N94- 31043

EFFECTS OF ORBITAL EXPOSURE ON RTV DURING THE LDEF MISSION

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ABSTRACT

Thermomechanical analysis (TMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were performed on samples of RTV 511 exposed on the Long Duration Exposure Facility (LDEF) mission for 6 years in orbit and unexposed RTV 511 control samples. Slices 20- to 400-microns thick were removed from the exposed surface down to a depth of 1,500 microns through the 3-mm thick samples. The TMA and DSC results, which arise from the entire slice and not just its surface, showed no significant differences between the LDEF exposed and the control samples. TMA scans were run from ambient to 500 °C; results were compared by a tabulation of the onset temperatures for flow. DSC scans were run from ambient to 600 °C; no endotherms or exotherms occurred over the range observed. What appear to be glass transition temperatures were compared for the samples as a function of section depth within the sample and between the exposed and control samples. The TGA scans from 25 to 900 °C, which arise from the surface of the sample initially, showed a slight increase in the top most 105-micron slice (the exposed, discolored side) in the weight loss at 600 °C in oxygen. This weight loss dropped to bulk values at the next slice below the top section, a mean depth of 258 microns. The control sample also showed an increase in weight loss as the top surface was approached, but the 600 °C weight losses were very inconsistent. The LDEF RTV sample appears to be mechanically undamaged, with a surface layer which oxidizes slightly faster as a result of orbital exposure.

INTRODUCTION

Early results of LDEF exposure on polymeric materials showed varying degrees of degradation, discoloration, and weight loss (refs. 1–4). Young and Slemp (ref. 5) reported no differences in DSC thermograms of FEP Teflon between exposed and control samples. They also reported no difference in TGA curves for Kapton films between the exposed and control samples. Brower, Holla, and Bauer (ref. 6) reported some difference among sections taken through the thickness of exposed Halar samples. The top 50 microns of the exposed Halar sample exhibited a significantly higher weight loss in oxygen than the bulk. Such a top surface effect was not observed in the Halar control sample. Brower et al. (ref. 6) found no difference between the control and exposed samples of Halar in DSC and TMA, in agreement with Young and Slemp's DSC and TGA results on Teflon and Kapton. Possibly, the surface effect in TGA reported by Brower et al. (ref. 6) on Halar was detectable due to the sectioning through the thickness of the film, which concentrated the surface damaged layer with respect to the bulk. Hurley and Jones (ref. 7) reported reflectance changes as a result of LDEF exposure on a number of polymer films. They also observed RTV 560 + 12 percent graphite adhesive bonds to fail in all cases.

RTV 511 in 3-mm thick film form was studied in the work reported here. The thrust of this investigation was to determine the depth profile of the LDEF orbital damage to the RTV 511 samples. TMA, TGA, and DSC were performed on slices of the RTV exposed and control samples to assess the depth of damage (if any) due to orbital exposure during the LDEF mission.

EXPERIMENTAL PROCEDURE

The procedure for preparing samples from the pieces of RTV 511 exposed and control samples was the same as that for the Halar samples as described previously (ref. 6). The measured areas of the pieces and their densities calculated from their measured weights and thicknesses are given in Table 1. From the measured weight of each microtomed slice from the given RTV piece, the measured density of the RTV piece, and the measured cross-sectional area of the slice, the mean thickness of each slice was calculated and is given in Table 1. This calculated thickness value was used instead of a measured thickness, due to the irregular thickness of each microtomed slice. The mean depth of each slice is given by the total thicknesses of the previous slices plus the half thickness of the present slice.

The test conditions during the various thermal analyses are given in Table 2. The heating rates were all the same, whereas the temperature range varied with the technique. TGA and DSC could be performed well above the glass transition temperature, but TMA could not. The TGA atmosphere was oxygen to measure the relative oxidation rates of the exposed and control RTV 511 slices.

RESULTS AND DISCUSSION

As opposed to the previous results with Halar (ref. 6), the density of the exposed RTV 511 was about 6 percent higher than the RTV 511 control (Table 1). If outgassing occurred during the LDEF exposure, the reverse should occur, unless shrinkage also occurred and volume contraction more than offset the mass loss.

The results are presented for each thermal analysis technique by showing typical thermograms in the figures included here and tables of peak temperatures or baseline shifts (weight changes and penetrations). The information from the TMA, DSC, and TGA thermograms of all the slices of the exposed and control RTV 511 is given in Tables 3, 4, and 5, respectively.

The penetration versus temperature TMA output plot is shown in Figure 1 for a section of the RTV 511 control sample. This plot was typical of all the TMA plots for both the exposed and control slices, showing thermal expansion upon heating giving way to contraction due to flow at the high temperatures. The temperature for the onset of flow is calculated by the method of intersecting tangents by the TMA software, and is shown in Figure 1. The onset temperatures are listed versus mean section depth in Table 3. Although visible discoloration was present in the top slice of the exposed RTV 511 piece, the onset temperatures showed no significant variation with slice depth in either the exposed or the control slices, Table 3. The average onset temperature for flow for the exposed slices of 401 °C is slightly higher than the average of the control slices of 393 °C. This agrees with the slightly higher density of the exposed piece.

A typical DSC thermogram is shown in Figure 2 for the top-most slice of the LDEF exposed RTV 511 sample. An apparent glass transition temperature onset calculated by the DSC software is shown at 309 °C. This shift was observable only after expanding the ordinate sensitivity such that significant noise is evident. Other slices of the exposed and control samples either exhibited similar shifts to that shown in Figure 2, or exhibited no shifts or peaks at all over the 25 to 600 °C temperature range scanned. The transition temperatures reported in Table 4 for all the DSC scans of all the slices are too few to identify any effect of slice depth or any significant difference between the exposed and control slices.

Figures 3 and 4 are typical TGA output plots for weight loss while heating in oxygen for the top-most LDEF exposed RTV sample slice and a slice 597-microns deep, respectively. Cumulative weight losses at 420 and 600 °C are given in Table 5. As can be seen by comparing Figures 3 and 4, the weight loss at 600 °C is 54 percent of the top-most exposed RTV slice, and only 40 percent for the 597-micron deep slice of the RTV 511 exposed sample. As shown in Table 5, the LDEF exposed RTV shows an increase in weight loss in the top slice, 54 percent, as compared to the average weight loss of 46 percent for all the slices. The control sample slices showed irregular TGA weight losses, Table 5. The top slice of the control sample, three other control slices, and one exposed slice showed anomalous step function drops in weight at around 525 °C, preventing a measurement of the 600 °C weight loss. Either an unexplainable TGA system error occurred, or these samples oxidized completely at 525 °C.

The TMA and DSC techniques measure the response of the whole sample section which is placed in the analyzer. Near surface effects that are truncated in several atom layers would not be resolvable in the roughly 50- to 200-micron thick sections. The TGA, however, measures the oxidation rate at the surface of the section placed in the analyzer. The top-most slice of the exposed RTV 511 had as its top surface the actual discolored top surface given the orbital exposure. The other side of the section was produced by the microtome. Thus, the TGA is the most surface sensitive of the three techniques employed, and it is the only technique to sense damage from orbital exposure in the RTV 511. The measured difference between top and bulk slices for the RTV 511 in TGA is much less pronounced than that observed for the Halar slices in TGA (ref. 6). However, due to the uncontrolled section depth produced by the microtome, the top Halar slice was 12-microns thick, while the top RTV 511 slice was 210-microns thick. The thicker RTV 511 slice would tend to mask surface damage detected by TGA.

CONCLUSIONS

In general, little difference between the LDEF exposed and control samples of RTV 511 was detected by thermal analysis. Some subtle differences are listed below.

1. A small difference between the top section of the LDEF exposed sample as compared to the lower sections appeared in TGA. The top section lost 54 percent of its weight by 600 °C, while the average section loss was 46 percent.

2. In TMA, the exposed sections had slightly higher flow temperatures than the control sections. There appeared to be no surface effect in either sample.

3. In DSC, no endotherms or exotherms were observed in either the sections of the exposed or the control samples. A glass transition like shift occurred in about half of the sections of each sample. There were no significant differences among the shifts in the samples.

4. The density of the RTV 511 exposed sample is 6 percent higher than the control sample.

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Table 1. Weight and density measurements for cut sections of RTV 511 LDEF and control samples. Thicknesses are calculated from the measured weight, density, and areas of the slices. The mean depth is reported at half the section thickness.

RTV in TGA

Control Piece No. 1

Area = 0.7971 cm^2
Density = 1.2646 gr/cm^3

Sample II	Wt (gr)	Thick (μm)	Mean Depth
R1C1	0.0020	19.8	9.9
R1C2	0.0023	22.8	32.3
R1C3	0.0056	55.6	70.4
R1C4	0.0051	50.6	123.5
R1C5	0.0125	124.0	210.8
R1C6	0.0016	15.9	280.8
R1C7	0.0027	26.8	302.1
R1C8	0.0286	283.7	457.3
R1C9	0.0345	342.3	770.3
R1C10	0.0283	280.8	1,081.8
51C11	0.0029	28.8	1,236.6
51C12	0.0392	388.9	1,445.4
Cutoff	0.4454	4,418.6	
Total	0.6107	6,058.5	
Original	0.6120	6,071	

RTV in TGA

Exposed Piece No. 2

Area = 0.6032 cm^2
Density = 1.3356 gr/cm^3

Sample ID	Wt (gr)	Thick (μm)	Mean Depth
R2C1	0.0169	209.8	104.9
R2C2	0.0077	95.6	257.6
R2C3	0.0149	184.9	397.8
R2C3A	0.0149	184.9	397.8
R2C4	0.0064	79.4	530.0
R2C5	0.0044	54.6	597.0
R2C6	0.0171	212.3	730.5
Cutoff	0.4135	5,132.6	
Total	0.4809	5,969.2	
Original	0.4931	6,121	

Table 2. Test conditions for RTV 511 samples for thermal analysis.

Technique	Test Atmosphere	Heating Rate (°C/min)	Temperature Range (°C)
TMA	Flowing Ar	10	25 to 500
TGA	Flowing O_2	10	25 to 900
DSC	Flowing Ar	10	25 to 600

Table 3. Thermomechanical analysis results on RTV 511.
Onset temperatures for flow over the range 320 to 430 °C.

Sample Number		Depth (microns)	Onset Temperature (°C)
Exposed	R2C1	105 (top)	402
	R2C2	258	394
	R2C3	398	402
	R2C4	530	403
	R2C6	730	403
			Avg = 401
Control	R1C5A	210	399
	R1C8	457	396
	R1C9B	770	398
	R1C12	1,445	397
			Avg = 393

Table 4. Differential scanning calorimetry results for RTV 511.
Glass transition temperatures over the range 3,275 to 350 °C.

Sample Number		Depth (microns)	Glass Transition Temperature (°C)	
			Onset	Midpoint
Exposed	R2C1	105 (top)	309	283
	R2C2	258	286	288
	R2C3	398	None	
	R2C4	530	None	
	R2C6	730	None	
Control	R1C3	70	None	
	R1C4	124	None	
	R1C5	211	330	330
	R1C6	281	293	305

Table 5. Thermogravimetric analysis results on RTV 511.

Sample Number		Mean Depth (microns)	Percent Weight Loss 25 to 420 °C	Percent Weight Loss 25 to 600 °C
Exposed	R2C1	105 (top)	5	54
	R2C2	258	3	44
	R2C3A	398	3	50
	R2C4	530	4	44
	R2C5	597	1	40
	R2C6	730	2	46
				Avg = 46
Control	R1C1	9.9 (top)	2	–
	R1C2	31.2	2	53
	R1C4A	123	2	32
	R1C6	280	2	30
	R1C8A	457	5	49
	R1C10	1,081	5	44
	R1C12	1,445	6	57
				Avg = 42

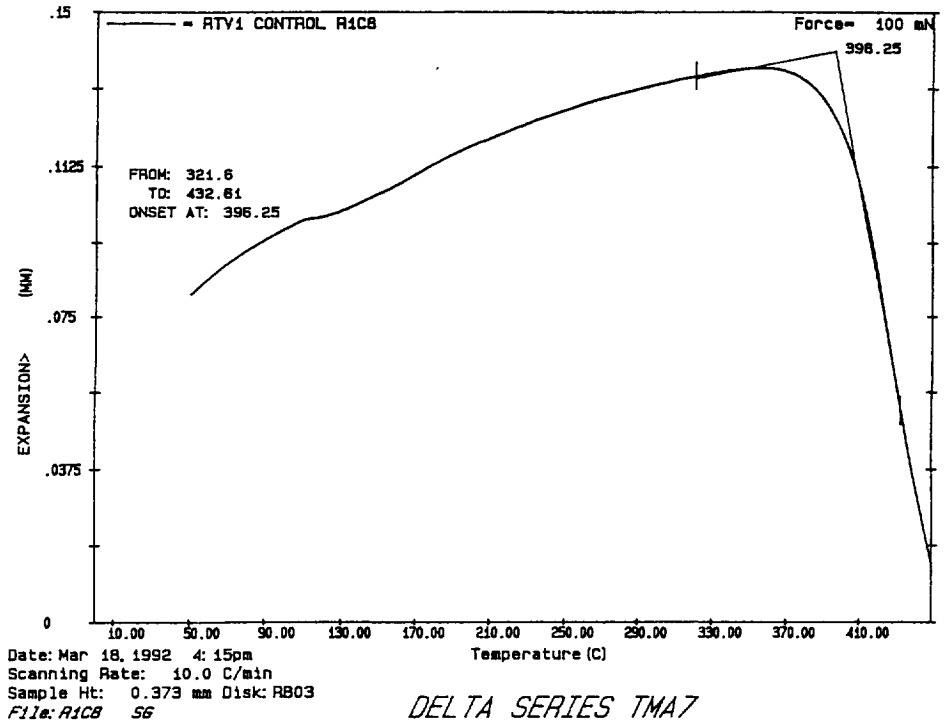

Figure 1. Typical TMA plot for a section of the RTV 511 LDEF sample showing the determination of onset temperature by the intersection of tangents.

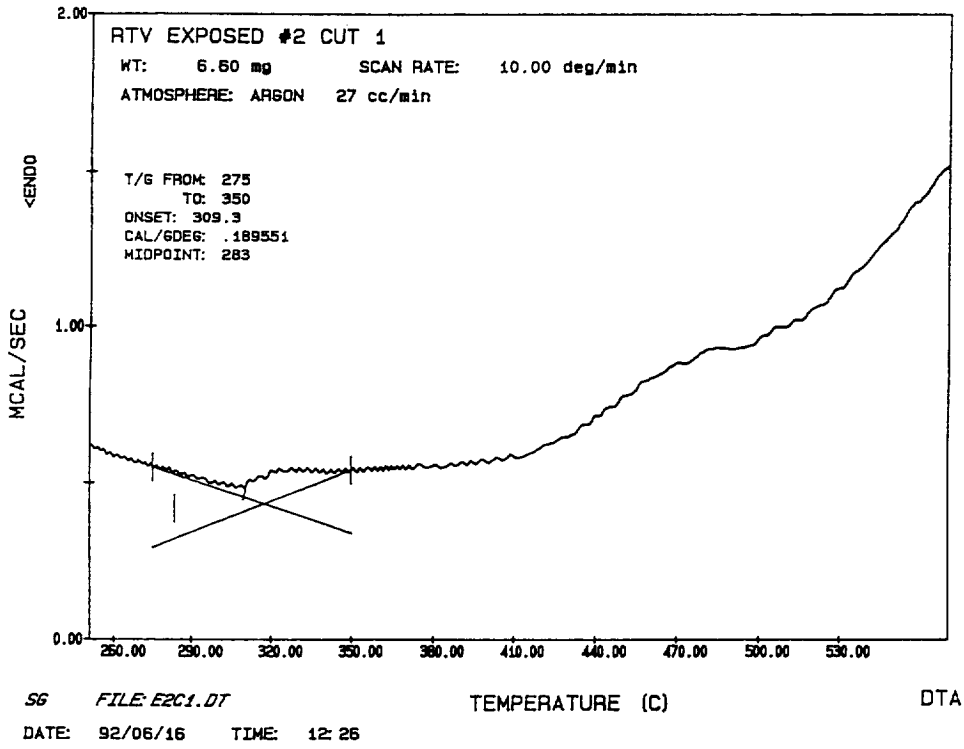

Figure 2. DSC plot for the top section of the RTV 511 LDEF exposed sample showing an apparent glass transition temperature with an onset of 309 °C and a midpoint of 283 °C.

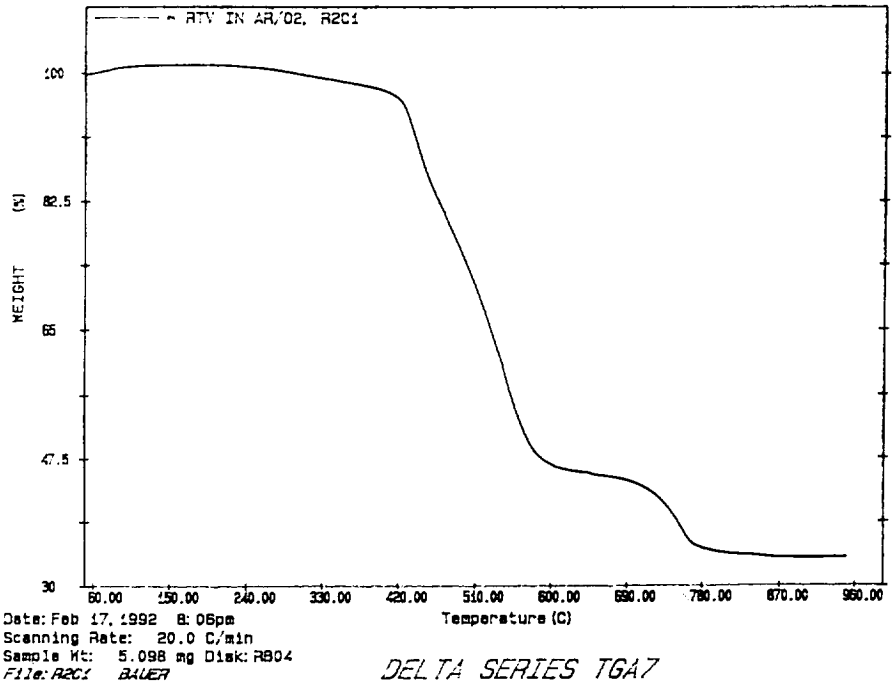

Figure 3. TGA plot for the top section of the RTV 511 LDEF exposed sample showing a 54-percent weight loss by 600 °C.

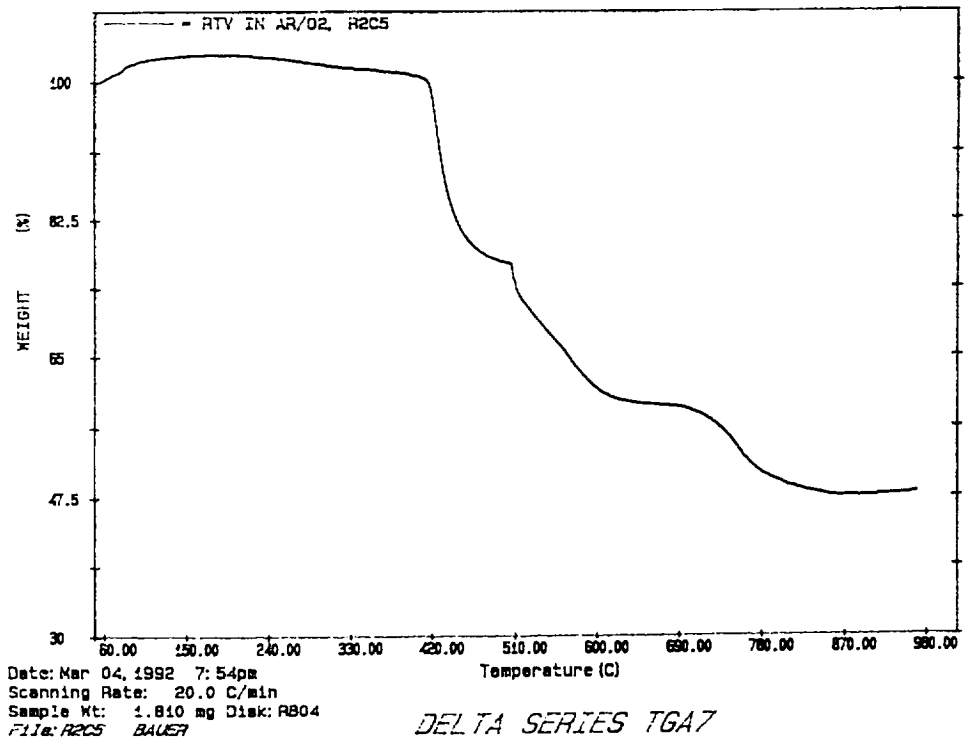

Figure 4. TGA plot for the section of the RTV 511 exposed at a mean depth of 597 microns showing a 40-percent weight loss by 600 °C.