tr>
<td>2</td>
<td>686</td>
<td>328</td>
<td>390</td>
<td>366</td>
<td>411</td>
</tr>
<tr>
<td>3</td>
<td>686</td>
<td>330</td>
<td>330</td>
<td>368</td>
<td>368</td>
</tr>
<tr>
<td>4</td>
<td>686</td>
<td>311</td>
<td>319</td>
<td>333</td>
<td>340</td>
</tr>
<tr>
<td>5</td>
<td>456</td>
<td>560</td>
<td>562</td>
<td>573</td>
<td>573</td>
</tr>
<tr>
<td>5 (with Al-foil coating)</td>
<td>456</td>
<td>560</td>
<td>563</td>
<td>573</td>
<td>575</td>
</tr>
<tr>
<td>6</td>
<td>1501</td>
<td>364</td>
<td>395</td>
<td>401</td>
<td>423</td>
</tr>
<tr>
<td>6 (screened)</td>
<td>1501</td>
<td>364</td>
<td>395</td>
<td>401</td>
<td>413</td>
</tr>
<tr>
<td>7</td>
<td>1501</td>
<td>365</td>
<td>413</td>
<td>403</td>
<td>447</td>
</tr>
<tr>
<td>8</td>
<td>1501</td>
<td>367</td>
<td>415</td>
<td>403</td>
<td>450</td>
</tr>
<tr>
<td>9 (exposed layer)</td>
<td>1501</td>
<td>351</td>
<td>411</td>
<td>361</td>
<td>427</td>
</tr>
<tr>
<td>9 (unexposed layer)</td>
<td>1501</td>
<td>351</td>
<td>411</td>
<td>361</td>
<td>419</td>
</tr>
<tr>
<td>10 (exposed layer)</td>
<td>1501</td>
<td>309</td>
<td>335</td>
<td>349</td>
<td>371</td>
</tr>
<tr>
<td>10 (unexposed layer)</td>
<td>1501</td>
<td>351</td>
<td>396</td>
<td>371</td>
<td>413</td>
</tr>
<tr>
<td>11 (exposed layer)</td>
<td>1501</td>
<td>320</td>
<td>323</td>
<td>361</td>
<td>373</td>
</tr>
<tr>
<td>11 (unexposed layer)</td>
<td>1501</td>
<td>320</td>
<td>326</td>
<td>361</td>
<td>371</td>
</tr>
</tbody>
</table>

Taking into account this phenomenon, the reason for increasing mechanical properties parameters of exposed PCM at higher temperature is evident: it is caused by binder postcuring.

Hence, from measuring mechanical properties parameters at 293 K and DMA-data for initial and exposed PCM specimens, one can predict the character of change in strain-stress parameters over a wide range of temperatures.

**Linear Dylatometry**

PCM based on epoxy compounds have comparatively low linear thermal expansion coefficients $\alpha_T$ [13, 19]. Fig. 6 depicts an example of outer space exposure effect on the thermal expansion $\Delta l/l_0$ of the layers for VPS-7 GFRP and KMU-31 CFRP which are components of hybrid No. 10. In the initial samples
of PCM in glassy state (when $T < T_{g1}$) one can observe thermal expansion. Due to the relaxation of internal stresses the slope of the curve $\Delta l/l_0$ reduces for GFRP at $T > T_{g1}$, but due to a negative value of carbon fibers the process of shrinkage (Table 5) is observed in CFRP [13, 19].

Fig. 6. Thermal expansion of VPS-7 glass fiber reinforced plastic (a) and KMU-31 carbon fiber reinforced plastic (b) which are components of hybrids No. 9 - No. 11:

a - initial state (1), unexposed layer in hybrid No. 11 (2), exposed layer in hybrid No. 11 (3), exposed layer in hybrid No. 10 (4);
b - initial state (1), exposed layer in hybrid No. 9 (2), unexposed layer in hybrid No. 10 (3)
Table 5. Effect of outer space exposure on linear thermal expansion coefficient [6]

<table>
<thead>
<tr>
<th>PCM</th>
<th>Composition, Exposure Conditions</th>
<th>$\alpha_T \times 10^6, K^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T &lt; T_{g_1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>initial after 1501 days</td>
</tr>
<tr>
<td>VPS-7</td>
<td>unexposed layer of hybrid No. 11</td>
<td>7.3 5.7</td>
</tr>
<tr>
<td></td>
<td>unexposed layer of hybrid No. 9</td>
<td>7.3 10.3</td>
</tr>
<tr>
<td></td>
<td>unexposed layer of hybrid No. 10</td>
<td>7.3 19</td>
</tr>
<tr>
<td>KMU-31</td>
<td>unexposed layer of hybrid No. 10</td>
<td>1.3 -0.8</td>
</tr>
<tr>
<td></td>
<td>unexposed layer of hybrid No. 9</td>
<td>1.3 -0.5</td>
</tr>
<tr>
<td>KMU-41</td>
<td>No. 7</td>
<td>1.4 0.6*</td>
</tr>
<tr>
<td></td>
<td>No. 8</td>
<td>0.9 0.9*</td>
</tr>
</tbody>
</table>

* - after 102 days of exposure

After 1501 days of exposure $\Delta l/l_0$ of VPS-7 unexposed layer is nearly halved as compared to initial specimens (Fig. 6a). In the exposed layer of hybrid No. 11 the magnitude $\alpha_T$ of VPS-7 increases greatly at $T < T_{g_1}$, (Table 5), during which the range of increase is greater in the exposed layer of VPS-7 in hybrid No. 10 due to softening the binder structure under the effect of SEF. Such a result is in excellent agreement with the microscopy data, as well as with the information on mass losses, change in mechanical properties and heat resistance.

Even approximate estimations show the following facts: for hybrid No. 10 due to VPS-7 layer expansion and KMU-31 shrinkage in the process of temperature cycling with the cycle amplitude in excess of 200 K, additional internal stresses occur. Their value ranges up from 15 to 25 MPa, i.e. 0.1-0.2 of fracture stress at temperatures of 373-393 K. From Fig. 6 it is evident that the level of internal stresses increases in hybrid No. 10 with increasing the exposure time.

In a similar way the thermal expansion of KMU-41 CFRP with orthogonal structure of layers (No. 7) decreases, while the effect of SEF is attenuated by inserting layers above $\pm 45^\circ$ in the reinforcement scheme (Table 5).

Conclusion

Binder postcuring is the main process which has an effect on the properties of PCM on long duration exposure to SEF. The phenomenon of postcuring depends on the composition and structure of composite material, its production technology, the initial degree of cross-linking, the maximum temperature of thermal cycles and the exposure time. The binder postcuring has a beneficial effect on the mechanical properties parameters of PCM. Excepting ORFP, strain-stress parameters of composite materials measured
at room temperature don't reduce after 456-1501 days of exposure to the space environment, and even increase at higher temperatures.

More detailed conclusions about the mechanism of physical, chemical and structural transformations are given in the papers [1-6]. The use of physical thermal methods of analysis allows us to gain a considerable body of information on the regularities concerning the behaviour of PCM under outer space conditions.

REFERENCES


OVERVIEW OF THE LDEF MSIG DATABASING ACTIVITIES
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Hampton, Va 23681-0001
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ABSTRACT

The Long Duration Exposure Facility (LDEF) and the accompanying experiments were composed of and contained a wide variety of materials, representing the largest collection of materials flown in low Earth orbit (LEO) and retrieved for ground-based analysis to date. The results and implications of the mechanical, thermal, optical, and electrical data from these materials are the foundation on which future LEO spacecraft and missions will be built. The LDEF Materials Special Investigation Group (MSIG) has been charged with establishing and developing databases to document these materials and their performance to assure not only that the data are archived for future generations but also that the data are available to the spacecraft user community in an easily accessed, user-friendly form. This paper gives an overview of the current LDEF Materials Databases, their capabilities and availability. An overview of the philosophy and format of a developing handbook on LEO effects on materials is also described.

INTRODUCTION

The LDEF is a reusable, unmanned spacecraft designed to accommodate a wide variety of technology and science experiments which require long-term exposure to a known LEO environment. The LDEF was designed to be transported into LEO via the Space Shuttle, free-fly for an extended time period, and be retrieved by the Space Shuttle for return to Earth. The LDEF was deployed on April 7, 1984 into a nearly circular 257 nautical mile orbit with a 28.4 degree inclination. On January 29, 1990, the LDEF was retrieved at a decreased altitude of 179 nautical miles after 69 months in space. During the mission life, the LDEF was exposed to the range of solar conditions including solar minimum and maximum. As LDEF was gravity gradient stabilized, the leading edge of the spacecraft saw the greatest atomic oxygen (AO) exposure, $5.8 \times 10^{22}$ atoms/in$^2$, with the trailing edge of the spacecraft having only minimal AO exposure. The environment that the LDEF was exposed to is described in reference 1.

The LDEF MSIG was formed to investigate the effects of long-term LEO exposure on structure and experiment materials which were not original test specimens. A significant part of the MSIG's charter is to establish and develop electronic databases which will eventually contain the wide variety and vast quantity of electrical, thermal, optical, and mechanical materials data being generated by the MSIG members and other LDEF investigators (ref. 1, 2). The MSIG chose to accomplish this task by a three-pronged approach as shown in figure 1. The first approach was to build on the Optical Materials Database developed by the Boeing Defense & Space Group under the auspices of the Systems Special Investigation Group (ref. 3). The Optical Materials Database was expanded and four other IBM/Macintosh software-based databases, commonly referred to as mini-databases, were developed. The second approach utilized a pre-existing global access database system, the Materials and Processes Technical Information System (MAPTIS), as the host for the LDEF Materials Database. The third approach was to develop a version of the LDEF Materials Database for use with PDA Engineering's.

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1 Work done under NASA Langley Research Center contract NAS1-19247.
M/VISION® software. An overview of the capabilities and requirements of the databases is discussed. Information on availability and how to access these databases is also given.

MINI-DATABASES

Under contract to the SSIG and MSIG, Boeing Defense & Space Group has developed a series of databases containing results from LDEF on specific topics. These databases were developed to provide the user community with early access to LDEF data. The databases were developed for use with IBM and Macintosh versions of Filemaker® Pro software. Filemaker Pro is a flat file database which means that the user can retrieve multiple data types such as tabular data, text, graphs, diagrams, and or picture files. The databases' simple interface allows for easy use of the database by the novice user. The individual databases are password protected, allowing the user full access privileges to read, print, or download the data but not allowing the user to edit the data. The software allows the user to search and retrieve specific information in a variety of layouts. Data can be exported to a variety of formats including ASCII. All data is traced back to its original data source. A more detailed report of the capabilities of these mini-databases can be found in reference 3.

The mini-databases cover the optical materials, silverized Teflon thermal blankets, treated aluminum hardware, thermal control paints, and the LDEF environment areas of interest. The Optical Materials Database is a compilation of the results on the optical materials flown on LDEF and was originally developed by the SSIG. The Silverized Teflon Thermal Blankets Database covers the results from the silverized Teflon thermal blankets utilized on LDEF. The Treated Aluminum Hardware Database is a compilation of data from the various types of aluminum hardware flown on or as part of the LDEF structure including different alloys, surface conditions, etc. The Thermal Control Paints Database contains information on the wide variety of paints flown on LDEF. The LDEF Environments Database contains information on the environment that LDEF was exposed to, including thermal profiles, and solar UV, and AO exposures levels. An order form for the mini-databases is given as figure 2.

MAPTIS VERSION OF THE LDEF MATERIALS DATABASE

NASA Marshall Flight Center has incorporated the LDEF Materials Database as a part of their automated storage, retrieval, and display database system. The preliminary version of the LDEF Materials Database was released on MAPTIS in June of 1992 and an updated version is currently available to all interested parties in the international space community. The goal of MAPTIS is to provide an efficient, reliable means of supplying the information needed for the selection and application of materials and processes to produce the hardware required for NASA's and industry's current and future space missions. MAPTIS uses ORACLE Corporation's relational data management system and can be accessed via modem and a 1-800 phone number or via Internet. There are several different databases in MAPTIS, one of which is the LDEF Materials Database.

The LDEF Materials Database allows the user to view and search a listing of the materials flown on LDEF, a listing of materials by specific material or material type, a listing of materials by property and property value, and original data source. All of the data is traced back to the original reference. Only tabular data is given as output of the MAPTIS version of the LDEF Materials Database. An order

2 The use of trademarks or names of manufacturers in this report is for accurate reporting and does not constitute an official endorsement, either expressed or implied, of such products or manufacturers by the National Aeronautics and Space Administration.

3 M/VISION is a registered trademark of PDA Engineering.

4 Filemaker Pro is a registered trademark of Claris Corporation.
form for the MAPTIS version of the LDEF Materials Database is given in figure 3.

M/VISION VERSION OF THE LDEF MATERIALS DATABASE

M/VISION is a materials software system, developed and marketed by PDA Engineering, which facilitates the organization and visualization of materials engineering data. M/VISION allows the user to analyze, manipulate, query, and graph materials data. The M/VISION software includes graphics, spreadsheet, imaging, and modeling capabilities as well as databasing capabilities. Multiple data types, such as tabular data, graphs, and raster images (e.g., C-scans, photomicrographs, etc ...) can be stored in a single M/VISION database. M/VISION is a hybrid hierarchical/relational database with both hierarchical and standard Structure Query Language (SQL) interfaces. An integrated engineering spreadsheet is included in the software that provides the user an efficient means to manipulate and visualize the information in the database. Databases can be manipulated via user-written FORTRAN and C codes.

A version of the LDEF Materials Database that runs on M/VISION is currently available to the international space materials community to run on their own licensed M/VISION software. The user can examine data based on specific materials, environmental parameters such as UV or AO exposure, experiment number, and data source. Once again all data is referenced to the original data source. Data from the LDEF Materials Database can be operated on and graphed using this software tool. An order form for the M/VISION version of the LDEF Materials Database is given in figure 4.

HANDBOOK

The results from LDEF and other LEO experiments and spacecraft are being used to determine the "rules of thumb" governing the relationship between the LEO environment and materials effects and life performance. The "rules of thumb" and the data to support them are being compiled into a handbook by TRW, Inc. under contract to NASA Langley Research Center. The principal audience for the handbook is the LEO spacecraft designer. The handbook is expected to be available in early 1995.

SUMMARY

Data from the materials and systems flown on LDEF experiments or as part of the LDEF structure is available in a variety of formats to suit the needs of the international space user community. All forms are available free-of-charge by filling out the request forms found in figs. 2-4.

ACKNOWLEDGMENT

The author would like to thank Dr. Gary Pippin and Gail Bohnhoff-Hlavacek of Boeing Defense & Space Group for their work on the mini-databases, Marshall Space Flight Space Center and their contractor's BAMSI, Inc. specifically John Strickland and Frankie Leath for their work on the LDEF Materials Database and PDA Engineering for their support of the M/VISION version of the LDEF Materials Database. The support of the LDEF principal investigators in allowing us to utilize their data is gratefully acknowledged.

REFERENCES


Figure 1. LDEF Materials databasing approach.
User Request Form for the Long Duration Exposure Facility (LDEF)

Materials Mini-Databases

Date: ___/___/___

Format: ______ IBM-compatible or ______ Macintosh

(runs on Claris Corporation's FileMaker® Pro version 2.0 or later software)

Databases requested:

_____ LDEF Optical Materials Database
_____ LDEF Treated Aluminum Database
_____ LDEF Thermal Control Coatings Database
_____ LDEF Silverized Teflon® Database
_____ LDEF Environment Database

Name: ________________________________________________________________

Company: ______________________________________________________________

Address: ___________________________________________________________________________

City: __________________ State: ____ Zip Code: _____________________________

Phone Number: (____)______-________________________

Complete and return this form along with one High Density Diskette (1.44MB) for each database requested to Gary Pippin, Boeing Defense & Space Group, P.O. Box 3999, M/S 82-32, Seattle, WA 98124. If you have any questions contact Gary Pippin (206) 773-2846 or Joan Funk at (804) 864-3092.

Figure 2. Request form for the mini-databases.
User Request Form for the Long Duration Exposure Facility (LDEF)

Materials Database on

the Materials and Processes Technical Information System (MAPTIS)

Date: ___/___/___

Employee Name: ___________________________ (first) ___________________________ (mi) ___________________________ (last)

Company/Mail Code: ___________________________

Work Address: ___________________________

City: ___________________________ State: _____ Zip Code: _____________

Office Telephone Number: (___)____-______ FAX: (___)____-_______

Do you have access to a NETWORK? (Yes/No) _____ Network: ___________________________

Check one only:

Govt Contractor ____ Industry User ____ NASA (MSFC) _______

Bamsi/BCSS Programmer ____ EH02 Personnel ____ NASA (other) ______

Signature ___________________________ Date: ___/___/___

Do Not Write Below This Line- System Information

User name: ___________________________ Uic:[________.________]

Password: ___________________________

NPSS/PSCN ID: ___________________________ Initial Password: ___________________________

Creation Date: ___/___/___ By: ___________________________

Deletion Date: ___/___/___ By: ___________________________

Complete and fax this form to Rene Hitson at (205)544-5786. If you have any questions contact Rene Hitson at (205)544-6972 or Joan Funk at (804)864-3092.

Figure 3. Request form for the MAPTIS version of the LDEF Materials Database.
User Request Form for the Long Duration Exposure Facility (LDEF) Materials Database in the M/VISION ® Format

Date: ___/___/___

Employee Name: ____________________________ ___. ____________________________ (first) (mi) (last)

Company/Mail Code: ________________________________________________

Work Address: _______________________________________________________

City: ____________________________ State: ______ Zip Code: ____________

Office Telephone Number: (___)___-______ FAX: (___)___-__________

Do you have access to a NETWORK? (Yes/No) ______ Network: ____________

Check one only:

Govt Contractor ____ Industry User ____ NASA (MSFC) ______

Bamsi/BCSS Programmer ____ EH02 Personnel ____ NASA (other) ______

Signature __________________________________________ Date: ___/___/___

Do Not Write Below This Line- System Information

User name: ____________________________ Uic: [_____, _______]

Password: ____________________________

NPSS/PSCN ID: ______________________ Initial Password: ______________________

Creation Date: ___/___/___ By: ______________________________________

Deletion Date: ___/___/___ By: ______________________________________

Complete and fax this form to Rene Hitson at (205)544-5786. If you have any questions contact Rene Hitson at (205)544-6972 or Joan Funk at (804)864-3092.

Figure 4. Request form for the M/VISION version of the LDEF Materials Database.
This volume is a compilation of papers presented at the Third Long Duration Exposure Facility (LDEF) Post-Retrieval Symposium. The papers represent the data analysis of the 57 experiments flown on the LDEF. The experiments include materials, coatings, thermal systems, power and propulsion, science (cosmic ray, interstellar gas, heavy ions, micrometeoroid, etc.), electronics, optics, and life science. In addition, papers on preliminary data analysis of EURECA, EOIM-3, and other spacecraft are included.