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Abstract

A cassette of uncured composite materials with epoxy resin matrixes was exposed in the stratosphere (40 km altitude) over three days. Temperature variations of –76 to 32.5 °C and pressure up to 2.1 torr were recorded during flight. An analysis of the chemical structure of the composites showed, that the polymer matrix exposed in the stratosphere becomes crosslinked, while the ground control materials react by way of polymerization reaction of epoxy groups. The space irradiations are considered to be responsible for crosslinking of the uncured polymers exposed in the stratosphere. The composites were cured on Earth after landing. Analysis of the cured composites showed that the polymer matrix remains active under stratospheric conditions. The results can be used for predicting curing processes of polymer composites in a free space environment during an orbital space flight.

Introduction

Future space exploration will require large lightweight structures for habitats, greenhouses, space bases, space factories and so on. A new approach enabling large-size constructions in space relies on the use of the technology of polymerization of fiber-filled composites with a curable polymer matrix applied in the space environment. For example, a fabric impregnated with a long-life matrix (prepreg) can be prepared in terrestrial conditions and, after folding, can be shipped in a container to orbit and unfolded there by inflating. Then the matrix polymerization reaction is initiated producing a durable composite wall or frame. Using such an approach, there are no restrictions on the frame size and form of the construction in space, and the number of deployment missions is kept at a minimum.

In the space environment, the material is exposed to high vacuum, dramatic temperature changes, plasma due to cosmic rays, Sun irradiation and atomic oxygen (in low Earth orbit), micrometeorites, electric charging and microgravity. The development of appropriate polymer matrix composites requires an understanding of the chemical processes of polymer matrix curing under the specific space conditions to be encountered.

Preliminary studies of polymerization processes in a high vacuum, space plasma, subject to temperature variations, indicate that for specific prepeg preparations the polymerization process is likely to be successful in space and that the composite cured in a space environment will have satisfactory mechanical properties (Refs. 1 to 17). However, the curing processes are sensitive to space factors such as high vacuum, flux of high-energy particles and temperature variations encountered.

Particularly pertinent observations from previous work include:

- The evaporation of active components can stop the curing reaction and evaporation can cause bubble formation in the curing polymer matrix and compromise the mechanical properties of the cured matrix.
- High-energy space irradiations can destroy macromolecules and create free radicals, which can accelerate the curing kinetics and strengthen the composite.
- Temperature variations change dramatically the curing kinetics and evaporation process.

Studies show that the curing process can proceed and a durable composite material can be polymerized under simulated space conditions. However in a laboratory environment it is not possible to simulate accurately the combinations of factors observed in space in order to assess how the various influences interact. To develop the appropriate polymer matrix composition for use in a particular space environment, the effects of the prevailing space conditions acting together must be taken into account. More detailed investigations of the curing process under real space conditions, where all the space factors act simultaneously during the curing process are required.

The goal of the flight experiment was an investigation of the effect of the stratospheric conditions on the uncured polymer matrix of the composite material. Stratospheric conditions are expected to have a strong impact on chemical processes in polymer materials. The unique combination of low atmospheric pressure, high intensity UV radiation including short wavelength UV, diurnal temperature variations and other aspects associated with solar irradiation strongly influences the chemical processes in polymeric materials. It is difficult to predict the impact on the curing chemistry, particularly important in designing polymers that could be shaped and cured in space for large-scale structural applications.

The flight experiment with uncured composites was a part of the NASA Scientific Balloon Flight Program conducted at the Australian Balloon Launch Station (ABLS) in Alice Springs, Australia. A flight cassette with the samples was installed on a 1200 kg payload carrying the telescope of the Tracking and Imaging Gamma-Ray Experiment (TIGRE). The payload was lifted with a "zero-pressure" stratospheric balloon filled with Helium. The dimension of the completely unfolded balloon is about 300 m. Columbia Scientific Balloon Facility (CSBF) provided the launch, flight telemetry and landing of the balloon and payload.

Experiment

Materials

The uncured composite prepreg with epoxy matrix SE70 (Gurit, Australia) filled with carbon fibers was purchased from Australian branch of Gurit. This prepreg has a long shelf life and the composites based on the prepreg are used in the aerospace industry. The prepreg was one layer of a 100×50 mm^2 size sheet and was kept in a refrigerator (4 °C) before using. The epoxy resins Polypox E 375 (based on Bisphenol F and epichlorhydrine, UPPC AG), Aldrich (CAS 25036-25-3, Poly(Bisphenol A-co-epichlorohydrin), glycidyl end-capped, $M_n = 374$), Epilox AF 8-50 (based on Bisphenol F and A, Leuna-Harze GmbH) and ED-20 (based on Bisphenol A, $M_n = 320$-340, Dzerzhinsk) were used. The hardener triethanolamine TEA (CAS 112-24-3, Aldrich) was added to the resins in 1:10 weight ratio and mixed for 1 min. These compositions are suitable for an analysis of curing processes as a model for most modern composites for space applications. The curing process in all these materials was investigated under vacuum and plasma conditions simulating the flight conditions in the stratosphere. The mixtures were prepared on the March, 29, 2010 in a chemical laboratory of St. Phillip College, Alice Springs. The prepared mixtures were kept in a refrigerator (2 °C) for 5 days before using. Then the mixtures were vacuumed for 2 min (up to foaming) and placed on glass fabric of size 300×25 mm^2. A 30 wt% content of polymer matrix on fabric was achieved after removing loose resin with filter paper sheets.

Stratospheric Flight

Three cassettes with uncured samples were prepared. The flight cassette consists of an aluminum base and a sleeve of black polyether fabric. The aluminum base was covered with paint filled with ZnO particulates (Dulux, Australia). The first data logger with a temperature sensor and a microprocessor data storage unit (EL-USB-1, model 23039-50, USA) was placed in an aluminum cylinder, sealed with aluminum disks and glued hermetically with Araldite epoxy resin (Fig. 1). The cylinder was covered by uncured SE70 Gurit prepreg. The top of base was covered with two layers of 0.05 mm thick low density polyethylene (LDPE) films.

Four sheets of uncured prepregs of SE70 were covered by Teflon mesh of 0.04 mm cells and stapled to the sleeve (Fig. 2, samples 1 to 4). A sheet of SE70 prepreg was cured in a thermo-box at 80 °C for 24 hr and then stapled to the sleeve as a control sample (sample 5 on (Fig. 2)). Four strips of uncured Polypox (a), Aldrich (b), Epilox (c) and ED-20 (d) prepregs were covered by Teflon mesh and stapled to opposite side of the sleeve (Fig. 2). Four high-density polyethylene (HDPE) envelopes of size 200×50 mm^2 were filled to 10 percent of their expanded volume with residual air and hermetically sealed. These were then inserted into the open HDPE envelope and inserted into the sleeve. The aluminum cylinder with a second temperature data logger was placed into a sleeve, which was fixed to the base. The sleeve was folded three times and fixed by Velcro adhesive stapled to the sleeve. The total weight of the flight cassette was about 1 kg.
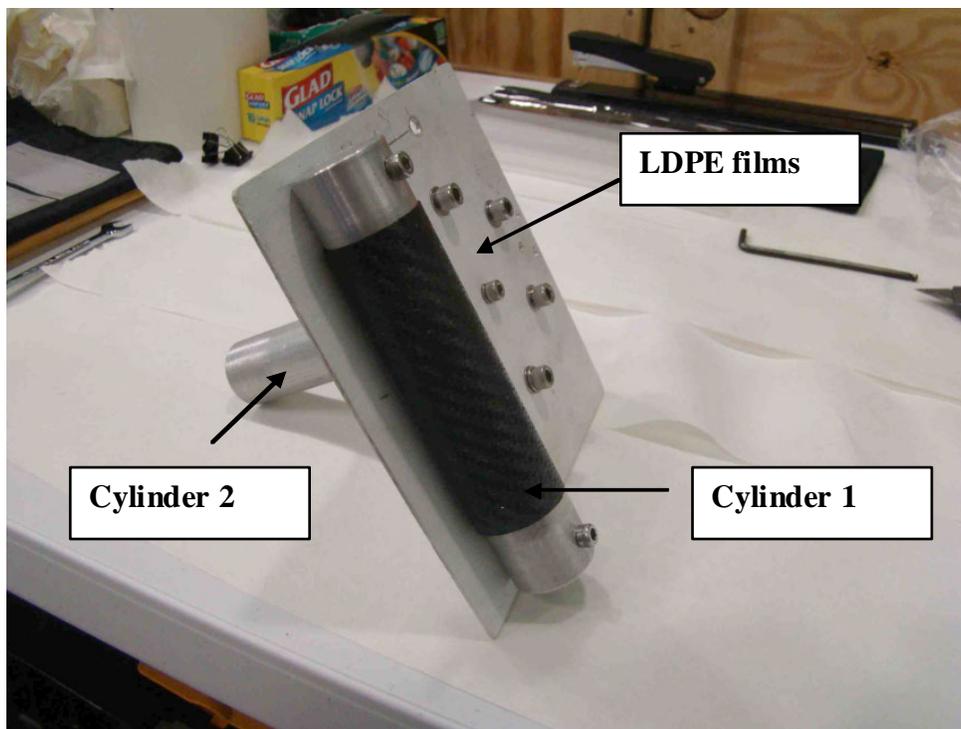

Figure 1.—The base of the flight cassette: the cylinder with thermometer 1 inside and Gurit prepreg on it (Cylinder 1). Two LDPE films are placed behind the cylinder and fixed with 7 screws. A second cylinder with thermometer 2 is under the base (Cylinder 2).
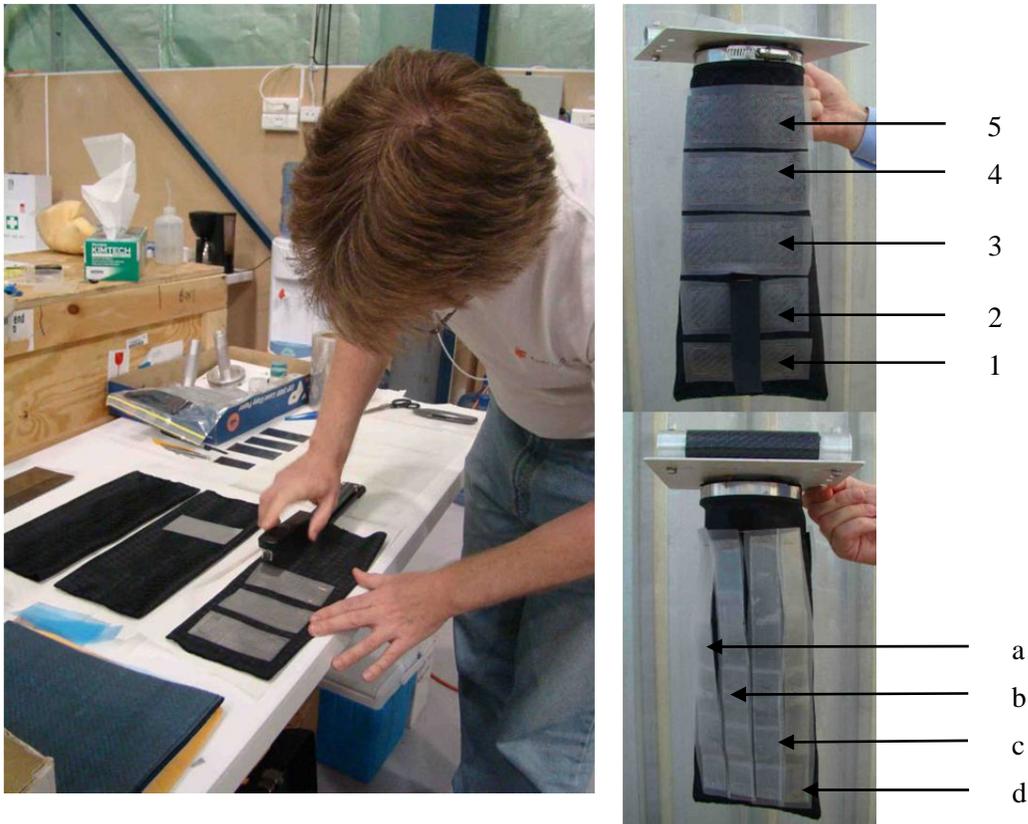
Figure 2.—Preparation of the sleeve: stapling of the SE70 samples covered with Teflon mesh to the sleeve and the control cassette with the samples. Samples 1 to 5 are SE70 prepregs, and samples a to d are prepregs with TEA hardener.

A ground control cassette was prepared at the same time with the same samples, excluding the cured SE70 prepreg, which was replaced by uncured prepreg. A third data logger was placed in the cylinder and fixed on the base.

A refrigerated control cassette was prepared at the same time with the same samples without base and data logger. The cassettes were prepared at 10 p.m. on April 3, 2010. This time and all further references to time in the text refer to the local, Northern Territory time.

The flight cassette was fixed on the payload to the GPS antenna bar (Figs. 3 and 4). The payload was moved out of the NASA base shed, moved to the airstrip and kept there from 1 a.m. to 7 a.m. on April 4, 2010. The launch was cancelled due to strong winds. The payload with cassette was moved back into the shed, the flight cassette was removed from the payload, and both flight and ground control cassettes were placed in a refrigerator (2 to 3 °C).

The next day at 1 a.m. the flight and ground control cassettes were taken out of the refrigerator. The flight cassette was fixed to the payload again and moved out of the shed. After 5 hr, the cassette was removed from the payload and both cassettes were placed back into the refrigerator. The launch was cancelled again due to strong winds (20 knots (10 m/sec)) at 400 m altitude since the maximum permitted was 10 to 12 knots (5 to 6 m/sec).

For the next 10 days the weather did not allow for the balloon launch with winds up to 50 knots (25 m/sec), thunderstorms and flooding. After the rain the soil had become too soft for the crane and heavy trucks with helium. The drying and hardening of the soil took two further days. The cassettes were kept in a refrigerator during this period.

Figure 3.—The flight cassette is fixed
on the metal bar of the GPS antenna
of the payload. The control sample,
which appears dark in the picture,
has been cured prior to the flight and
is not covered with a Teflon mesh.
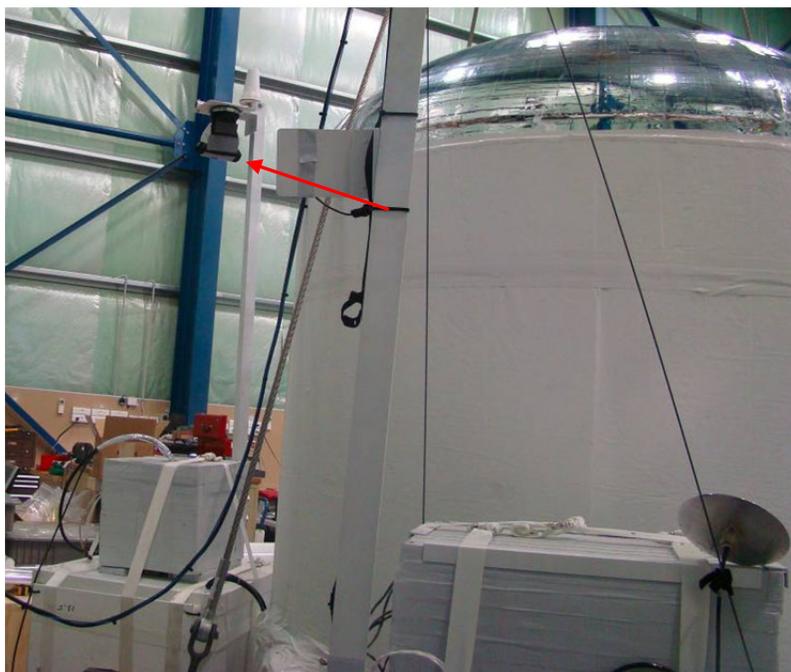
Figure 4.—The array shows the back of the video camera. The camera
was used to view the cassette during the flight.
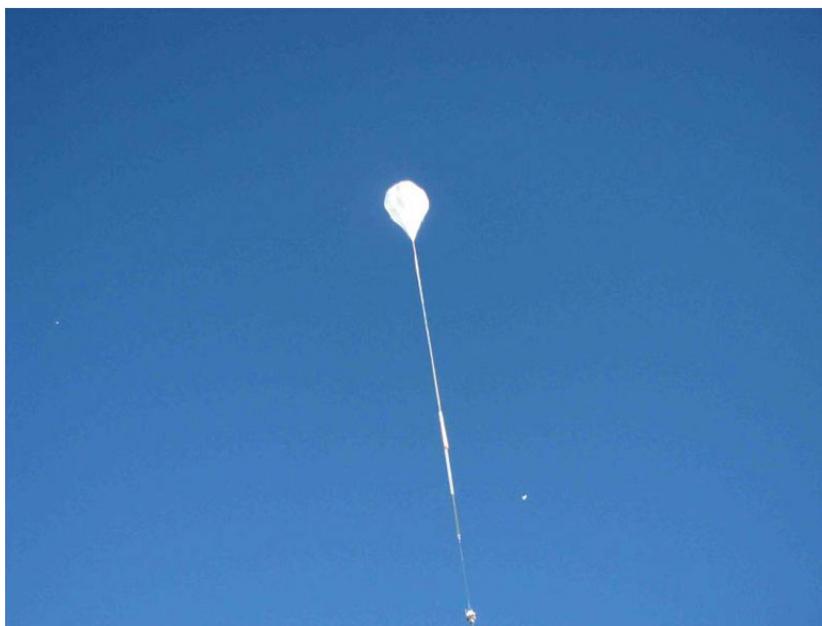
Figure 5.—Balloon launch with payload.

Figure 6.—The view of the cassette sent by telemetry during the flight at 40 km altitude.

At 1 a.m. on April 16 the flight and ground control cassettes were taken from the refrigerator. The flight cassette was fixed on the payload and moved out to the airstrip. The balloon was launched from Alice Springs Seven Mile airport, Northern Territory, Australia on April 16, 2010 at 9:00 a.m. (Fig. 5). After 4 min of flight (at the altitude of 1.6 km) the HDPE bags inside the sleeve expanded due to low pressure outside the sleeve, the Velcro adhesive peeled off and the flight cassette unfolded. After 2 hr of flight the balloon achieved an altitude of 40 km.

Over the next three days the altitude of balloon varied between 40 km (day time) and 35 km (night time). The position of the balloon, altitude, pressure, temperature and signal from the video camera were monitored with telemetry (Fig. 6). The payload was rotated by a motor at a rate of 1 turn per 4 min during

two days of flight. On the third day of flight, the rotation was stopped and the orientation of the payload was no longer controlled. After three days of flight, the payload was separated from the balloon and descended by means of a parachute. After 3 hr of descent the payload landed about 100 km to the west from Longreach, Queensland, Australia (latitude 24° 2.71' S, longitude 143° 54.5' E), 990 km from the launch site, at 6:11 p.m. on April 18, 2010. The speed at landing was about 4 to 5 m/sec. At landing, the payload fell on the side where the cassette was. The top of the cylinder was in contact with the soil. The day after landing the payload was found and transported to Longreach airport. The flight cassette was removed from the payload and stored in a refrigerator (2 °C).

The ground control cassette was placed outside the NASA base shed at the time of launch and exposed to sunlight during the balloon flight. As soon as the balloon landed, the ground control cassette was enclosed in a dark container at room temperature. The ground control cassette was placed in the refrigerator at the same time as the flight cassette was removed from the payload and placed in the refrigerator. The two cassettes were transported to Sydney in a refrigerator and stored in a refrigerator prior to analysis. Data loggers recorded the temperature on both cassettes during the waiting period before launch, during flight and transportation.

Measurements During the Flight

Pressure, temperature and altitude were recorded and logged during the flight. These data were sent to the ground station using telemetry. The air temperature was measured by a sensor placed in a white painted box at the bottom of the payload near the battery box. It showed that the temperature decreased after launch from 20 °C on the ground to –76.7 °C at an altitude of 17600 m. During the flight at 40 km altitude, the temperature remained in the range of –20 to 5 °C during the day and –30 to –45 °C at night (Figs. 7 and 8).
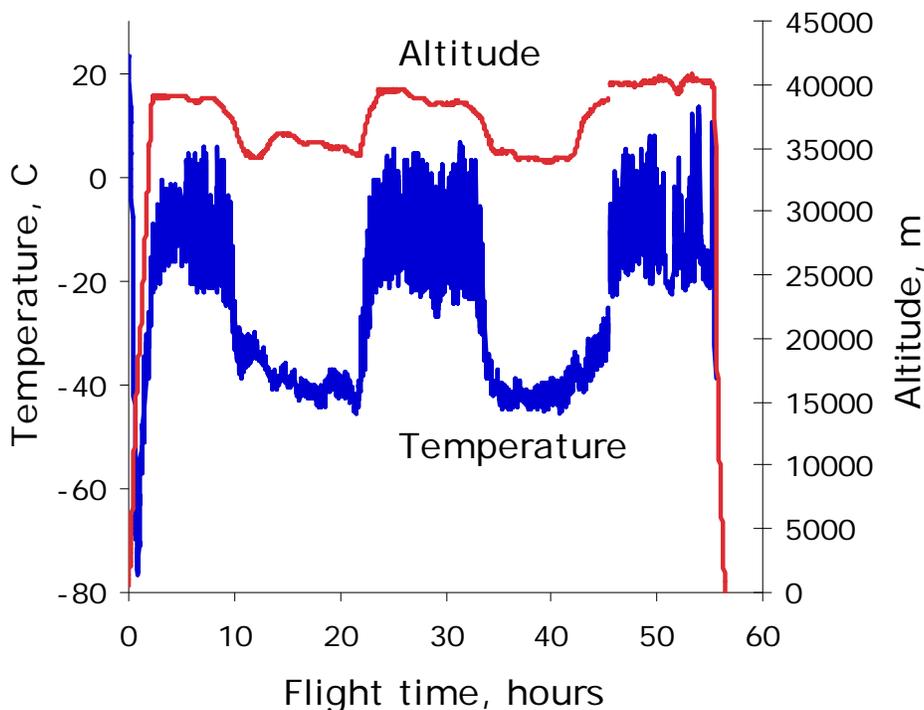

Figure 7.—Temperature and altitude of the payload during the flight. The break of the curve at 45 hr 40 min is due to change of the telemetry signal from the Alice Springs station to the Longreach station.
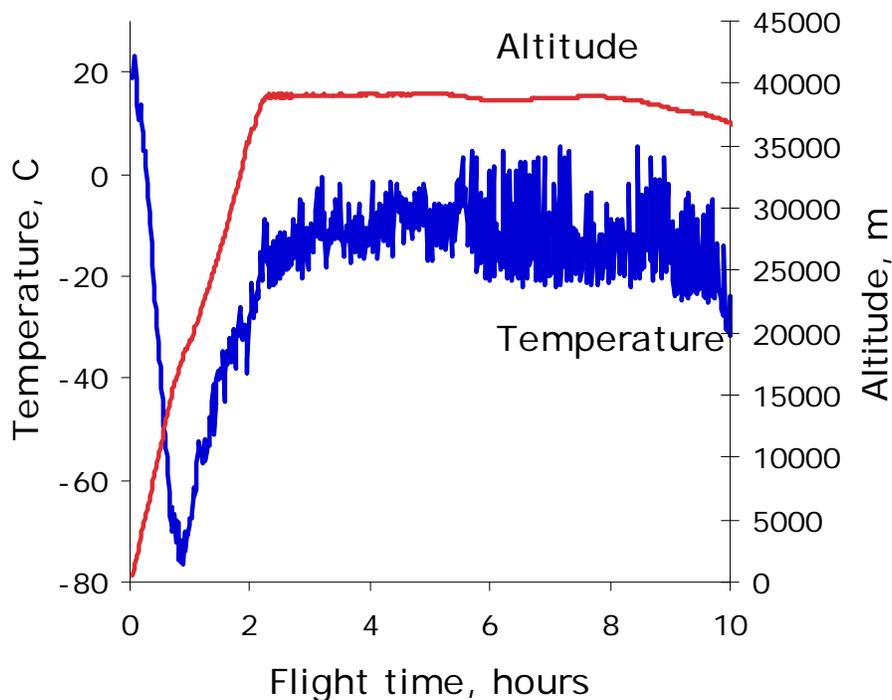
Figure 8.—Temperature and altitude of the payload during the launch and first day of flight.

The daytime temperature varied periodically with time. The cycle of temperature variation corresponded to the rotation of the payload. Therefore, the high temperature corresponds to an orientation of the temperature sensor to the Sun, when sunlight heated the sensor. The low temperature corresponds to the temperature of air.

On the third day, the rotation of the payload stopped and the temperature varied between –22 and 13 °C randomly depending on the orientation of the payload with respect to the Sun (Fig. 9).

The pressure decreased with elevation of the balloon (Fig. 10). At daytime, the balloon was heated by solar irradiation. The altitude of the balloon remained in the range 38 to 39 km during the first and second days of flight and then increased to 40 km on the third day of flight. The pressure at daytime decreased to 2.5 to 2.1 torr while at night time, the balloon was cooled, reducing the buoyancy on the balloon and the altitude decreased to the range 34 to 35 km. Consequently, the pressure increased to 5 torr at night time (Figs. 10 and 11).

Figure 12 shows the temperature measured inside the cylinder and sleeve of the flight cassette. At point "a", the cassette was taken from the refrigerator and attached to the payload. The cassette heated up to 22 to 23 °C which was the ambient temperature in the NASA base shed. Then the payload was moved out of shed and the temperature decreased to the air ambient temperature (8 to 9 °C). At point "b" the balloon was launched, the temperature decrease to –39 °C as the balloon rose. The temperature then increased to 26 °C in the cylinder and to 20.5 °C in the sleeve due to solar irradiation at higher altitude. At night time, the temperature decreased below –40°C. Temperatures lower than –40 °C were not recorded because this is the lower limit of the measurement range for our thermometers.

At 7:25 a.m., on the second day, thermometer 2 in the sleeve stopped recording (point c). Perhaps, the battery froze. The maximum temperature of the flight cassette (32.5 °C) was observed on the third day of the flight. The low (–38 °C) temperature observed on the third day corresponds to a descent of the payload to an altitude of 20 km. At point "d", the payload landed.

The temperature of ground control cassette (3) was consistently higher than the flight cassette. The maximum temperature of the ground cassette was 37.5 °C.
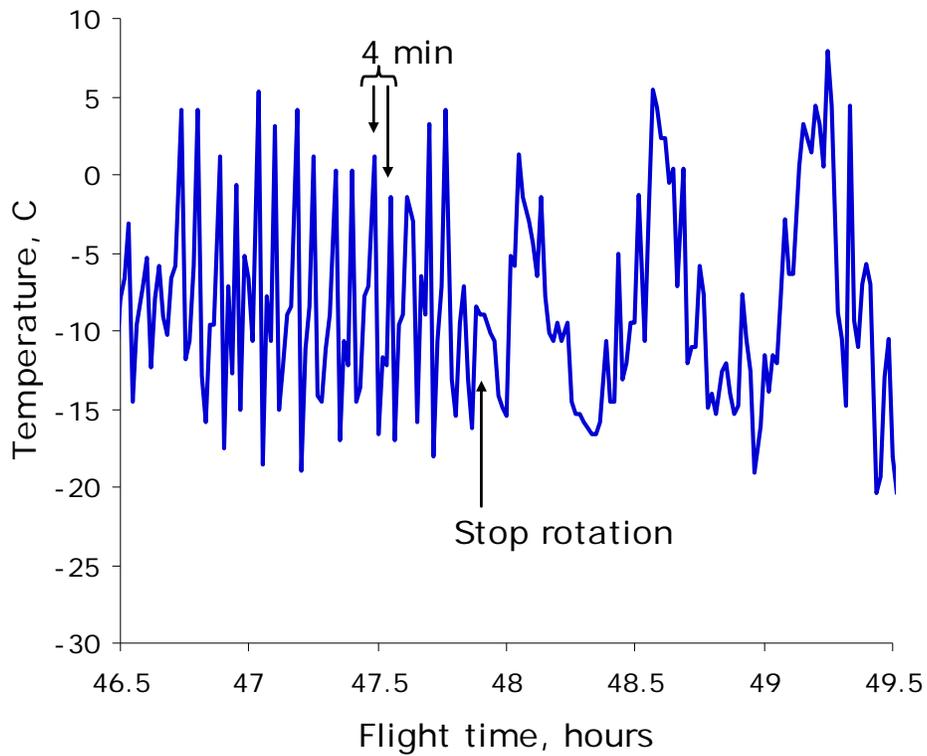
Figure 9.—Variation of the temperature of the payload during the third day of flight. The cycling of temperature up to 47 h 54 min is due to the rotation of the payload. After this time the payload was not rotated and the temperature variations correspond to its random orientation with respect to the Sun.
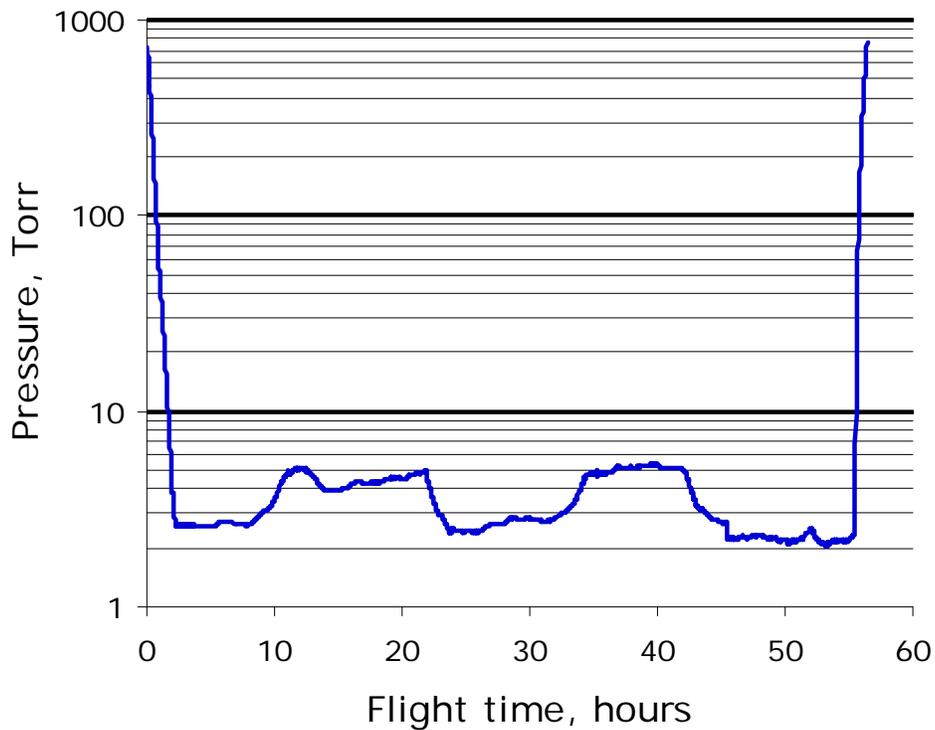
Figure 10.—Air pressure near the payload as a function of time during the stratospheric flight.
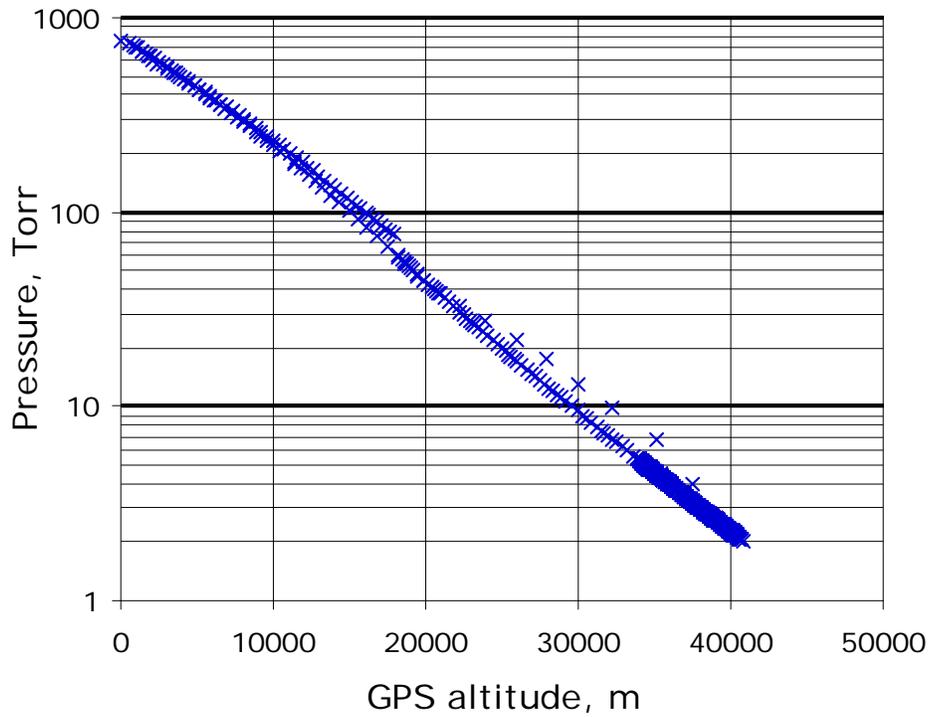
Figure 11.—Variation of air pressure near the payload with altitude of the balloon.
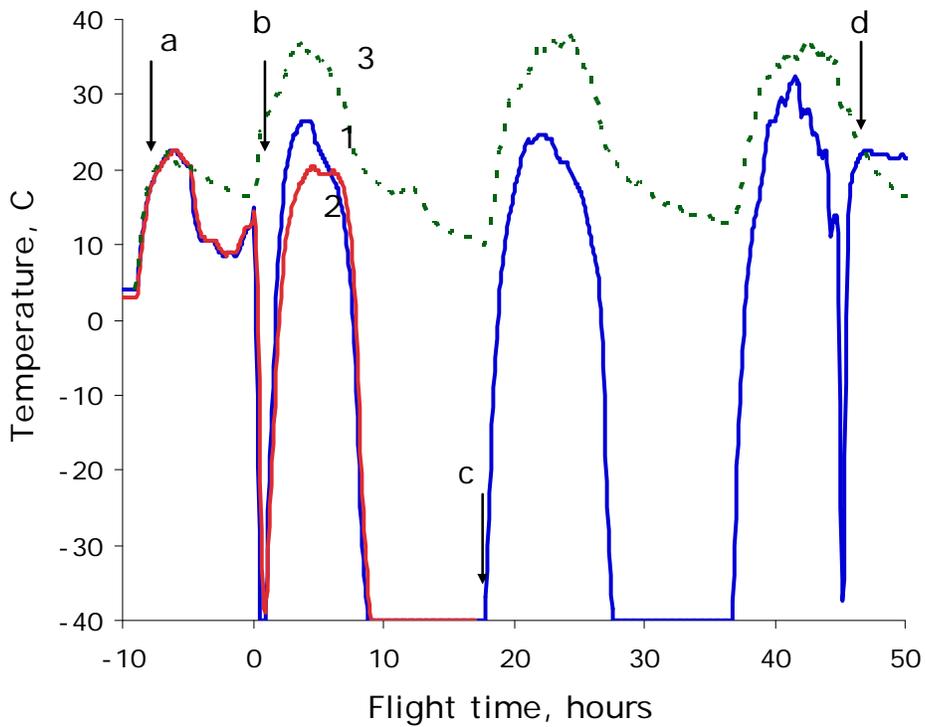
Figure 12.—Temperature measured in the flight cassette (1–blue line, 2–red line) and in the ground control cassette (3–green dash line). Thermometer 1 was placed on the top of the base, thermometer 2 was placed in the sleeve of the flight cassette. Times marked are a–cassettes taken from the refrigerator, time b–launch, time c–thermometer 2 ceased recording, time d–landing of the payload.

The refrigerated control cassette was kept in refrigerator (2 to 3 °C) during the entire experiment prior to analysis.

During the flight (April 16–18, 2010) the space weather was monitored using NOAA/SWPC Boulder, CO USA data received from the GOES-13 satellite on geostationary orbit. The electron flux and proton flux correspond to low level solar activity (Table 1). The X-ray intensity was 10^{-8} to 10^{-9} W/m^2 for 0.5-4 Å wavelengths, 2-0.2×10^{-7} W/m^2 for 1-8 Å wavelengths. No space weather events and Sun spots during the flight days were registered by U.S. Dept. of Commerce, NOAA, Space Weather Prediction Center.

The solar irradiance data were taken at Laboratory for Atmospheric and Space Physics (LASP). The SORCE spacecraft measurement data set was used. This data set included daily averaged SSI measurements from three instruments: Spectral Irradiance Monitor (SIM): 310 to 2400 nm, SOLar STellar Irradiance Comparison Experiment (SOLSTICE): 115 to 310 nm, XUV Photometer System (XPS): 0.1 to 40 nm. Solar irradiation spectra on April 16, 2010 is presented on Figure 13. The spectra during all days of the stratospheric flight are similar. The total level of the solar irradiation was 1361.09±0.01 W/m^2 during all days of flight.

TABLE 1.—FLUXES OF ELECTRONS AND PROTONS AT FLIGHT DAYS OF APRIL 16–18, 2010 MEASURED IN GEOS-13 SPACECRAFT ON GEOSTATIONARY ORBIT (NOAA DATA)

|	Energy	Average flux in a day			Range of variations
		Particles/cm^2/day/sr			Particles/cm^2/sec/sr
Electrons	> 0.8 MeV	8.83×10^8	7.86×10^8	7.89×10^8	3000 to 20000
	> 2 MeV	1.35×10^7	1.57×10^7	1.80×10^7	80 to 300
Protons	> 1 MeV	2.25×10^5	2.39×10^5	2.76×10^5	0.1 to 0.3
	> 10 MeV	1.74×10^4	1.72×10^4	1.78×10^4	0.09 to 0.2
	> 100 MeV	7.07×10^3	6.72×10^3	7.16×10^3	0.03 to 0.1
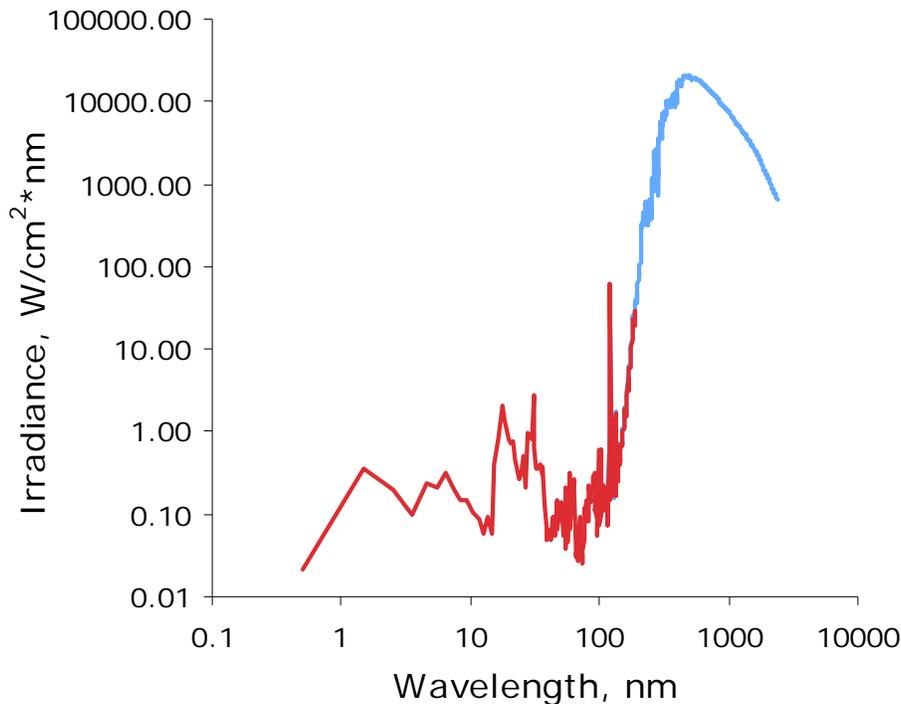
Figure 13.—Solar irradiation spectra at 16 April, 2010: first day of flight.
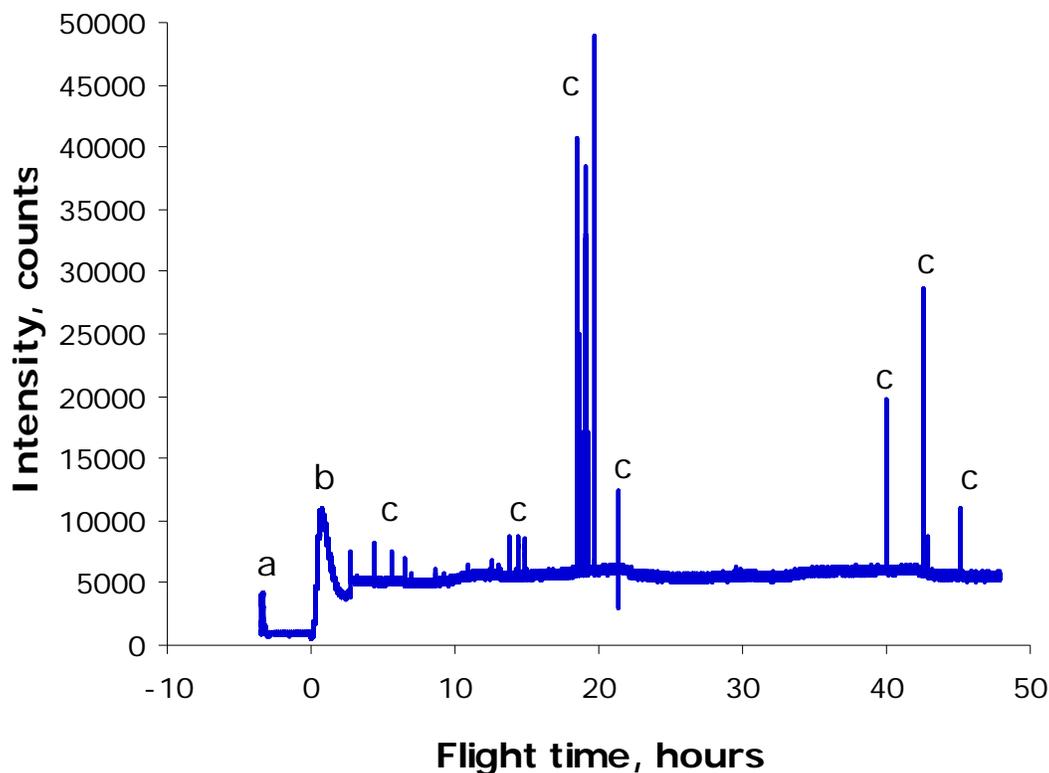
Figure 14.—The intensity of cosmic rays during the flight measured on first layer of silicon detector. The a spike is a response of the detector from a test isotopic source. The b spike shows the high level of irradiation in the Pfotzer maximum at 20000 m altitude. The c spikes are responds on electrical break of photomultiplier tube. The recording was stopped after 2 days of flight due to low battery voltage. The data were presented by Prof. A. Zych.

During the flight the cosmic rays intensity was measured using a Compton telescope the Tracking and Imaging Gamma Ray Experiment (TIGRE) with multi-layers of thin silicon strip detectors to convert and track gamma-ray events (Fig. 14).

The level of radiation on ground is mostly provided by muons and corresponds to about 1000 counts per 1.31 sec. The cosmic rays intensity in the stratosphere is about 5000 counts per 1.31 sec. This level is provided by cosmic rays like high-energy protons, electrons, X-rays and γ-rays. These irradiations and UV light penetrated into the samples during the balloon flight at 40 km altitude that was above ozone layer (20 to 25 km).

Analysis of the Samples

The polyethylene films were used for analysis of the radiation environment during the flight in stratosphere and on ground. Electron paramagnetic resonance spectra (ESR) were recorded on a Bruker Elexsys E500 EPR spectrometer operating in X band with a microwave frequency of 9.75 GHz and a central magnetic field of 3480 G, at room temperature. The spectrometer was calibrated using a weak pitch sample in KCl and also with DPPH (α,α'–diphenyl-β-picrylhydrazyl). The LDPE film were rolled and placed into a glass tube. The tube was placed into the spectrometer cavity for the recording of spectra. The spectrum of the tube without LDPE film was recorded before the measurement.

The radiation damage and oxidation of LDPE film was monitored with Fourier Transform Infrared (FTIR) Attenuated Total Reflectance (ATR) spectroscopy. FTIR ATR spectra from the samples were recorded using a Digilab FTS7000 FTIR spectrometer fitted with an ATR accessory (Harrick, USA) with

trapezium germanium crystal and incidence angle of 45°. To obtain sufficient signal/noise ratio and resolution of spectral bands, we used 500 scans and a resolution of 4 cm^{-1}. The spectra of both side of the film were recorded. A peak intensity of the spectral lines was used for quantitative analysis. The error bars were calculated from the noise level of the spectra.

The composite samples have been analyzed with FTIR ATR spectra with the same spectrometer and ATR accessory. The absorbance of the 915 cm^{-1} line of the epoxy group vibration was used for the analysis of the concentration of epoxy groups in the samples. In order to compare between spectra the absorbance was normalized to the absorbance of the 1509 cm^{-1} line corresponding to aromatic ring vibrations, which is not affected by the curing. The FTIR ATR spectra of the samples were recorded on April 24, 6 days after landing.

The swelling degree of the samples in acetone was calculated according to

$$S = (M_1 - M_f)/(M_2 - M_f) \hspace{4cm} (1)$$

where M_1 is weight of the sample swelled in acetone after soaking for 3 days in acetone but prior to drying. M_2 is the weight of the sample after soaking for 3 days in acetone and then drying. M_f is the weight of the carbon fibers, calculated according to the known content of fibers in the original sample.

The gel-fraction was measured by dissolving of the uncured epoxy matrix in acetone. The gel-fraction content was calculated as

$$G = (M_2 - M_f)/(M_3 - M_f) \hspace{4cm} (2)$$

where M_3 is weight of the sample before exposure to solvent.

The gel-fraction and swelling degree for each sample sheet was measured for 4 pieces (15×20 mm^2) cut from the sheet and the results were averaged. The first measurement of the gel-fraction was performed on April 24, 2010 six days after landing. The second measurement of the gel-fraction was performed on May 5, 17 days after landing. The samples were kept in refrigerator at +2 to 3 °C prior to all measurements.

DMA measurement was carried out using the ARES analyzer (Rheometric Scientific, Inc., USA). Sample plates of $50 \times 10 \times 0.35$ mm were tested. The rate of heating was 5 °C/ min, strain was 0.1 radian with frequency of 1 Hz. Samples were heated and cooled continuously with the heating rate of 5 °C/min in dry N_2 gas flow, from –50 to 150 °C. The G' and G'' modulus and tan(δ) values were recorded. Orchestrator software was used for analysis.

Results

The ESR spectra show that the initial LDPE film (refrigerated control cassette) has free radicals with g-factor of 2.0025 caused by environmental radiation effects at storing of the LDPE film (Fig. 15). The spectra of LDPE film exposed in ground cassette shows the same signal with g-factor of 2.0025 and additional signal with g-factor of 2.008 as result of radiation damages of polyethylene macromolecules under Sun radiation on ground. The ESR spectra of the film exposed in stratosphere showed similar signal with g-factor of 2.0025 and strong signals with g-factor of 2.005 and 2.016. These additional free radicals appeared due to radiation damages of polyethylene macromolecules in stratosphere.

The FTIR ATR spectra of exposed films show additional lines of vibrations in unsaturated hydrocarbon groups and in oxygen containing group. The unsaturated hydrocarbon groups such as vinyl, vinylidene and vinylene groups appeared in exposed LDPE films after reactions of free radicals. The quantitative analysis of the unsaturated hydrocarbon concentration was done by absorbance of vinyl group at 910 cm^{-1} (Fig. 16). The absorbance of 910 cm^{-1} line was normalized on absorbance of 1462 cm^{-1} line of methylene groups. The vinyl groups exist in initial LDPE film as a result of radiation damage caused by environmental effects during storing. The absorbance in the initial film is shown as background (dashed line). The concentration of vinyl groups in the film exposed on ground is higher than in the initial
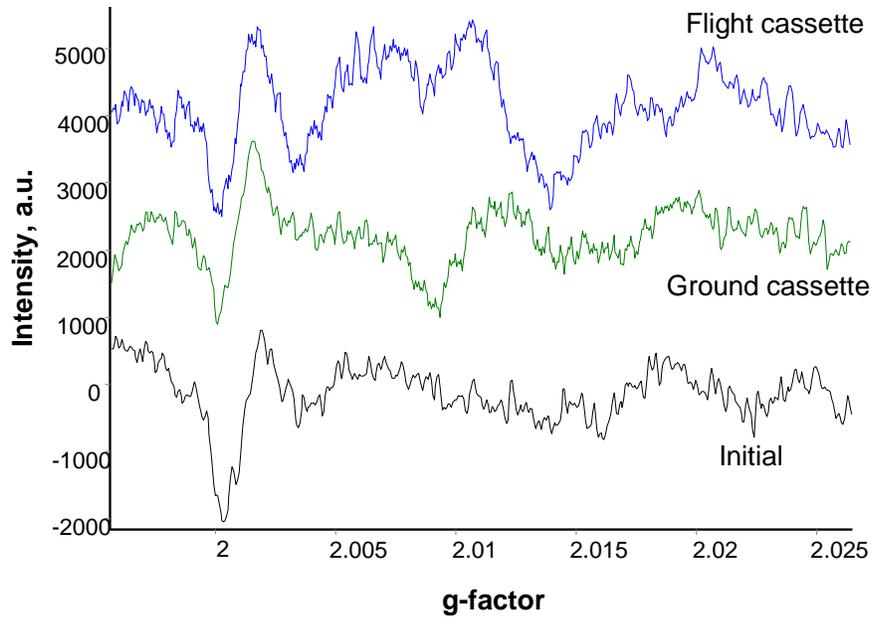
Figure 15.—ESR spectra (first derivative) of LDPE as initial, exposed in ground cassette and in flight cassette.
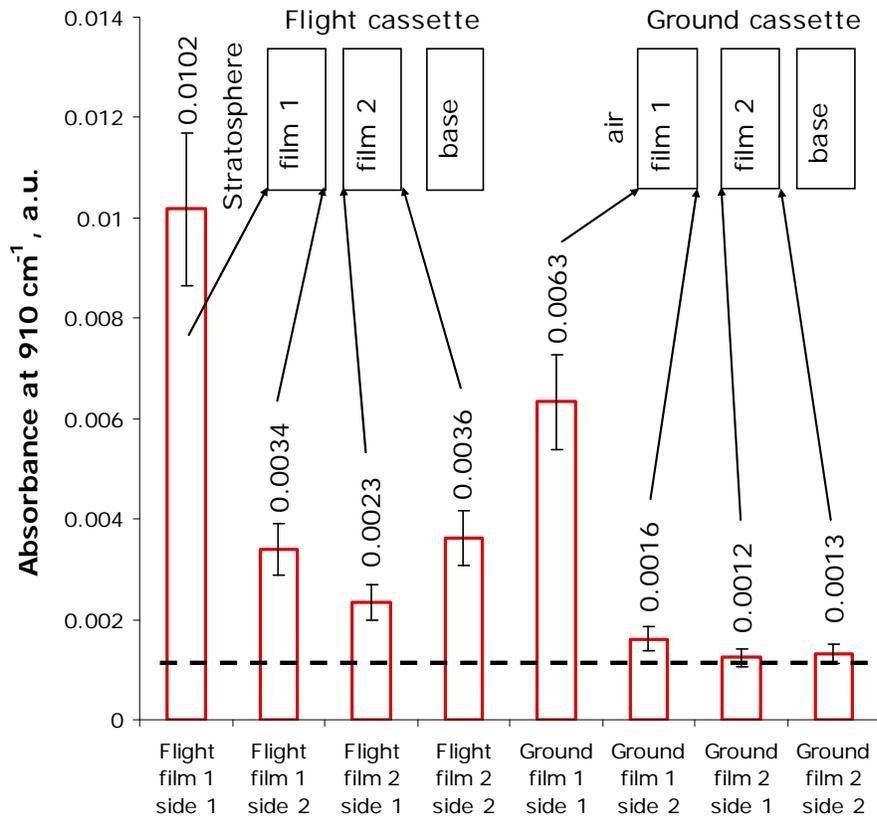
Figure 16.—Absorbance of vinyl vibration group line in FTIR ATR spectra of LDPE surface exposed in stratosphere (flight cassette) and on ground (ground cassette). Two films of LDPE attached together on the base of the cassette were exposed. The spectra were recorded from both sides of both films. Dashed line shows an absorbance of vinyl group vibrations in initial unexposed LDPE film.

film due to radiation damage under sunlight. The high concentration is observed in the external surface of the first film which was directly illuminated by sunlight. The backside of the first film and second film do not show significant increase of the unsaturated groups. The concentration of vinyl groups in the film exposed in stratosphere is higher than in films exposed on ground. The highest concentration is observed in the external side of the first film that was under Sun irradiation and cosmic rays during the flight experiment. However, a clear increase in the concentration is observed on all sides of all films exposed in stratosphere.

The oxygen containing groups appeared after free radical reactions with atmospheric oxygen. The analysis of oxidation was done on absorbance of carbonyl group at 1735 cm^{-1}. The absorbance of 1735 cm^{-1} line was normalized on absorbance of 1462 cm^{-1} line of methylene groups.

The carbonyl groups exist in the initial LDPE film as a result of radiation damage caused by environmental effects during storing. The absorbance of the carbonyl groups in the initial film is shown as background (dashed line) (Fig. 17). The concentration of carbonyl groups in the film exposed on ground is higher than in the initial film due to radiation damage under sunlight. The high concentration is observed in the external surface of the first film that was directly illuminated by sunlight. The backside of the first film and the second film show an increase of the carbonyl groups. The concentration of carbonyl groups in all films exposed in the stratosphere is slightly higher than in the films exposed on ground. The highest concentration is observed in the external side of the first film and the lowest concentration is observed in the internal side of the second film.
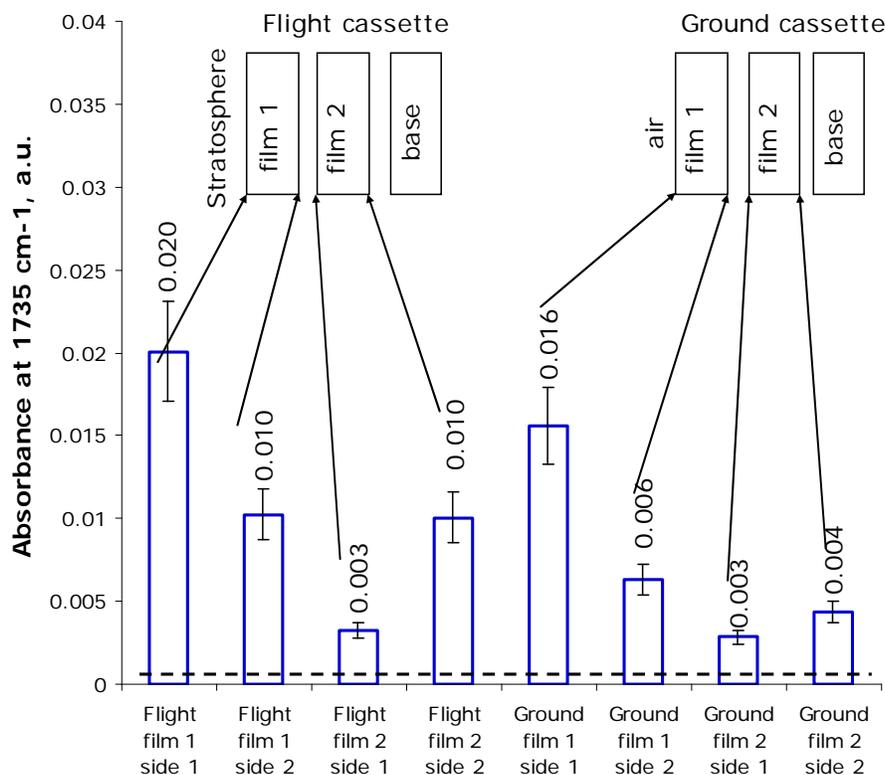

Figure 17.—Absorbance of carbonyl vibration group line in FTIR ATR spectra of LDPE surface exposed in stratosphere (flight cassette) and on ground (ground cassette). Two films of LDPE attached together on the base of the cassette were exposed. The spectra were recorded from both sides of both films. Dashed line shows an absorbance of carbonyl group vibrations in initial unexposed LDPE film.

The observed increase of unsaturated and carbonyl groups concentrations correspond to 3rd day expositions in direct sunlight on ground and in stratosphere. A similar level of the radiation damage is expected in uncured composite materials exposed in stratosphere and on ground.

The samples of composite materials from the flight cassette, the ground control cassette and the refrigerator control cassette were analyzed. Progress of the curing reaction was monitored with FTIR ATR spectroscopy. The degree of crosslinking was assessed by gel-fraction and swelling measurements.

The gel-fraction content in the flight samples on the sleeve is higher, than in the ground control samples and the refrigerated control samples (Fig. 18). The gel-fraction content in the flight sample on the cylinder is the same as in the ground control sample. The error bars of gel-fraction content in the flight sleeve samples are significantly higher than in the ground and refrigerated samples. These differences in flight and control samples are observed in the first measurement after 6 days after landing and in the second measurement after 17 days after landing.

The swelling degree results correlate with gel-fraction content results (Fig. 19). The epoxy matrix in the control samples swells to a higher degree, than the matrix of the flight samples on the sleeve. The swelling of the flight sample on the cylinder is the same as for the control sample. The higher content of gel-fraction and lower swelling degree in the flight samples shows, that there is more crosslinking in the flight samples than in the ground control.
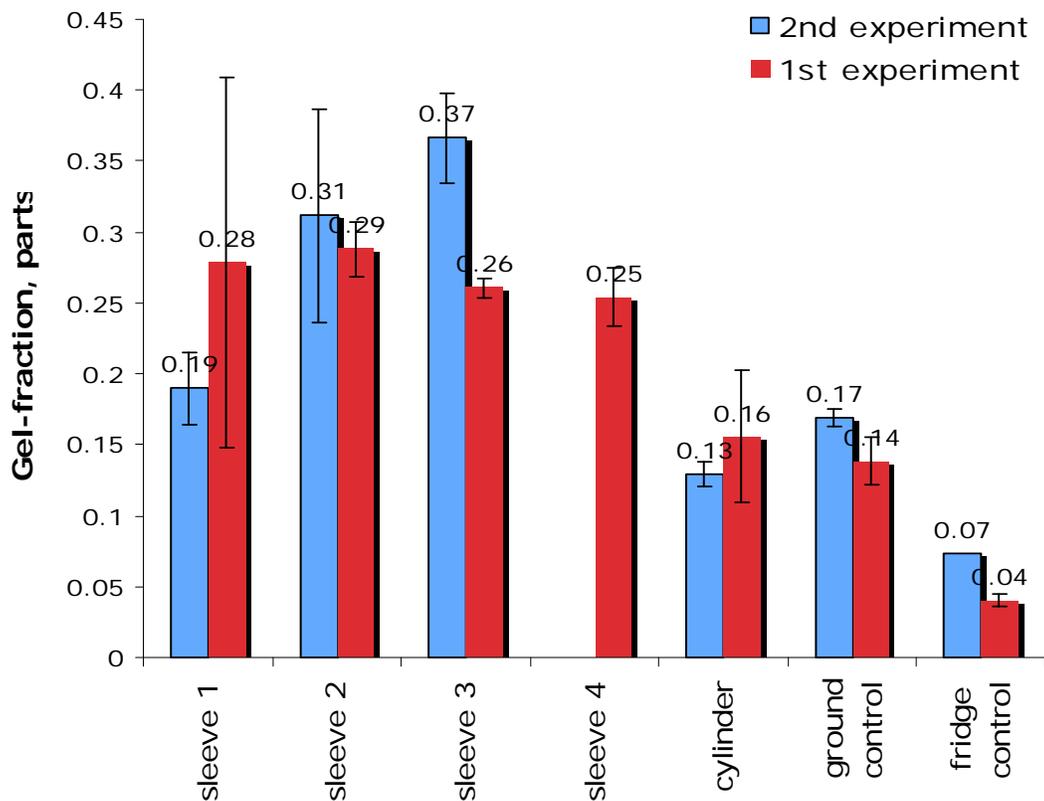
Figure 18.—Gel-fractions of uncured SE70 prepreg samples in acetone. 1 to 4 sleeve sheets and the sheet from the cylinder are flight samples. The control samples are from the ground cassette and from the cassette stored in the refrigerator. The first measurement of the gel-fraction measurement was done 6 days after landing. The second measurement of the gel-fraction was done 17 days after landing. The samples after landing were kept in the refrigerator at 2 to 3 °C prior to all measurements.
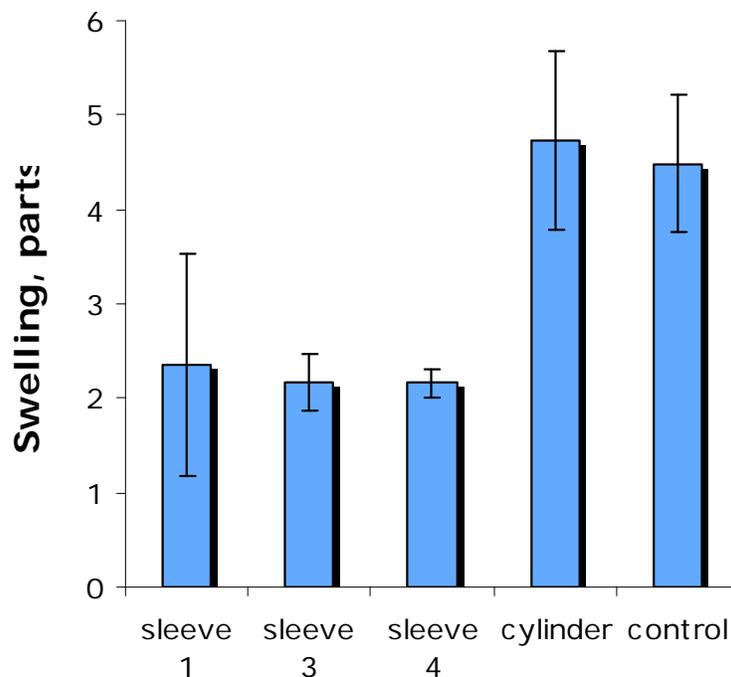
Figure 19.—Swelling of uncured SE70 prepreg in acetone: sleeve
1 to 4 and cylinder samples are from the flight cassette, the control
is from the ground cassette.

The absorbance of epoxy group vibrations in FTIR ATR spectra shows, that the epoxy group concentration in the uncured flight cassette samples and in the uncured ground control samples is similar (Fig. 20). The absorbance of epoxy groups in both kinds of the samples is high and close to the absorbance of 0.22 for the initial uncured prepreg. It shows that the curing reaction of epoxy groups with active groups of hardener in epoxy matrix occurred slowly in the flight and ground control samples due to the low temperatures experienced by the flight and ground control cassettes.

The FTIR ATR spectra of gel-fraction of the samples after washing in acetone show the residual epoxy groups, and are attributed to crosslinked macromolecules of the epoxy resin (Fig. 21). The low absorbance of residual epoxy groups in the gel-fraction of the ground control sample (0.038) is similar to the absorbance of residual epoxy groups in the sample cured before the flight (0.041). It shows that the gel-fraction in the ground control samples is formed due to the reaction of epoxy groups with hardener as in the usual curing of the epoxy resin composite.

The absorbance of residual epoxy groups in the gel-fraction of the flight samples is higher than in the gel-fraction of the ground control samples. This means that the high degree of crosslinking of the macromolecules in the flight samples is not due to the curing reaction of epoxy groups. There are clearly additional reactions, which cause crosslinking in the flight samples.

An important parameter of the uncured prepreg after exposure in the stratosphere is the remaining chemical activity for curing. The flight and control samples were cured in the thermobox at 80 °C over a period of 3 days. The completeness of the curing reaction was tested by FTIR ATR spectroscopy (Fig. 20). The FTIR ATR spectra of the cured samples show the absorbance of residual epoxy groups in the composite after the curing reaction. The absorbance of residual epoxy groups in the cured ground control samples is similar to the absorbance of epoxy groups in flight sample 5 which was cured before the flight. The absorbance of the residual epoxy groups in the cured flight samples is higher, than in the ground control samples. This means that the epoxy groups in the flight samples were not completely reacted during the curing.
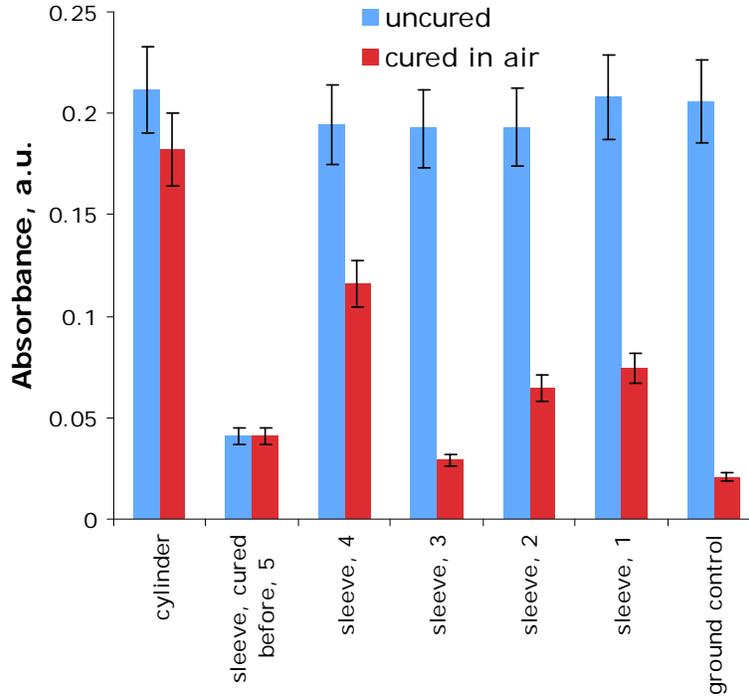
Figure 20.—Normalized absorbance at 915 cm^{-1} line in the FTIR ATR spectra of uncured SE70 prepreg and SE70 composite cured in air at 80 °C over 3 days: 1 to 4 sleeve samples and sample on the cylinder in the flight cassette; sleeve 5 is the flight cassette sample cured before the flight; control is the sample in the ground cassette.
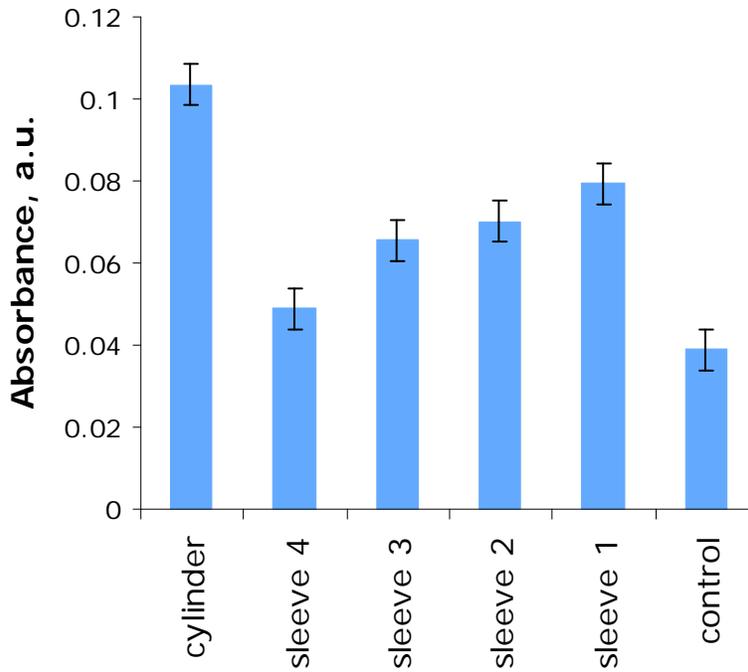
Figure 21.—Absorbance at 915 cm^{-1} from FTIR ATR spectra of the gel-fraction in the SE70 prepregs: 1 to 4 sleeve samples and the sample on cylinder are from the flight cassette, the control is the ground cassette.

TABLE 2.—GLASS TRANSITION TEMPERATURE OF THE
SAMPLES CURED AT 80 °C DURING 3 DAYS

| Sample	T_g, °C
Aldrich composition, flight cassette	97.5
Aldrich composition, ground cassette	95
Aldrich composition, refrigerated cassette	97.5
ED 20 composition, flight cassette	76.3
ED 20 composition, ground cassette	88.7
ED 20 composition, refrigerated cassette	93.7
EPILOX composition, flight cassette	90
EPILOX composition, ground cassette	87.2
EPILOX composition, refrigerated cassette	89.8
Polypox composition, flight cassette	81.3
Polypox composition, ground cassette	57.4
Polypox composition, refrigerated cassette	82.7
SE70 composition, flight cassette, cylinder end	113.6
SE70 composition, flight cassette, sleeve 1	110.1
SE70 composition, flight cassette, sleeve 2	113.5
SE70 composition, flight cassette, sleeve 3	113.7
SE70 composition, flight cassette, cylinder center	111.1
SE70 composition, ground cassette, sleeve 1	112.5
SE70 composition, refrigerated cassette, sleeve 1	116.2

The final test of curing ability of the compositions after exposure in stratosphere was done with using of Dynamical Mechanical Analysis (DMA) of the cured samples. The flight, ground control and refrigerated control samples were cured in the thermobox at 80 °C over a period of 3 days. The glass transition temperature (T_g) was determined (Table 2).

The glass transition temperature of cured composites based on Aldrich and Epilox resins and SE70 composite does not show a significant difference between the flight, ground control and refrigerated control samples. This means that the reaction in flight and control samples proceeded similarly.

The composition based on Polypox becomes darker after storing in the ground cassette. Probably, this is caused by a specific reaction of the resin induced by humidity. The glass transition temperature of the ground control sample is significantly lower than the refrigerated control and flight samples. T_g of flight sample and refrigerated control sample are similar, and shows successful curing in flight sample.

The composition based on ED-20 resin shows significant decrease of T_g in the flight sample in comparison with ground and refrigerated control samples. Probably, some additives of the resin were evaporated or the resin is not stable under cosmic rays. It means that this composition cannot be recommended for curing after an exposure in stratosphere.

Discussion

The flight samples remained uncured in stratosphere and were successfully cured after landing. The conditions in the stratosphere did not interfere with the curing capability of the samples. Therefore, the uncured samples can be delivered and stored in the stratosphere before curing.

The temperature records during the flight show that the uncured samples were exposed to temperatures in the range from –76 to 32 °C. The prepreg used has a slow curing reaction rate at such low temperatures, as noted in the Gurit Information Sheet for the SE70 prepreg. The small decrease of the epoxy group concentration in the samples in the ground cassette and in the flight cassette from the original uncured sample shows that the curing reaction proceeded minimally in accordance with the low

curing rate. The temperature of the ground cassette was higher than the temperature of the flight cassette, but the temperature difference was too small to observe a difference in epoxy group conversion between the ground control and flight cassette samples. However, the analysis of gel-fraction and swelling degree shows that the flight cassette samples have a significantly higher degree of crosslinking. The gel-fraction of the control samples is formed as the result of epoxy group conversion and this residual concentration is equal in the completely cured samples and the incompletely cured samples. In the flight samples, the concentration of residual epoxy groups is higher, indicating that the gel-fraction is formed due to epoxy group reactions as well as additional reactions which leave the epoxy groups unchanged.

The gel-fraction in the flight samples is due to two reactions: the reaction of epoxy groups with the active groups of the hardener, as in the usual curing process, and additional chemical reactions, where the epoxy groups do not take part. These additional reactions are initiated by radiation damage in the epoxy matrix due to high-energy particles (electrons and ions), X-rays, γ-rays, ultraviolet and short wavelength ultraviolet sunlight as per the specific conditions in the stratosphere. Space radiation can cause damage of the polymer macromolecules producing free radicals, which facilitate crosslinking between macromolecules without conversion of the epoxy groups of the macromolecules. The intensity of these space radiations at a height of 40 km in the stratosphere above the ozone layer is higher than on the ground, therefore, the flight samples were irradiated with a higher intensity than the ground control samples.

In summary, our results show that the stratospheric conditions give additional pathways for crosslinking of the polymer matrix. Similar effects of radiation damage on curing reactions were observed in previous laboratory investigations in which prepregs were exposed to plasma and ion beam (Refs. 9, 10, and 17). Similarly additional crosslinking reactions in uncured composites can be expected in a low Earth orbit space environment.

Conclusions

This is the first time that uncured epoxy matrix composites were exposed in the stratosphere at a height of 40 km over 3 days. Analysis of the gel-fractions and epoxy group concentrations showed that curing reactions in the flight samples and in the ground control samples are different. Additional crosslinking reactions caused by space radiations are observed in the flight samples. The uncured samples of SE70 prepreg and compositions based on Aldrich, Epilox and Polypox resins remain curable after an exposure in stratosphere.

References

1. Kondyurin A.V., Building the shells of large space stations by the polymerisation of epoxy composites in open space, Int. Polymer Sci. and Technol., v.25, N4, 1998, p. T/78.
2. Briskman V., A. Kondyurin, K. Kostarev, V. Leontyev, M. Levkovich, A. Mashinsky, G. Nechitailo, T. Yudina, Polymerization in microgravity as a new process in space technology, Paper IAA-97-IAA.12.1.07, 48th International Astronautical Congress, October 6–10, 1997, Turin Italy.
3. Kondyurin A., G.Mesyats, Yu.Klyachkin, Creation of High-Size Space Station by Polymerisation of Composite Materials in Free Space, J. of the Japan Soc. of Microgravity Appl., v.15, Suppl.II, 1998, p. 61–65.
4. Kondyurin A., Kostarev K., Bagara M.V., Polymerization processes of epoxy plastic in free space conditions, Paper IAF-99-I.5.04, 50th International Astronautical Congress 4-8- Oct., 1999, Amsterdam, The Netherlands.
5. Kondyurin A., High-size space laboratory for biological orbit experiments, Advanced space research, v.28, N4, 2001, pp. 665–671.
6. Kondyurin A., Kostarev K., Bagara M., Polymerization processes of epoxy plastic in simulated free space conditions, Acta Astronautica, vol. 48, N2-3, 2001, pp. 109–113.

7. Briskman V.A., Yudina T.M., Kostarev K.G., Kondyurin A.V., Leontyev V.B., Levkovich M.G., Mashinsky A.L., Nechitailo G.S., Polymerization in microgravity as a new process in space technology, Acta Astronautica, vol.48, N2-3, 2001, pp. 169–180.
8. Kondyurin A., B. Lauke, I. Kondyurina and E. Orba, Creation of biological module for self-regulating ecological system by the way of polymerization of composite materials in free space, Advances in Space Research, 2004, v. 34/7, p. 1585–1591.
9. Kondyurin A., B. Lauke, E. Richter: Polymerization Process of Epoxy Matrix Composites under Simulated Free Space Conditions, High Performance Polymers. 16, 2004, p. 163–175.
10. Kondyurin A., B. Lauke: Curing of liquid epoxy resin in plasma discharge, European Polymer Journal. 40/8, 2004, p. 1915–1923.
11. Kondyurina I., A. Kondyurin, B. Lauke, L. Figiel, R. Vogel, U. Reuter, Polymerisation of composite materials in space environment for development of a Moon base, Advances in space research, 37, 2006, p. 109–115.
12. Kondyurin A., B. Lauke, R. Vogel, Photopolymerisation of composite material in simulated free space environment at low Earth orbital flight, European Polymer Journal 42 (2006) 2703–2714.
13. A. Kondyurin, B. Lauke, R. Vogel, G. Nechitailo, Kinetics of photocuring of matrix of composite material under simulated conditions of free space, Plasticheskie massi, 2007, v.11, pp. 50–55.
14. A.V. Kondyurin, L.A. Komar, A.L. Svistkov, Modelling of curing of composite materials for the inflatable structure of a lunar space base, Mechanics of composite materials and constructions, 15 (4), 512–526, 2009.
15. A.V. Kondyurin, G.S. Nechitailo, Composite material for Inflatable Structures Photocured under Space Flight Conditions, Cosmonautics and rockets, 3 (56), 182–190, 2009.
16. A. Kondyurin, M. Bilek, Ion Beam Treatment of Polymers. Application aspects from medicine to space, Elsevier, Oxford, 2008.
17. A. Kondyurin, M. Bilek, Etching and structure transformations in uncured epoxy resin under rf-plasma and plasma immersion ion implantation, Nuclear Instruments and Methods in Physics Research, B 268 (2010) 1568–1580.