

## OUTGASSING AND DIMENSIONAL CHANGES OF POLYMER MATRIX COMPOSITES IN SPACE

R. C. Tennyson and R. Matthews  
 University of Toronto Institute for Aerospace Studies  
 North York, Ontario, Canada, M3H 5T6  
 Phone: 416/667-7710, Fax: 416/667-7799

## SUMMARY

This report describes a thermal-vacuum outgassing model and test protocol for predicting outgassing times and dimensional changes for polymer matrix composites. Experimental results derived from a "control" sample are used to provide the basis for analytical predictions to compare with the outgassing response of LDEF flight samples.

## THERMAL-VACUUM OUTGASSING AND DIMENSIONAL CHANGES OF LDEF POLYMER MATRIX COMPOSITES (AO180)

The UTIAS experiment consisted of a variety of graphite, aramid and boron fiber reinforced epoxy matrix composites located at station D-12 on LDEF (i.e.,  $\sim 82^\circ$  relative to velocity vector). Selected samples were instrumented with strain and temperature gauges that were sampled every 16 hours over the first 370 days in orbit. Data were stored on a magnetic tape cassette using a space-qualified data acquisition system designed and constructed at UTIAS. Details on this aspect of our experiment can be obtained from ref. 1. It was found that the strain/thermal gauge measuring system worked flawlessly, as evidenced by the measured response of a stainless steel calibration specimen which remained unchanged throughout the 5.75 years in orbit. Typical time/temperature and strain/temperature data for one material (graphite/epoxy, 5208/T300) are shown in Figs. 1 and 2, respectively. This data can be re-plotted as strain vs. temperature as given in Fig. 3 for the  $90^\circ$  laminate. It can be seen that a "total" dimensional strain change of  $\sim 1600 \times 10^{-6}$  occurred after about 80 days in orbit. It should be noted that no microcracks were observed in this laminate and full recovery of the dimensional change occurred once the sample was returned to Earth and exposed to the ambient environment.

From this data, it is possible to estimate the coefficient of thermal expansion (CTE) from the final slope once all outgassing is essentially finished. Using this CTE value, one can correct for the temperature variations on-orbit, giving the strain change of the sample, over time, independent of temperature. The formula used to do this is:

$$\Delta_t = \epsilon_t - (T_t - T_{\text{Ref}}) \cdot \alpha \quad (1)$$

where

$\Delta_t$  = strain change at time t  
 $\epsilon_t$  = measured strain at time t  
 $T_t$  = temperature at time t  
 $T_{\text{Ref}}$  = reference temperature =  $75^\circ\text{F}$   
 $\alpha$  = CTE of material.

$\Delta_t$  was then plotted against time and an adjustment factor ( $\Delta$  adj) was added to every point. This had the effect of shifting the graph so that the final strain was zero, allowing the total strain change to be read easily. Figure 4 shows the adjusted  $\Delta_t$  versus time curve for graphite/epoxy (5208/T300). From this graph it is

evident that outgassing was completed in about 80~100 days. It is clear that outgassing was very rapid over the first 25 days, then slowed due to the low temperatures encountered (see Fig. 1). Outgassing then increased after 50 days as the sample temperature increased, and eventually no further measured dimensional change occurred after about 80~100 days exposure. Similar behaviour was exhibited by the other composite materials (ref. 1). The outgassing time required to reach an equilibrium state in space depends on such factors as the initial moisture concentration, the volatile content, laminate thickness, ambient temperature and constituent material diffusion properties.

## MOISTURE DESORPTION AND DIMENSIONAL CHANGES

As with many other published analyses, the moisture desorption can be estimated using Fick's law, given by (for example, ref. 2):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where

c = moisture concentration at x  
t = time  
x = thickness coordinate  
h = thickness  
D = diffusion coefficient in the x-direction

and the following boundary conditions apply:

$$c(x, 0) = c_0 \text{ (initial concentration)}$$

$$c(0, t) = c(h, t) = c_\infty \text{ (ambient concentration)}$$

$$c(x, \infty) = c_\infty$$

Noting that the total mass change over time is given by

$$M = \int_0^h c(x, t) dx \quad (3)$$

a solution was obtained to Eq. (2) in terms of the moisture content variation with time:

$$M(T, t) = M_0(1 - G) \quad (4)$$

where  $M_0$  = initial moisture content (wt %), assuming the final moisture content = 0 in space, and

$$G = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \left( \frac{1}{(2k+1)^2} \exp \left[ \frac{-(2k+1)^2 \pi^2 D t}{h^2} \right] \right)$$

$$\approx 1 - \exp \left[ -7.3 \left( \frac{D t}{h^2} \right)^{0.75} \right] \quad (5)$$

where

$$D = \text{diffusion coefficient} = D_0 \exp(-E_d/RT) \quad (\text{from ref. 3}) \quad (6)$$

R = gas constant  
T = absolute temperature  
E<sub>d</sub> = activation (diffusion) energy

For constant temperature, Shen and Springer (ref. 4) have shown that the diffusion coefficient (D) can be calculated knowing the moisture content at different times, i.e.,

$$D_{T=\text{const}} = \frac{\pi h^2}{16 M_0^2} \left[ \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right]^2 \quad (7)$$

where

$$M_0 = \text{initial moisture content at start of desorption test}$$

$$M_1, M_2 = \text{moisture contents at times } t_1 \text{ and } t_2, \text{ respectively}$$

Rather than measure moisture content during a test, one can employ strain data. Noting that

$$\epsilon = M \beta \quad (8)$$

where  $\beta$  = coefficient of moisture expansion (CME), then substituting into Eq. (4) yields:

$$\epsilon(T, t) = \epsilon_0(1 - G) \quad (9)$$

Substituting Eq. (8) into Eq. (7) also gives

$$D_{T=\text{const}} = \frac{\pi h^2}{16 \epsilon_0^2} \left[ \frac{\epsilon_2 - \epsilon_1}{\sqrt{t_2} - \sqrt{t_1}} \right]^2 \quad (10)$$

## PREDICTING MOISTURE OUTGASSING FOR VARYING TEMPERATURES

To develop a model for predicting outgassing of materials in space, it is necessary to take temperature into account. However, Fick's law as previously described applies to constant temperature, constant

humidity environments. In space, the humidity level (i.e., vacuum) is constant. It is possible to determine the diffusion coefficient by performing outgassing tests at different temperatures ( $T_1$  and  $T_2$ ). Using the Arrhenius relation given by Eq. (6), one obtains the following two equations:

$$\ln(D_1) = \ln(D_0) - \frac{E^*}{T_1} \quad (11)$$

$$\ln(D_2) = \ln(D_0) - \frac{E^*}{T_2} \quad (12)$$

where  $E^* = E_a/R$ . Solving for  $E^*$  and  $D_0$  yields:

$$E^* = \frac{[\ln(D_2) - \ln(D_1)]}{\left[\frac{1}{T_1} - \frac{1}{T_2}\right]} \quad (13)$$

$$D_0 = \exp \left[ \left( \frac{\ln(D_2) - \ln(D_1)}{1 - \frac{T_1}{T_2}} \right) + \ln(D_1) \right] \quad (14)$$

Substituting back into Eq. (6) gives:

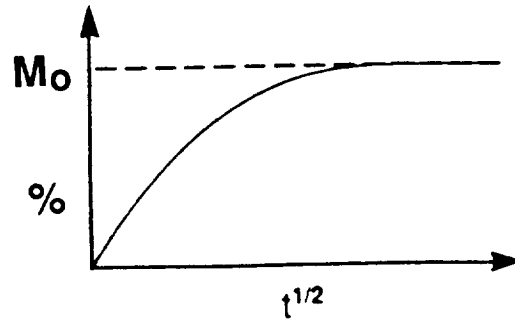
$$D(T) = \exp \left[ \frac{\ln(D_2) - \ln(D_1)}{1 - \frac{T_1}{T_2}} + \ln(D_1) \right] \cdot \exp - \left[ \frac{(\ln(D_2) - \ln(D_1))}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \cdot T} \right] \quad (15)$$

This equation can be used to calculate the diffusion coefficient at any temperature,  $T$ , as long as the diffusion coefficients  $D_1$  and  $D_2$  at temperatures  $T_1$  and  $T_2$  are known. All of the above temperatures must be absolute (K).

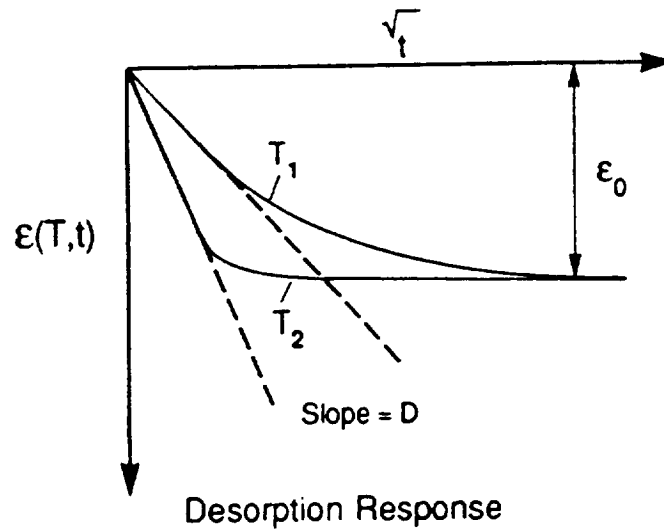
## APPLICATION TO LDEF SAMPLES

### Experimental Input

1. Control samples were subjected to vacuum outgassing at elevated temperature to obtain their “dry weight” values.
2. For given temperature ( $T$ ) and % RH, record moisture uptake (%) for given material from its “dry” state as a function of time ( $t$ ) to saturation.



3. Measure sample strain ( $\epsilon$ ) as a function of time ( $t$ ) in vacuum for a given temperature ( $T_1$ ). Repeat experiment at another temperature ( $T_2$ ). Both experiments employ samples having the same  $M_0$ .



#### Analytical Procedure

1. Using the  $\epsilon(T, t)$  curves, calculate the initial slope from Eq. (10) to obtain  $D_1(T_1)$  and  $D_2(T_2)$ .
2. Determine  $D(T)$  from Eq. (15) based on  $D_1(T_1)$ ,  $D_2(T_2)$ ,  $T_1$  and  $T_2$ .
3. Using the LDEF temperature/time profile obtained in-orbit (see Fig. 1), calculate the dynamic strain change  $\epsilon(t)$  for given time steps ( $\Delta t$ ), using the above  $D(T)$  equation evaluated at the appropriate temperature. The  $\epsilon(t)$  function is given by

$$\epsilon_t = \epsilon_{t-1} - \epsilon_{t-1} \left( 1 - \exp \left[ -7.3 \left( \frac{D(T_t) \cdot \Delta t}{h^2} \right)^{.75} \right] \right) \quad (16)$$

where  $T_t$  = average temperature over  $\Delta t$ , assuming  $\epsilon_0$  is known at  $t = 0$  from the outgassing test. By using this equation at every time step over the temperature history, it is possible to calculate the strain change of the sample due to outgassing, taking into account temperature effects.

## COMPARISON WITH LDEF DATA

Before starting the outgassing tests, the samples were completely dried out under vacuum at elevated temperature. The dry weight and length of each sample were measured and recorded. The samples were then placed in a hygroscopic chamber to absorb moisture. Each sample was left until it absorbed the same amount of moisture as was outgassed from the equivalent LDEF sample. This value was determined by measuring the CME ( $\beta$ ) of each material and then dividing the strain change measured on-orbit by  $\beta$  to give the total change in moisture content. Typical moisture absorption curves for three polymer matrix composites flown on LDEF are shown in Fig. 5. At this point in time, results will be presented only for one graphite/epoxy system — T300/5208, having the form of a 4 ply, 90° laminate [90]<sub>4</sub>. The ground-based simulator tests were conducted on two tubes: a control sample (5T5) that had remained under ambient laboratory conditions since the manufacture of the LDEF flight specimens and a flight sample (2T13). Both 22°C and 50°C outgassing tests were performed on the control and flight samples. From CME calculations, it was determined that the flight data from sample 3T6 (Fig. 3) indicated a total moisture content change of .50%. Therefore, for all the tests on the T300/5208 [90]<sub>4</sub> samples, a moisture content as close as possible to this value was used, as summarized in Table I. The initial straight-line portions of the tests are plotted in Figs. 6 to 9 and a comparison of the  $\beta$  and D results presented in Table I. The nonlinearity at the beginning of these curves is due to temperature corrections. For about the first hour the samples had not reached equilibrium. On average, the 22°C and 50°C tests took about 13 days and 6 days to complete, respectively. Note that the diffusion coefficients of the control and flight samples agree quite well, indicating no significant changes occurred after 69 months of space exposure.

Using the temperature history of the flight sample (3T6) shown in Fig. 1, it was possible to predict its outgassing behaviour based on the results in Table I and Eqs. (15) and (16). A comparison with the flight data is given in Fig. 10. It is obvious that the predicted values do not fit the actual results very closely. However, if the predicted diffusion coefficient is reduced to 13.4% of its measured value, the predicted response is extremely close to the actual data as shown in Fig. 11. This indicates that the model itself is correct. The discrepancies may be due to differences between the test conditions and the space environment, such as a higher pressure or the presence of surface contaminants. It is also important to note that there is a large variability in the thickness and uniformity of the samples. Manufacturing variations may have caused the different diffusion coefficients of the samples. Ideally, it would be best to measure D(T) from sample 3T6, and see how well this prediction fits the flight data. Unfortunately, it was not yet possible to perform this test, although this will be done in the near future.

## ACKNOWLEDGEMENTS

This research was sponsored by the Canadian Space Agency (CSA) under contract 025SR.9F009-1-1435, and two Ontario Centres of Excellence: the Institute for Space and Terrestrial Science and the Ontario Centre for Materials Research. Special thanks are extended to Dr. D. G. Zimcik of the CSA for his continued support of our work.

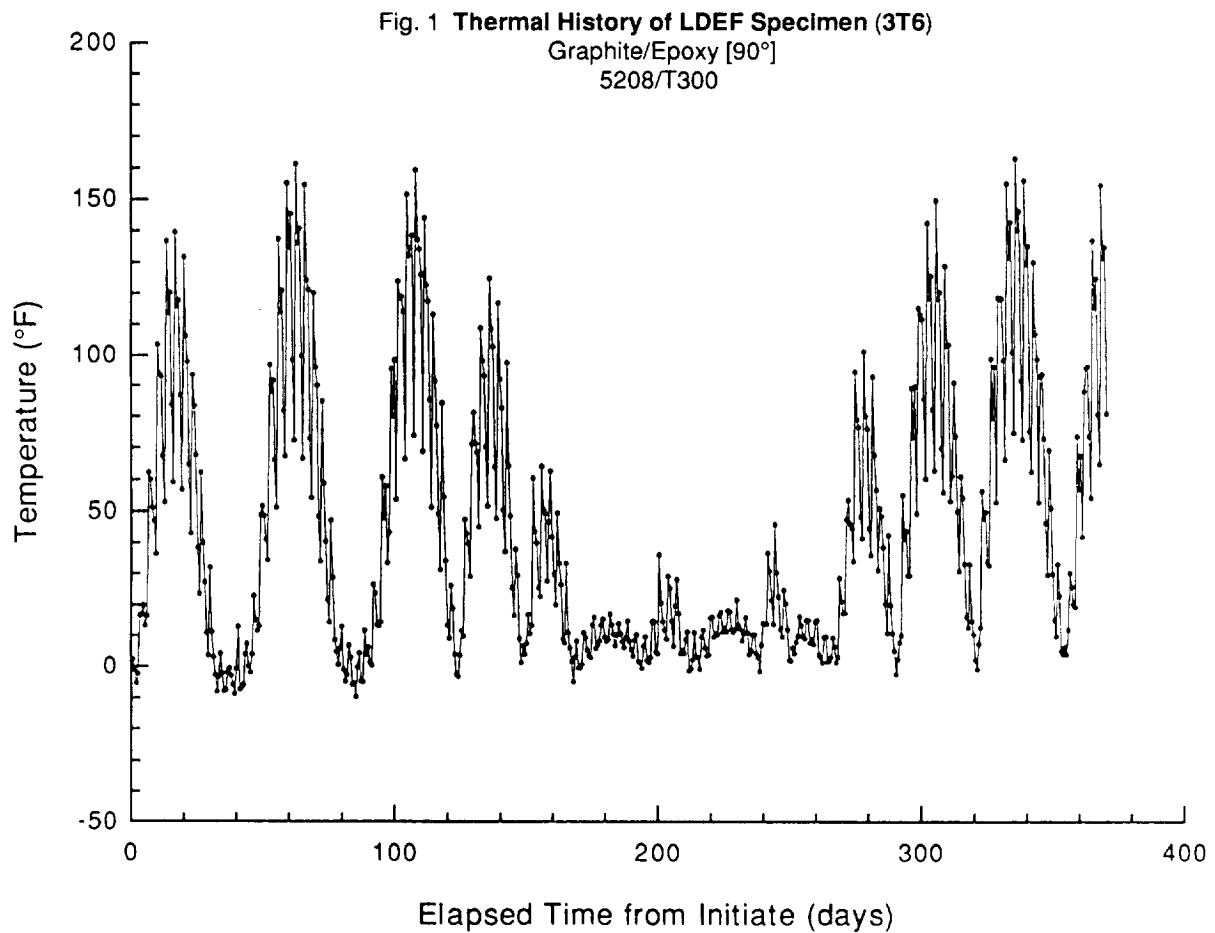
## REFERENCES

1. Tennyson, R. C.: Composite Materials in Space — Results from the LDEF Satellite. *J. Canadian Aeronautics and Space Institute*, vol. 37, no. 3, Sept. 1991.
2. Crank, J.; and Park, G. S.: *Diffusion in Polymers*. Academic Press, London, 1968.

3. Whitney, J. M.; and Browning, C. E.: Some Anomalies Associated with Moisture Diffusion in Epoxy Matrix Composite Materials. *Advanced Composite Materials - Environmental Effects*, ASTM STP 658, J. R. Vinson, ed.; American Society for Testing and Materials, 1978.
4. Shen, Chi-Hung.; and Springer, George S.: Moisture Absorption and Desorption of Composite Materials. *J. Composite Materials*, vol. 10, Jan. 1976.

Table I. Summary of Simulator Outgassing Test Results for Graphite/Epoxy (T300/5208) Tube Laminates [90]<sub>4</sub>

Sample No.	Type	Temp [°C]	M <sub>i</sub> [%]	Δε [με]	CME [με/%]	D [mm <sup>2</sup> /h]
5T5	Control	22	.49	-1200	-2449	.0001
5T5	Control	50	.55	-1939	-3525	.00047
2T13	Flight	22	.505	-1212	-2400	.00013
2T13	Flight	50	.632	-1517	-2400	.00078



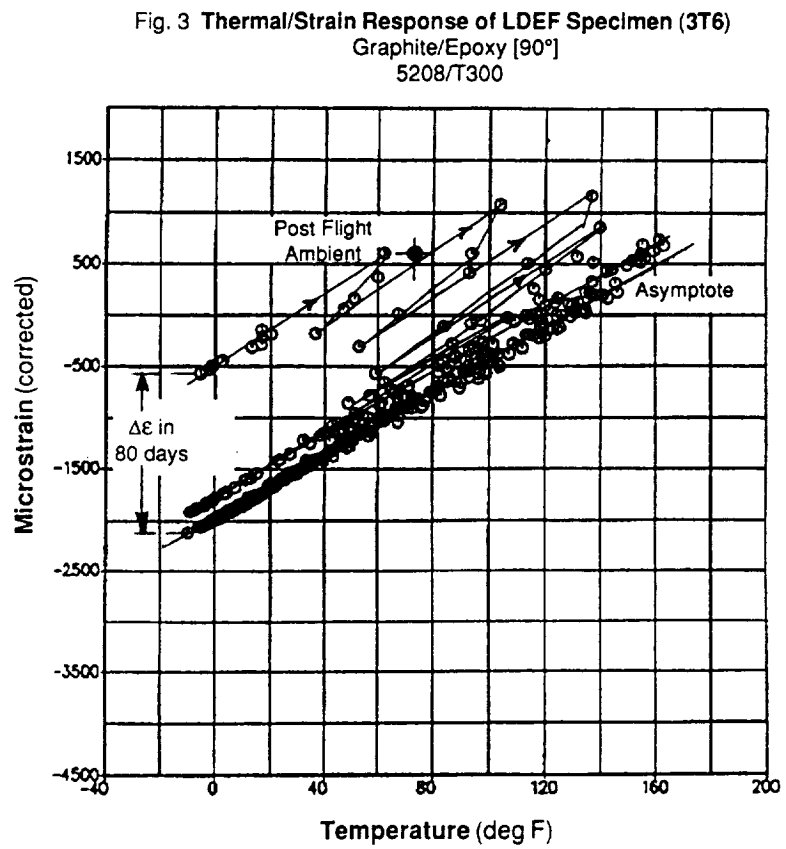
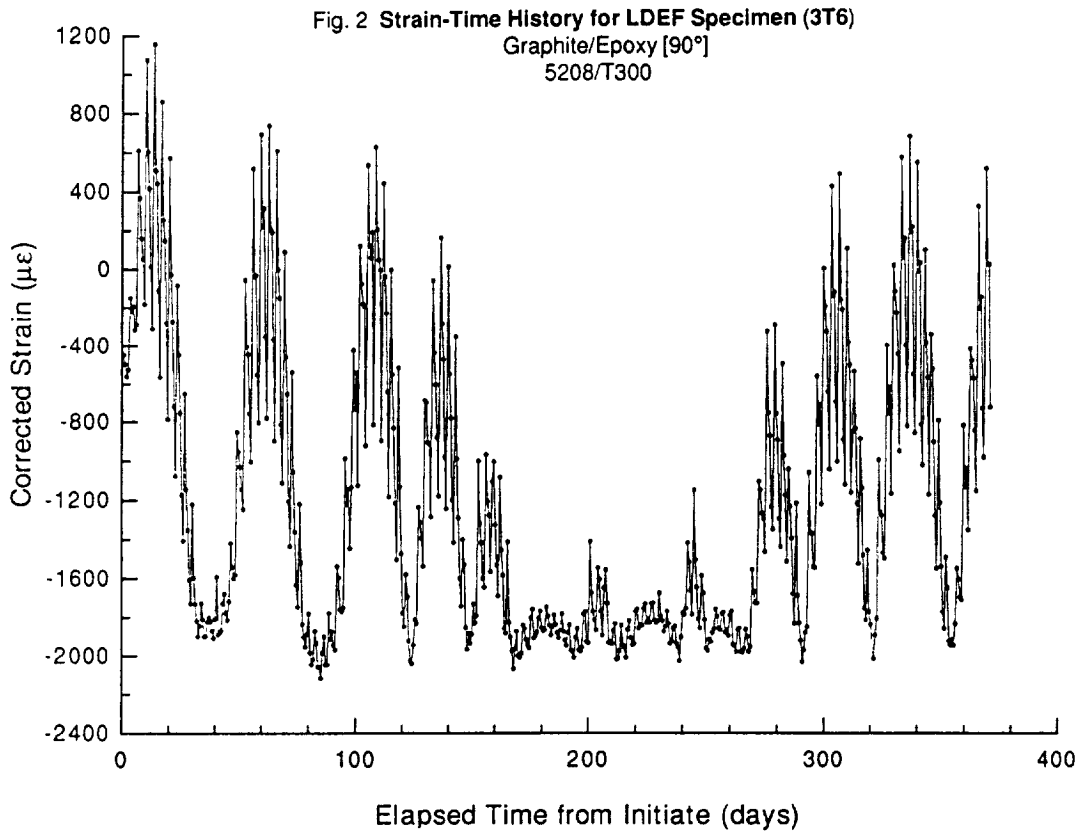




Fig. 4 Plot of  $\Delta$  Strain vs Time in Orbit  
for LDEF Specimen (3T6)

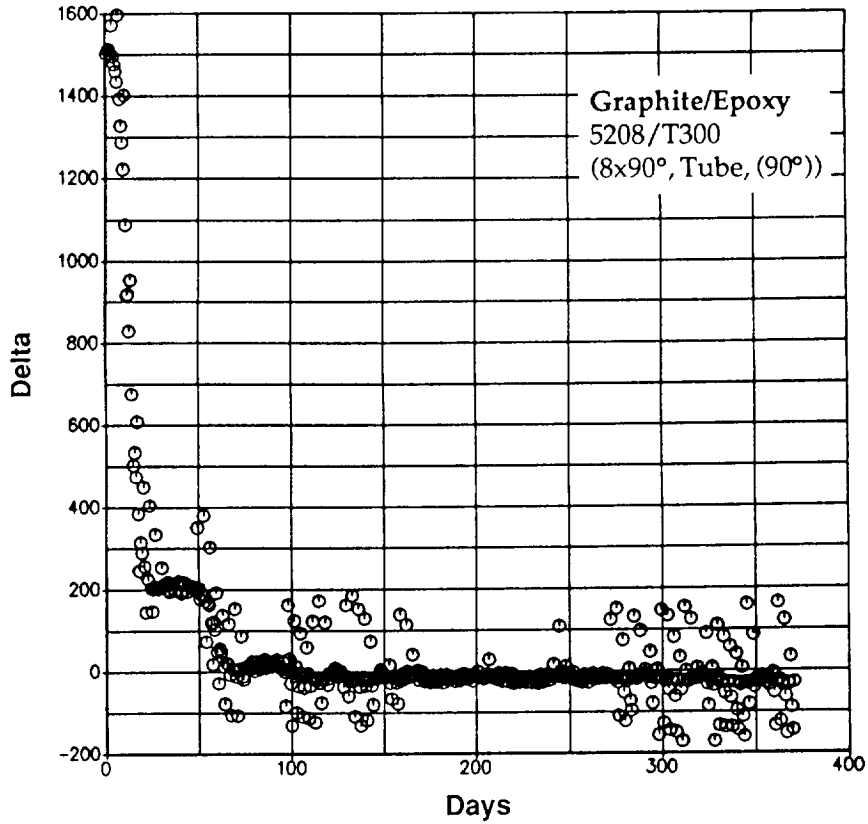


Fig. 5 LDEF Control Moisture Absorption Test  
4 Ply 90 deg — 50 C — 75% RH

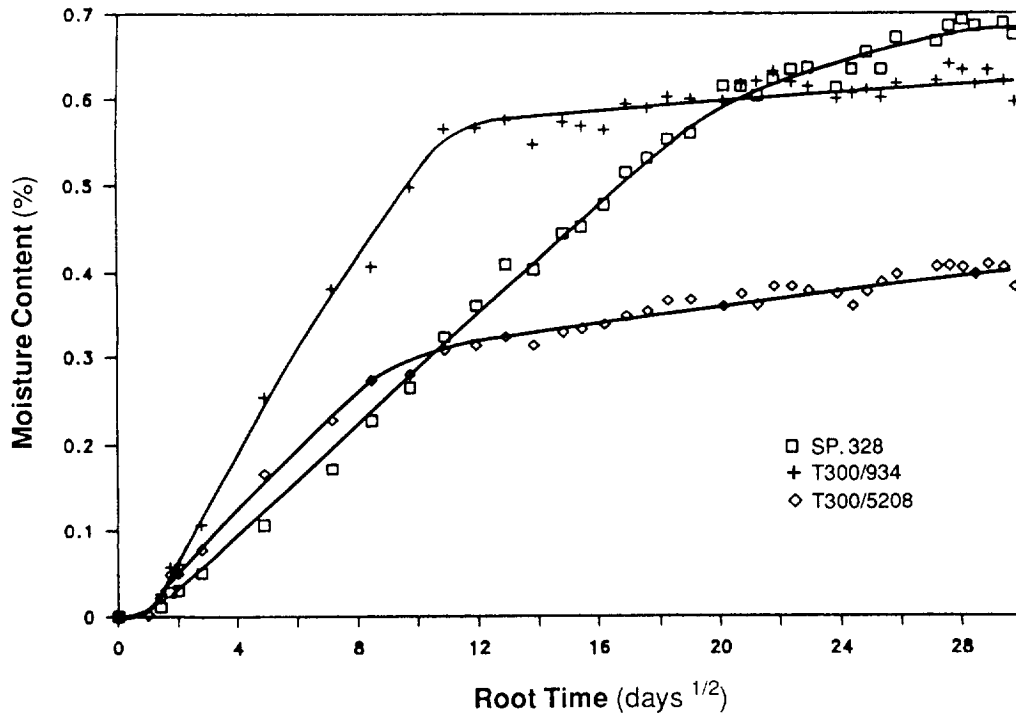


Fig. 6 Outgassing Test on Control Specimen (5T5) @ 22°C  
Graphite/Epoxy [90°]  
5208/T300

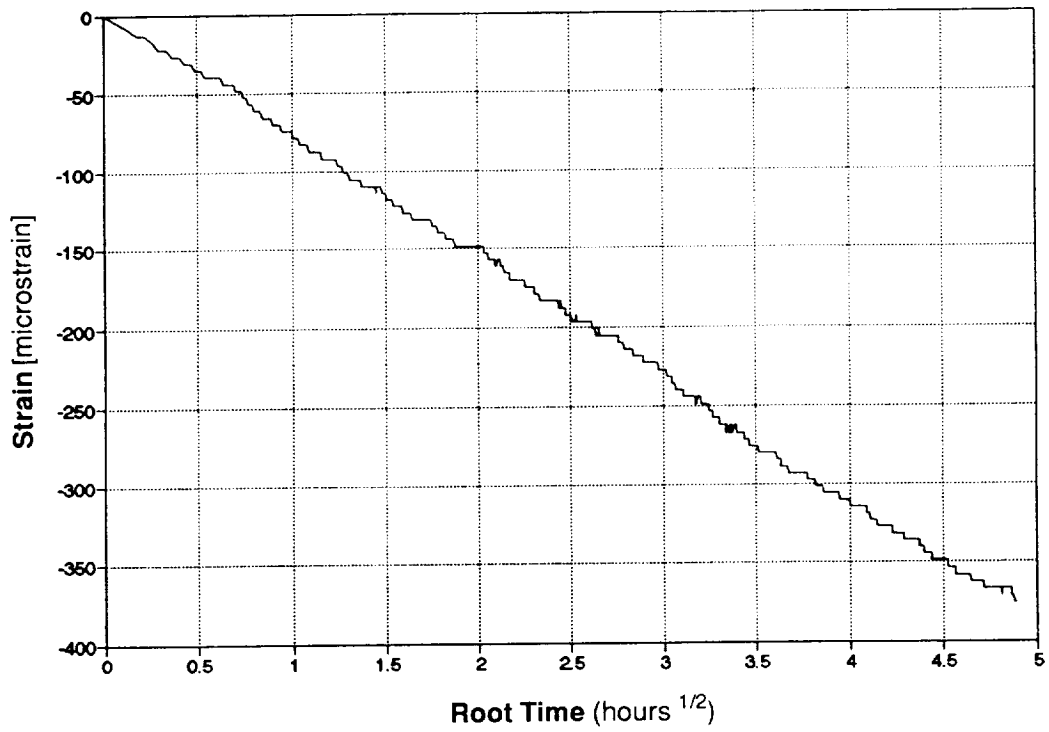


Fig. 7 Outgassing Test on Control Specimen (5T5) @ 55°C  
Graphite/Epoxy [90°]  
5208/T300

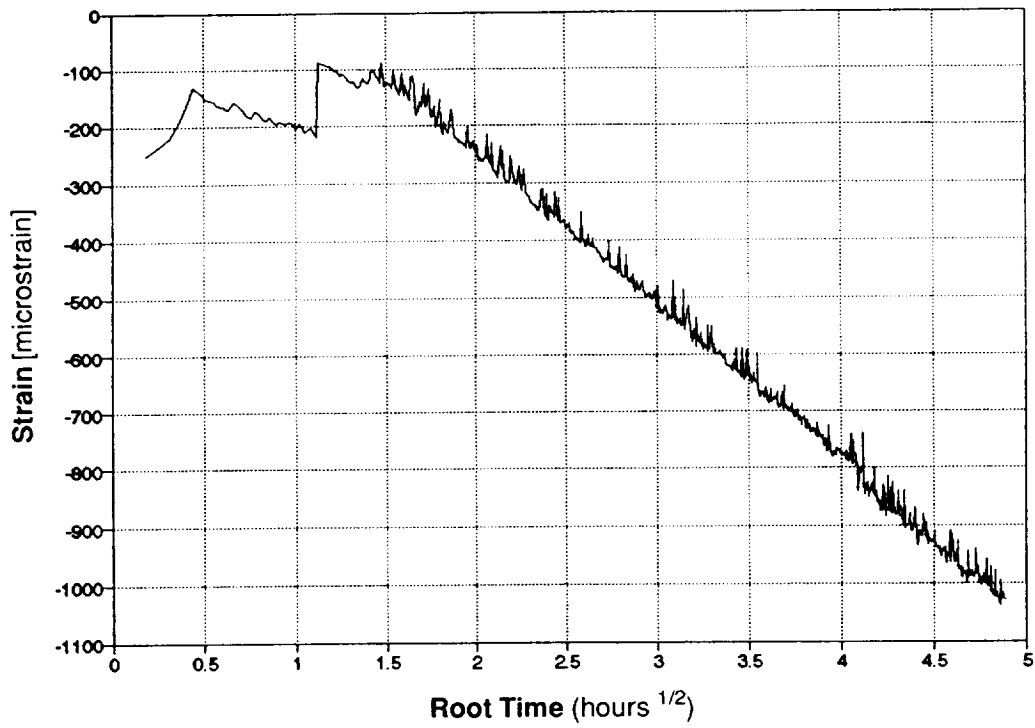


Fig. 8 Outgassing Test on LDEF Flight Specimen (2T13) @ 22°C  
Graphite/Epoxy [90°]  
5208/T300

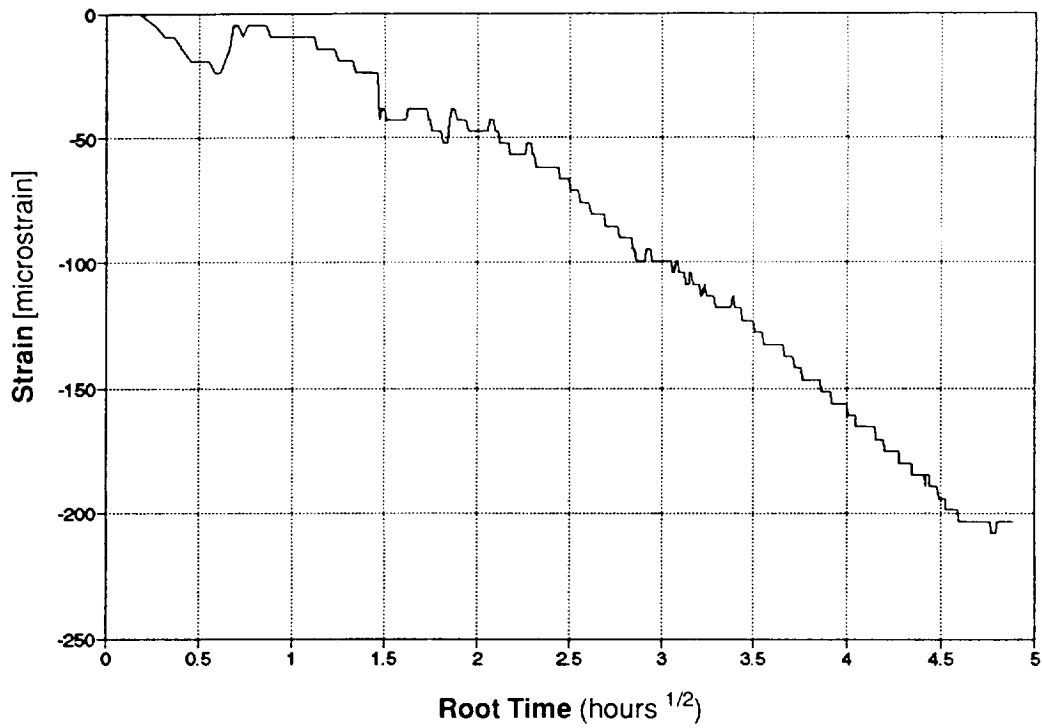


Fig. 9 Outgassing Test on LDEF Flight Specimen (2T13) @ 50°C  
Graphite/Epoxy [90°]  
5208/T300

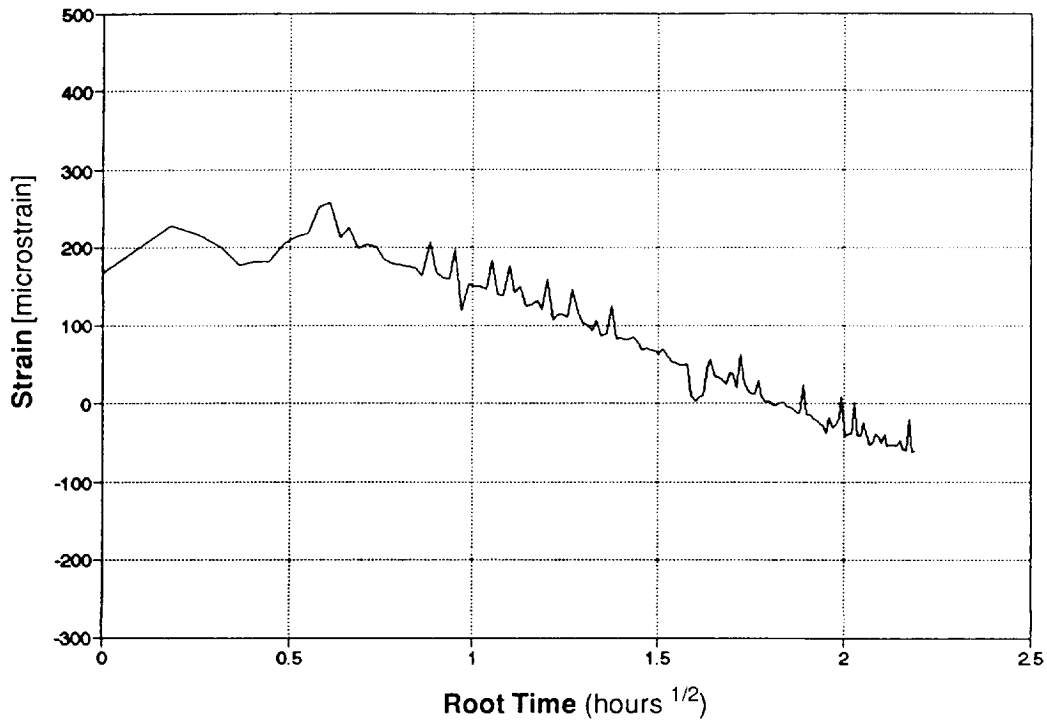


Fig. 10 Comparison of Predicted Strain/Time Response in Space  
with LDEF Flight Specimen  
Graphite/Epoxy [90°]  
5208/T300

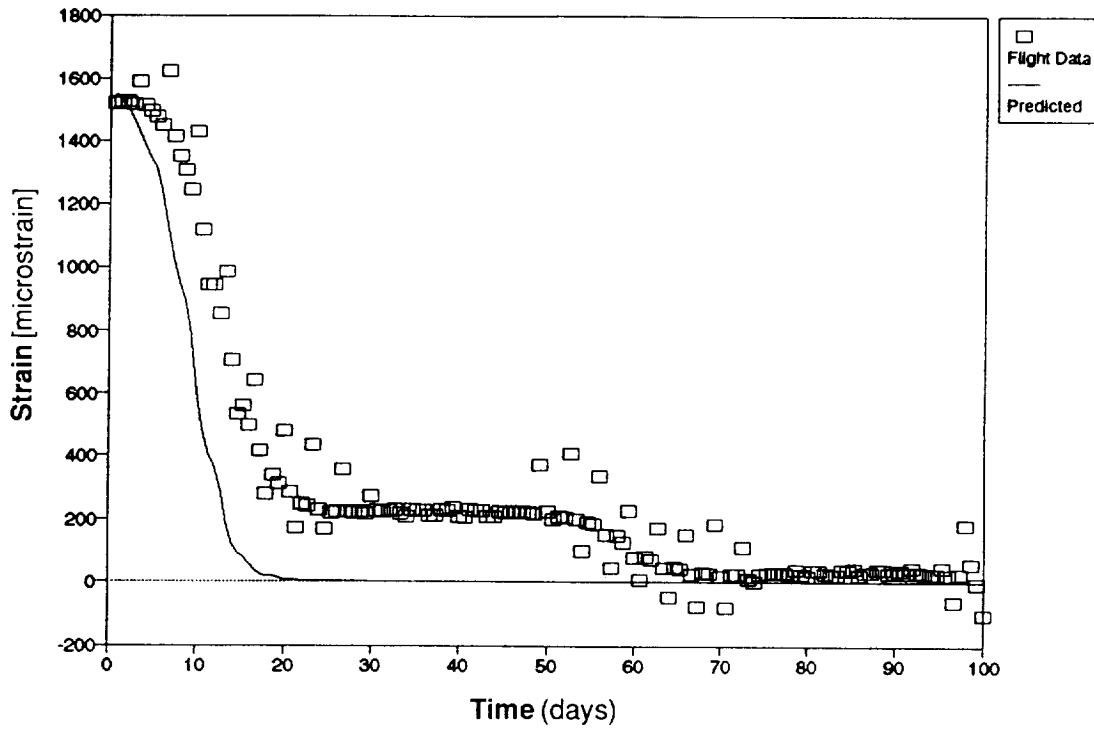


Fig. 11 Comparison of Corrected Prediction of Strain/Time Response in Space  
with LDEF Flight Specimen ( $D^* = 0.134D$ )  
Graphite/Epoxy [90°]  
5208/T300

