EFFECTS OF ORBITAL EXPOSURE ON HALAR 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 Halar exposed on the LDEF Mission for 6 years in orbit and unexposed Halar control samples. Sections 10-100 microns thick were removed from the exposed surface down to a depth of 1,000 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 differences between the LDEF and the control samples. TMA scans were run from ambient to 300 C; results were compared by a tabulation of the glass transition temperatures. DSC scans were run from ambient to 700 C; the enthalpy of melting was compared for the samples as a function of section depth within the sample. The TGA results, which arise from the surface of the sample initially, showed a sharp increase in the topmost 50 micron section (the exposed, discolored side) in the weight loss of 170 C in oxygen. This weight loss dropped to bulk values in the range of depth of 50-200 microns. The control sample showed only a slight increase in weight loss as the top surface was approached. The LDEF Halar sample appears to be mechanically undamaged, with a surface layer which oxidizes faster as a result of orbital exposure.

INTRODUCTION

The first reports of the effects of prolonged orbital exposure by Whitaker (1) showed some weight loss data for a range of solar array materials. Tennyson et al (2) reported dimensional changes and changes in thermal expansion coefficients for a range of composite samples. B. J. Dunbar (3) reported on the general effects encountered by the LDEF samples - atomic oxygen, particle strikes, and UV exposure. Some of the Mylar 5 mil coatings were completely gone; this result gives added interest to the Halar and RTV studies of this investigation. Steckel and Le (4) were the first to report degradation as a function of depth in the sample, although their results were calculated from bulk weight loss data. The thrust of this investigation was to determine the depth profile of the damage to the Halar and RTV LDEF samples. Results for the Halar samples are reported here. Thermomechanical Analysis (TMA), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) were employed to assess the effects of orbital exposure during the LDEF Mission.

EXPERIMENTAL PROCEDURE

The procedure for preparing samples from the piece of LDEF exposed Halar and the Halar control is shown schematically in Figure 1. First, 1 cm x 1/4 cm pieces were cut from the full Halar pieces. These pieces were best suited for sectioning in the Edmund Model DK-10 microtome. Although the nominal minimum section thickness was 10 microns for the micrometer, the typical section was 50 microns thick. Wide variations in section thicknesses between sections and within a section occurred as shown in Tables 3-8,* due to bending of the microtome blade, play in the micrometer drive, and the inherent toughness of the Halar. Table 1 shows the dimensions of the samples that were cut from the fully exposed and control samples of Halar. The density, calculated from the measured volume and the measured weight of the cut samples, did not appear to vary between the exposed and the control. Piece

*Tables 1 through 8 are cited in text.

7 (exposed) did have a significantly lower density than the rest of the exposed sample and the control samples. It is hard to imagine such a sharp variation of density within the exposed sample of Halar. 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 assess oxidation rates.

RESULTS AND DISCUSSION

The results are presented for each technique by showing some thermograms, the output of the thermal analysis run. Tables of peak temperatures, peak integrals, or baseline shift amounts (weight changes, penetrations) have been compiled from all the thermograms. All the thermograms used to obtain the data in Tables 3-8 are given in Appendices A, B, and C. These temperatures, integrals, or shifts are then plotted versus section depth for the three techniques employed; TMA, TGA, and DSC. Since the section thicknesses varied within the section itself, each section was weighed, and its depth is given in the tables as the calculated average depth from the weight of the section and the density of the Halar from Table 1.

The penetration versus temperature TMA thermogram is shown in Figure 2 for the top section of the LDEF Halar sample. Although visible discoloration was present in this top section, the glass transition temperature, 253 C in Figure 2, was essentially the same as the control, 254 C, as shown in Figure 3. The glass transition temperatures for all the sections analyzed in the TMA are given in Table 3 for the LDEF exposed Halar sample, and in Table 4 for the control Halar sample. The temperatures were determined by the inflection points of the plots within the transition. Figure 4 is a plot of the transition temperatures as a function of section depth in the sample. All the temperatures are within +/- 2 C. There is no trend with depth, and the control is essentially the same as the LDEF exposed sample.

Figure 5 is the TGA thermogram for weight gain or loss while heating in oxygen for the topmost LDEF exposed sample. Significant weight losses occurred at 170 C and in the range 300-500 C. As can be seen in Figure 6, the weight loss at 170 C is far less for the top-most control sample than for the exposed Halar sample, while the weight loss at the higher temperature range is similar for both samples. TGA weight losses at 170 C, 290 C, and 420 C are given in Table 5 for all the LDEF exposed Halar sections and in Table 6 for all the Halar control sections. The plot of weight loss at 170 C versus section depth is shown in Figure 7. The LDEF exposed Halar shows a dramatic increase in weight loss as compared to the control samples for the first two sections from the top. Discoloration was evident in both of the top two TGA sections of the exposed sample. Apparently the oxidation rate differs from the control for the LDEF exposed Halar only to a depth of about 50 microns.

The DSC thermogram is shown in Figure 8 for the topmost LDEF exposed sample. A noisy melting endotherm is evident at 235 C, and a strong exotherm at 446 C. The top-most control sample, Figure 9, showed a weak melting endotherm at 234 C. The second section of the control sample, Figure 10, showed an endotherm at 235 C very similar to the LDEF sample. Plots of melting temperature versus section depth and melting enthalpy (the integral of the melting endotherm) versus depth are shown in Figures 11 and 12. In both cases, there appears to be no difference between the LDEF and the control samples. No significant variation with section depth is evident for either melting temperature or for enthalpy of melting.

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 micron thick sections. The TGA, however, measures the oxidation rate at the surface of the section placed in the analyzer. The top-most section had as its top surface the actual 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. This 50 micron damage depth is in rough agreement with the observation of severe damage to 125 micron thick Mylar (3).

CONCLUSIONS

The orbital exposure during the LDEF Mission did not appear to mechanically damage the Halar sample. To a surface section resolution of about 50 microns, no thermodynamic damage was detectible via differential thermal analysis. The top 50 microns of the LDEF exposed sample did exhibit a higher oxidation rate than the control samples, which correlates to the depth of the discoloration.

References

(1) A. F. Whitaker, "Coatings Could Protect Composites From Hostile Space Environments," Adv. Materials & Processes, 4 (1991), 30-32.

(2) R. C. Tennyson, G. E. Mabson, W. D. Morison, and J. Kleinman, "LDEF Mission Update: Composites in Space," Adv. Materials & Processes, 5 (1991), 33-36.

(3) B. J. Dunbar, "A Materials Scientist in Space," MRS Bulletin, May (1991), 36-41.

(4) G. L. Steckel and T. D. Le, "LDEF Mission Update: Composites Survive Space Exposure," Adv. Materials & Processes, 8 (1991), 35-38.

Table 1 **Thickness and Density Measurements for Cut Halar LDEF and Control Samples Before Sectioning**

Dimensional Characteristics of Halar Samples

Measured Thickness

Pc#1 Control (inches)	Pc#2 Control (inches)	Pc#3 Control (inches)	Pc#4 Exposed (inches)	Pc#5 Exposed (inches)	Pc#6 Control (inches)	Pc#7 Exposed (inches)
0.1209	0.1220	0.1257	0.1215	0.1224	0.1256	0.1180
	0.1218	0.1256	0.1202	0.1218	0.1241	0.1202
	0.1218	0.1254	0.1196	0.1198	0.1252	0.1202

Calculated Density

Pc#1 Control (gr/cc)	Pc#2 Control (gr/cc)	Pc#3 Control (gr/cc)	Pc#4 Exposed (gr/cc)	Pc#5 Exposed (gr/cc)	Pc#6 Control (gr/cc)	Pc#7 Exposed (gr/cc)
1.651	1.549	1.558	1.515	1.568	1.573	1.205

Table 2 **Test Conditions for LDEF Samples for Thermal Analysis**

Technique	Test Atmosphere	Heating Rate, C/min	Temp Range,C
TMA	flowing Ar	10	25-300
TGA	flowing O2	10	25-700
DSC	flowing Ar	10	25-600

Table 3 Glass Transition Temperatures as Determined by Thermomechanical Analysis for Halar LDEF Samples

Halar in TMA Transition temp. determined by inflection pt

Exposed
Piece #4

Area= 0.248 cm^2
Density= 1.515 gr/cm^3

Sample ID	Wt (gr)	Thick (um)	Depth (um)	Temp C
H4C1	0.0027	71.9	36.0	253.3
H4C1A	0.0027	71.9	36.0	251.0
H4C2	0.0047	125.1	134.4	254.1
H4C3	0.0013	34.6	214.3	252.2
H4C4	0.0030	79.8	271.5	251.1
H4C5	0.0038	101.1	362.0	252.0
H4C6	0.0045	119.8	472.4	252.0
H4C7	0.0044	117.1	590.9	
H4C8	0.0014	37.3	668.1	
H4C9	0.0080	212.9	793.1	
H4C10	0.0028	74.5	936.9	
H4C11	0.0051	135.7	1042.0	
H4C12	0.0019	50.6	1135.2	
H4C13	0.0053	141.1	1231.0	
H4C14	0.0039	103.8	1353.4	
H4C15	0.0050	133.1	1471.8	
H4C16	0.0019	50.6	1563.7	
H4C17	0.0078	207.6	1692.7	
cutoff	0.0486	1293.5		
total	0.1161	3161.9		
original	0.1148	3053.0		

Table 4 Glass Transition Temperatures as Determined by Thermomechanical Analysis for Halar Control Samples

Halar in TMA Transition temp. determined by inflection pt

Control
Piece #3

Area= 0.3035 cm^2
Density= 1.558 gr/cm^3

Sample ID	Wt (gr)	Thick (um)	Depth (um)	Temp C
H3C1	0.0016	33.8	16.9	253.7
H3C2	0.0010	21.1	44.4	254.1
H3C3	0.0050	105.7	107.8	253.4
H3C4	0.0007	14.8	168.0	252.7
H3C5	0.0182	384.9	367.8	253.2
H3C6	0.0011	23.3	572.0	
H3C7	0.0001	2.1	584.7	
H3C8	0.0095	200.9	686.2	252.7
H3C9	0.0007	14.8	794.0	
H3C10	0.0090	190.3	896.6	252.7
H3C11	0.0052	110.0	1046.7	
H3C12	0.0006	12.7	1108.0	
H3C13	0.0084	177.6	1203.2	
H3C14	0.0003	6.3	1295.2	
H3C15	0.0100	211.5	1404.0	
H3C16	0.0016	33.8	1526.7	
cutoff	0.0734	1552.3		
total	0.1464	3096.1		
original	0.1508	3190.0		

Table 5 Weight Losses at Various Temperature Ranges as Determined by Thermogravimetric Analysis for Halar LDEF Samples

Halar in TGA Weight changes occur after onset temperatures

Exposed
Piece #7

Area= 0.270 cm^2
Density= 1.205 gr/cm^3

Sample ID	Wt(gr)	thick (um)	mean depth	170 C d %wt	290 C d %wt	420 C d %wt
H7C1	0.0004	12.3	6.2	23.0	61.6	14.3
H7C2	0.0029	89.1	56.9	3.9	68.7	27.3
H7C3	0.0003	9.2	106.0	0.0	78.0	20.6
H7C4	0.0048	147.5	184.4	1.1	74.7	24.8
H7C5	0.0006	18.4	267.4	0.0	82.6	24.2
H7C6	0.0040	122.9	338.1	0.5	72.8	26.8
H7C7	0.0006	18.4	408.8	0.0	84.9	22.0
H7C8	0.0066	202.9	519.4	0.4	64.1	35.7
H7C9	0.0029	89.1	665.4	0.0	67.7	31.8
H7C10	0.0047	144.5	782.2	0.3	65.3	34.7
H7C11	0.0011	33.8	871.4	0.0	69.5	29.8
H7C12	0.0044	135.2	955.9	nd	68.5	31.3
H7C13	0.0037	113.7	1080.4			
H7C14	0.0039	119.9	1197.2			
H7C15	0.0007	21.5	1267.9			
H7C16	0.0057	175.2	1366.2			
H7C17	0.0008	24.6	1466.1			
cutoff	0.0509	1564.5				
total	0.0990	3042.9				
original	0.0994	3053				

Table 6 Weight Losses at Various Temperature Ranges as Determined by Thermogravimetric Analysis for Halar Control Samples

Halar in TGA Weight changes occur after onset temperatures

Control
Piece #6

Area= 0.2639 cm^2
Density= 1.573 gr/cm^3

Sample ID	Wt(gr)	thick (um)	mean depth	170 C d %wt	290 C d %wt	420 C d %wt
H6C1	0.0046	110.8	55.4	1.3	66.2	32.5
H6C2	0.0040	96.4	159.0	0.8	72.5	27.1
H6C3	0.0049	118.0	266.2	0.2	68.0	31.8
H6C4	0.0030	72.3	361.3	0.0	66.7	32.8
H6C5	0.0008	19.3	407.1	0.0	74.9	25.1
H6C6	0.0047	113.2	473.4	0.0	67.4	32.2
H6C7	0.0006	14.5	537.2			
H6C8	0.0040	96.4	592.6	0.0	65.9	34.0
H6C9	0.0033	79.5	680.5			
H6C10	0.0030	72.3	756.4	0.0	68.6	31.4
H6C11	0.0007	16.9	801.0			
H6C12	0.0039	93.9	856.4	0.0	69.3	30.7
H6C13	0.0005	12.0	909.4			
H6C14	0.0041	98.8	964.8	0.1	66.5	33.5
H6C15	0.0007	16.9	1022.6			
H6C16	0.0043	103.6	1082.8	0.0	67.4	33.7
H6C17	0.0022	53.0	1161.1			
H6C18	0.0059	142.1	1258.7	0.3	65.0	34.6
cutoff	0.0803	1934.4				
total	0.1355	3264.2				
original	0.1320	3180				

Table 7 Transition Temperatures and Enthalphy of Melting as Determined by Differential Scanning Calorimetry for Halar LDEF Samples

Halar in DSC Temperatures determined by peaks

Exposed
Piece #5

Area= 0.1281 cm^2
Density= 1.568 gr/cm^3

Sample ID	Wt (gr)	Thick (um)	Depth (um)	temp C	temp C	H
H5C1	0.0042	209.1	104.6	445.6	235.1	
H5C2	0.0018	89.6	253.9	449.7	237.5	6.26
H5C3	0.0039	194.2	395.8	445.4	235.9	4.35
H5C4	0.0021	104.6	545.2	435.6	237.7	3.24
H5C5	0.0048	239.0	716.9	441.0	235.6	5.80
H5C6	0.0019	94.6	883.7	449.3	236.2	2.49
H5C7	0.0034	169.3	1015.6			
H5C8	0.0032	159.3	1179.9			
H5C9	0.0022	109.5	1314.3			
H5C10	0.0070	348.5	1543.4			
H5C11	0.0016	79.7	1757.4			
H5C12	0.0034	169.3	1881.9			
H5C13	0.0038	189.2	2061.1			
H5C14	0.0013	64.7	2188.1			
H5C15	0.0076	378.4	2409.6			
H5C16	0.0010	49.8	2623.7			
H5C17	0.0027	134.4	2715.8			
cutoff	0.0388	1931.7				
total	0.0947	4714.7				
original	0.0883	3094.0				

Table 8 Transition Temperatures and Enthalphy of Melting as Determined by Differential Scanning Calorimetry for Halar Control Samples

Halar in DSC Temperatures determined by peaks

Control
Piece #2

Area= 0.265 cm^2
Density= 1.549 gr/cm^3

Sample ID	Wt (gr)	Thick (um)	Depth (um)	temp C	temp C	H
H2C1	0.0012	29.2	14.6	448.8	234.7	3.02
H2C2	0.0058	141.3	99.8	452.0	235.1	6.78
H2C3	0.0006	14.6	177.8			
H2C4	0.0053	129.1	249.6	448.0	238.0	
H2C5	0.0003	7.3	317.8			
H2C6	0.0053	129.1	386.0	447.7	236.0	3.60
H2C7	0.0067	163.2	532.2			
H2C8	0.0048	116.9	672.2	450.2	235.5	3.32
H2C9	0.0023	56.0	758.7			
H2C10	0.0042	102.3	837.8	449.5	236.7	2.23
H2C11	0.0066	160.8	969.4			
H2C12	0.0005	12.2	1055.9			
H2C13	0.0059	143.7	1133.8			
H2C14	0.0024	58.5	1235.0			
H2C15	0.0025	60.9	1294.7			
H2C16	0.0020	48.7	1349.4			
H2C17	0.0023	56.0	1401.8			
H2C18	0.0027	65.8	1462.7			
cutoff	0.0463	1127.9				
total	0.1077	2623.7				
original	0.1207	3094.0				

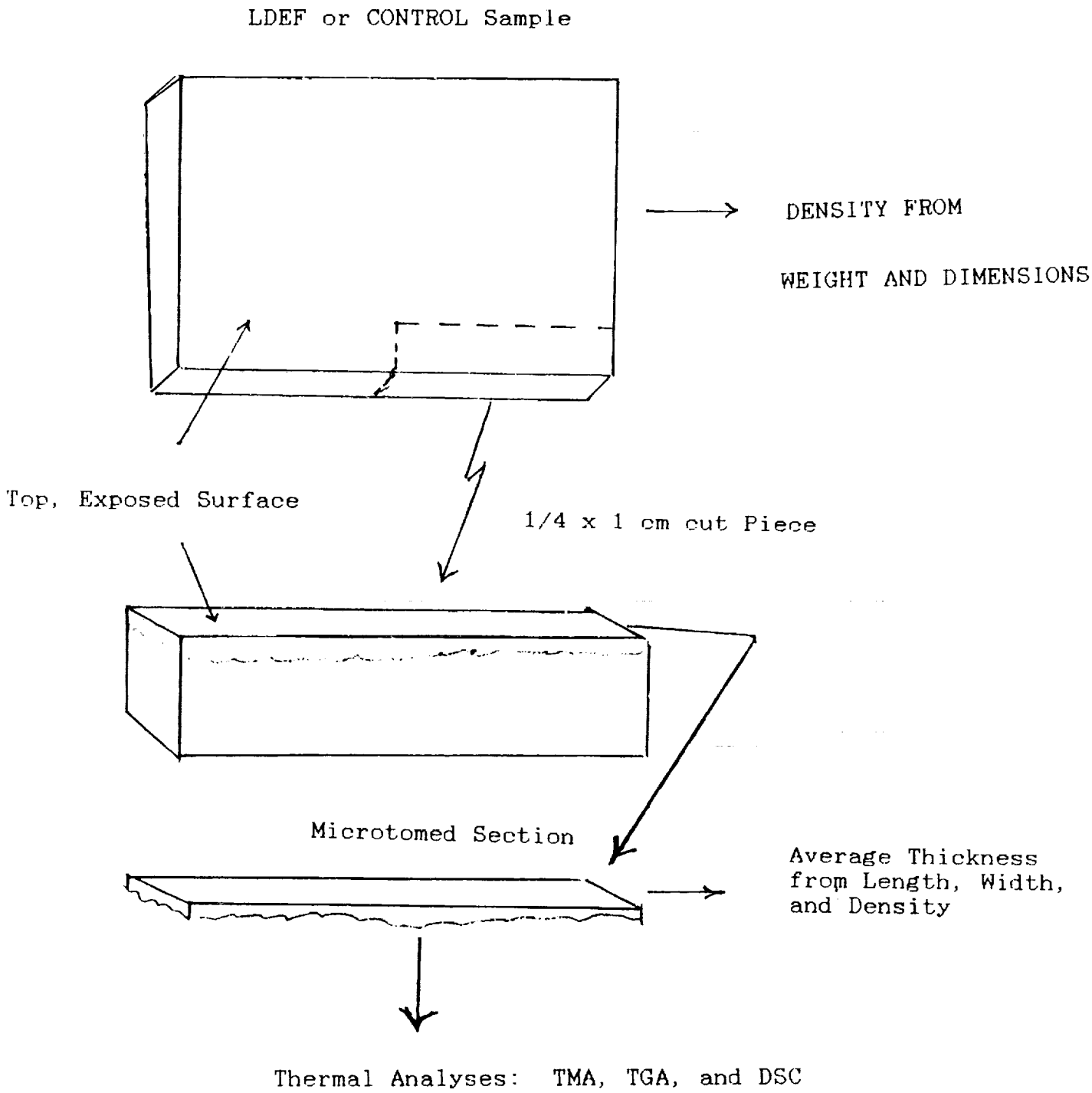

Figure 1 Schematic Diagram of LDEF Sample Sectioning Procedure

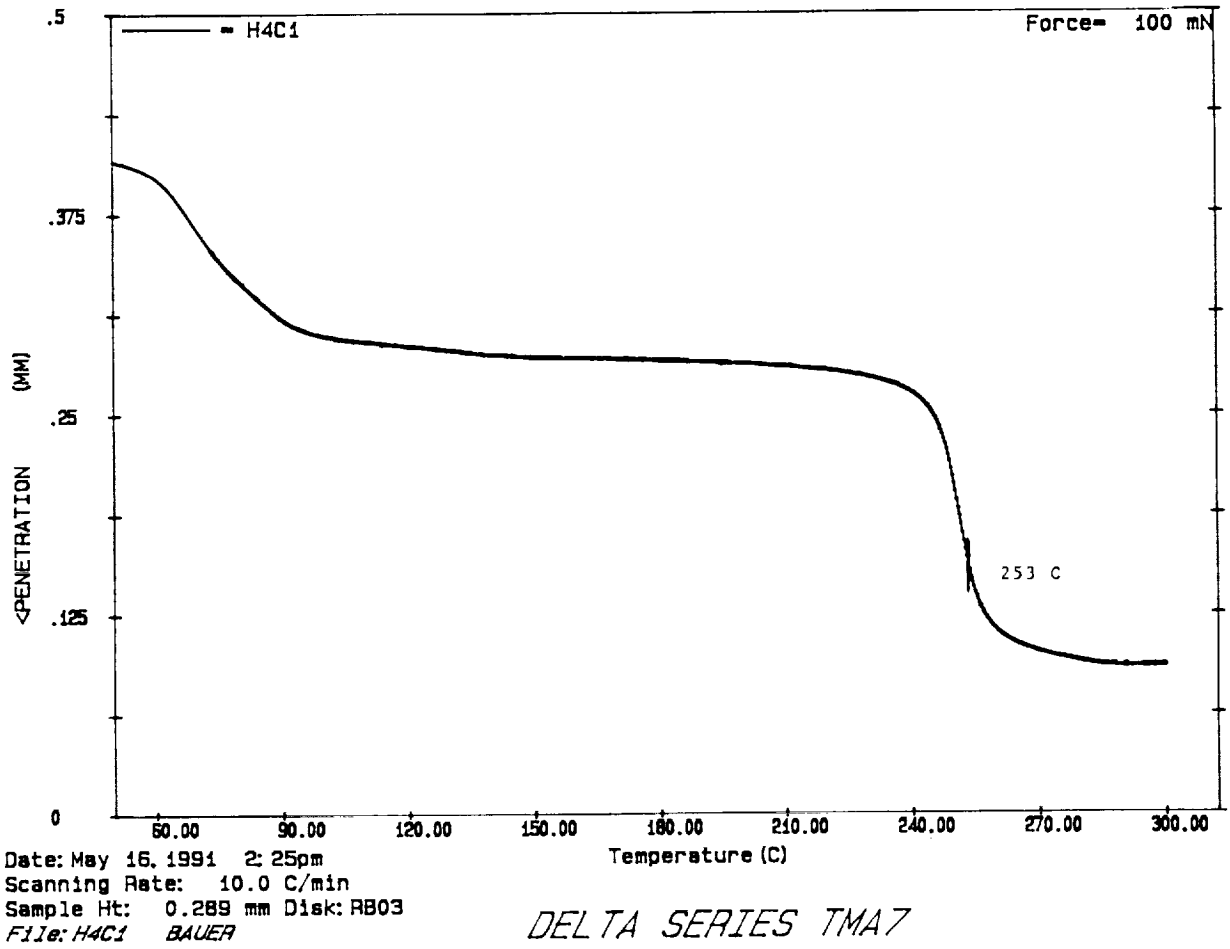

Figure 2 TMA Plot for the Top Section of the Halar, LDEF Sample Which Showed Visible Discoloration

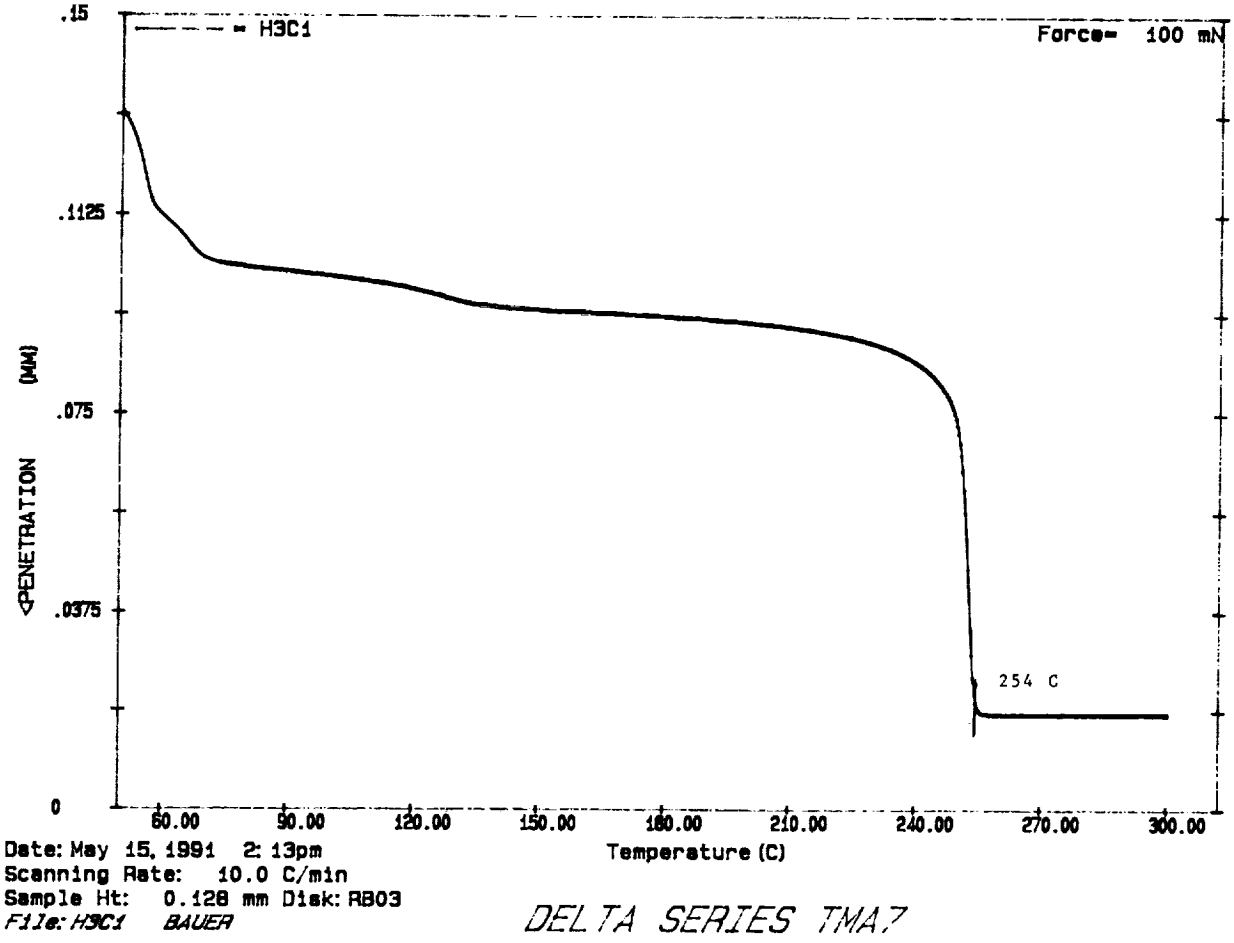

Figure 3 TMA Plot for the Top Section of the Halar Control Sample

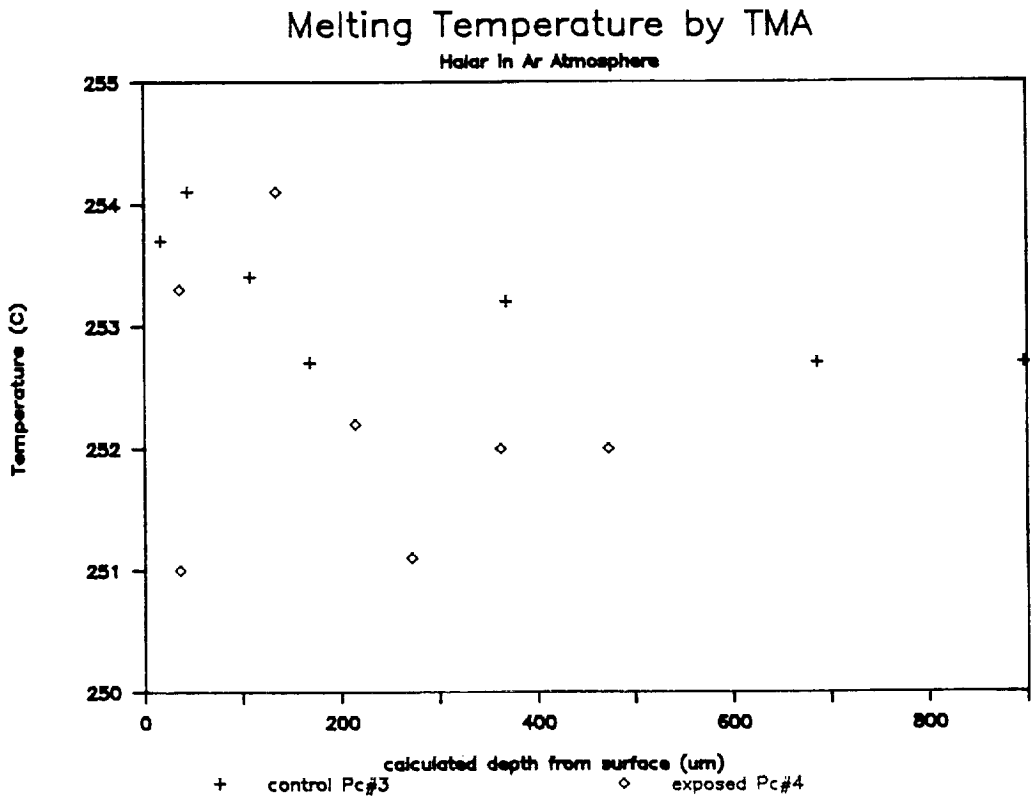

Figure 4 TMA Glass Transition Temperature as a Function of Section Depth for Halar LDEF and Control Samples

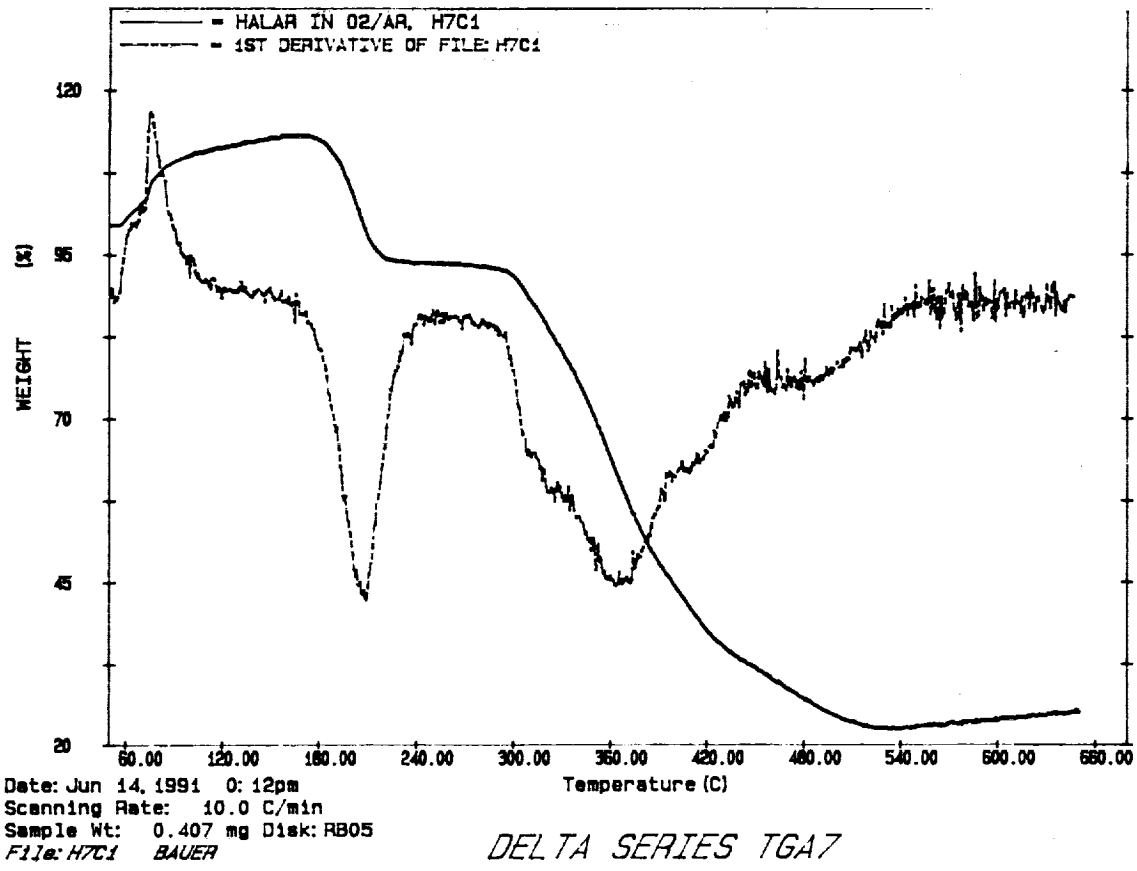

Figure 5 TGA Plot for the Top Section of the Halar LDEF Sample Showing a Large Weight Loss at 170° C

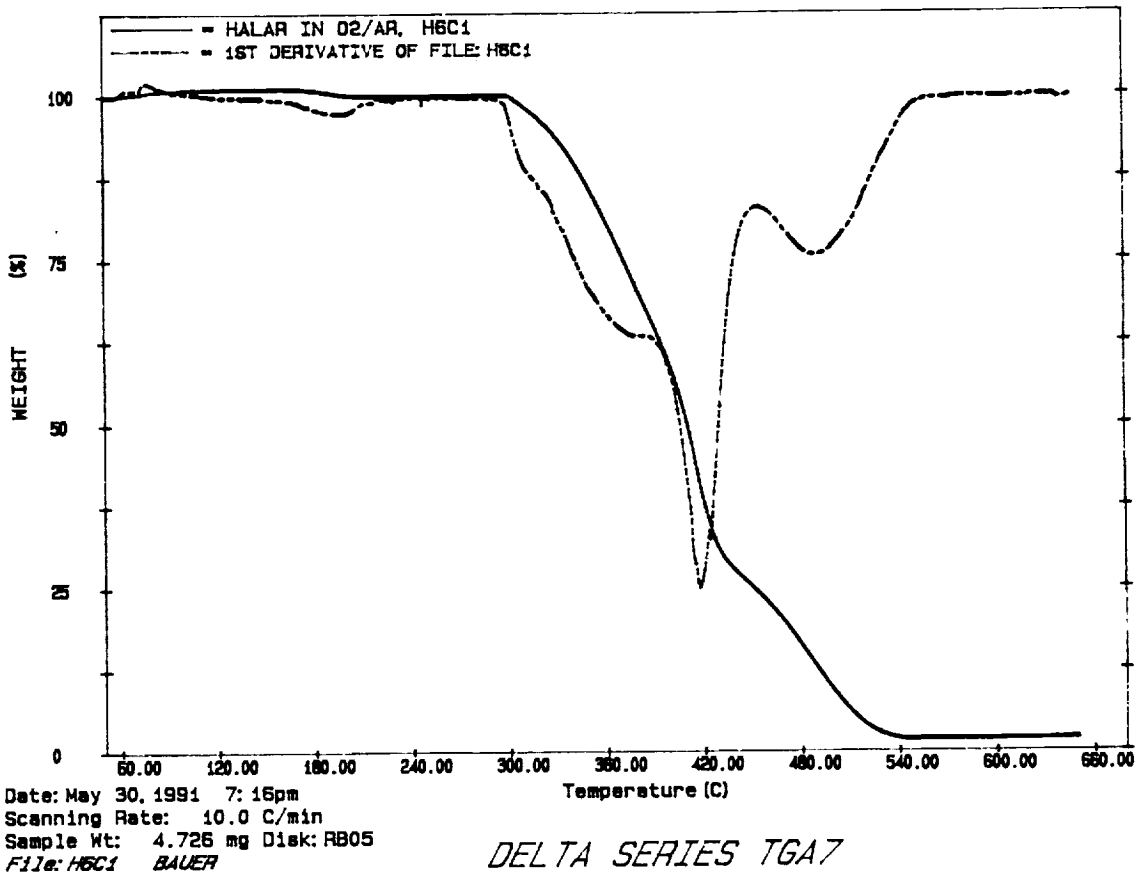

Figure 6 TGA Plot for the Top Section of the Halar Control Sample

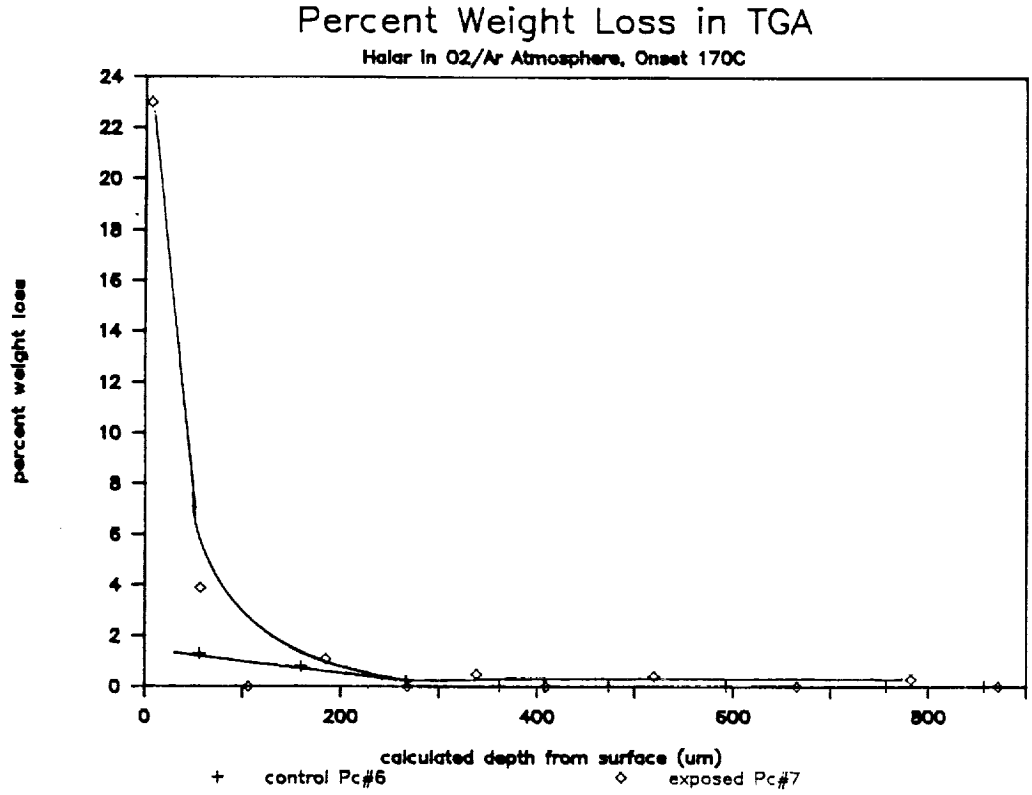

Figure 7 TGA Weight Loss at 170° C as a Function of Sectioning Depth for Halar, LDEF and Control Samples

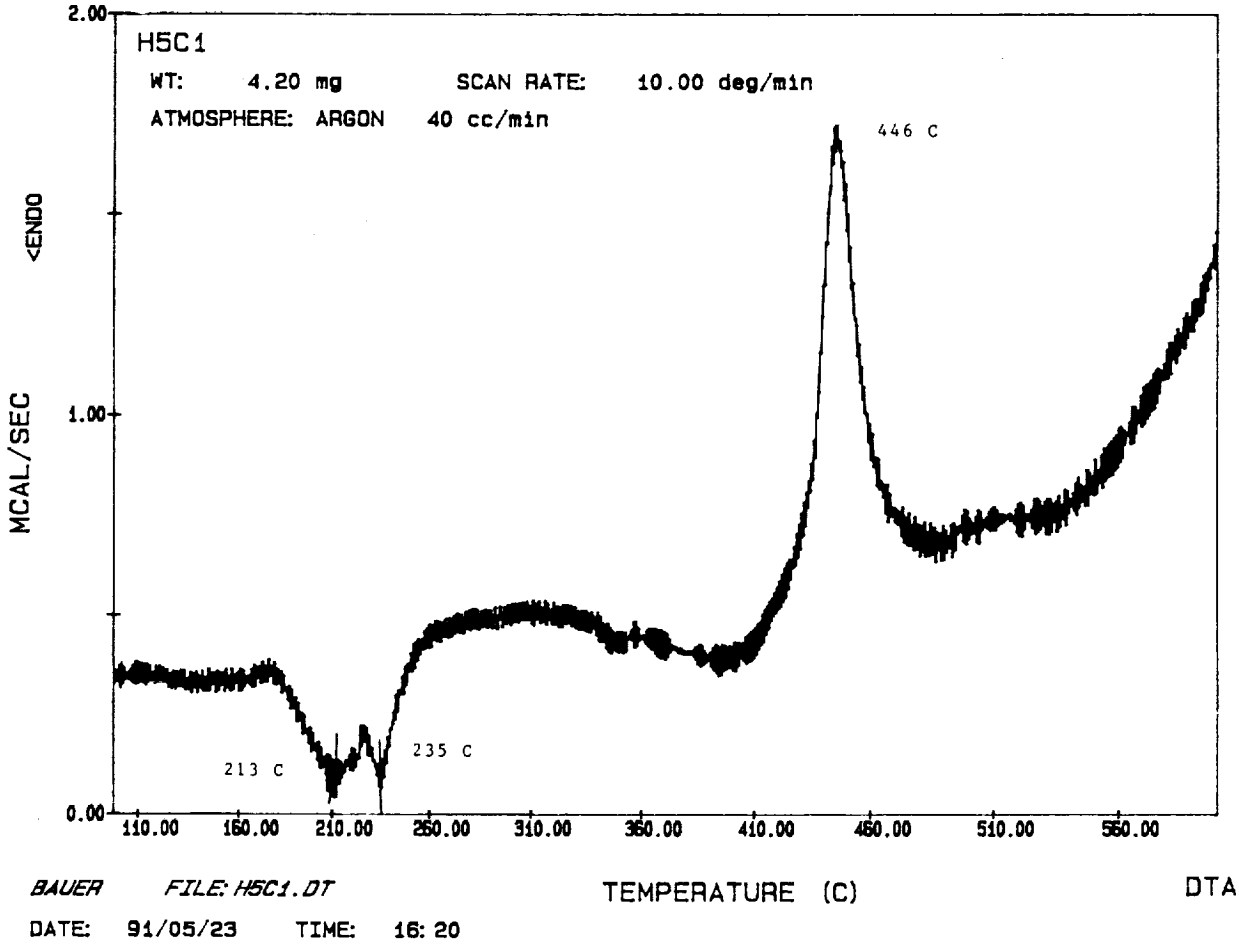

Figure 8 DSC Plot for the Top Section of the Halar LDEF Sample Showing an Endotherm at 235° C and an Exotherm at 446° C

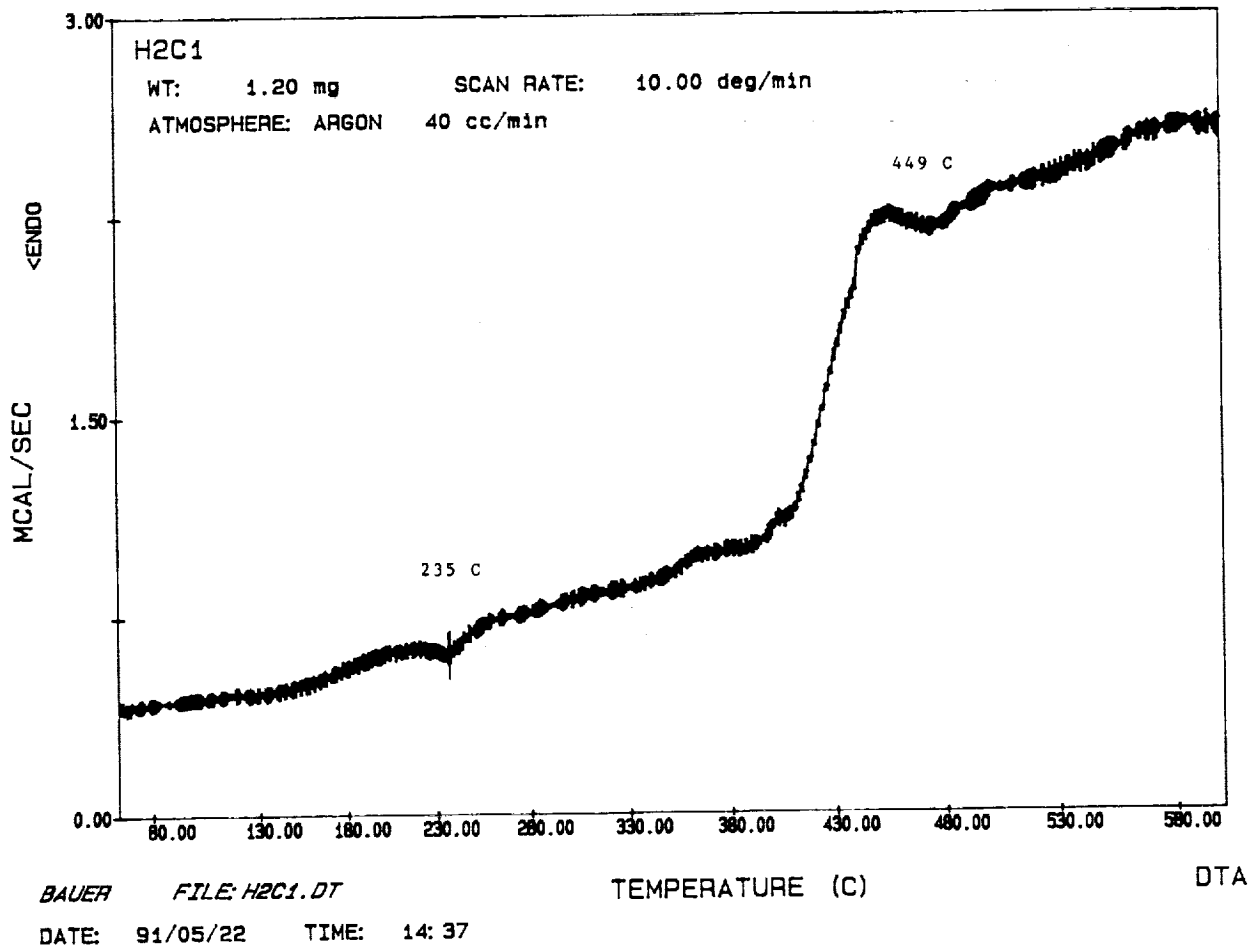

Figure 9 DSC Plot for the Top Section of the Halar Control Sample Showing a Weak Endotherm at 234° C and a Weak Exotherm at 449° C

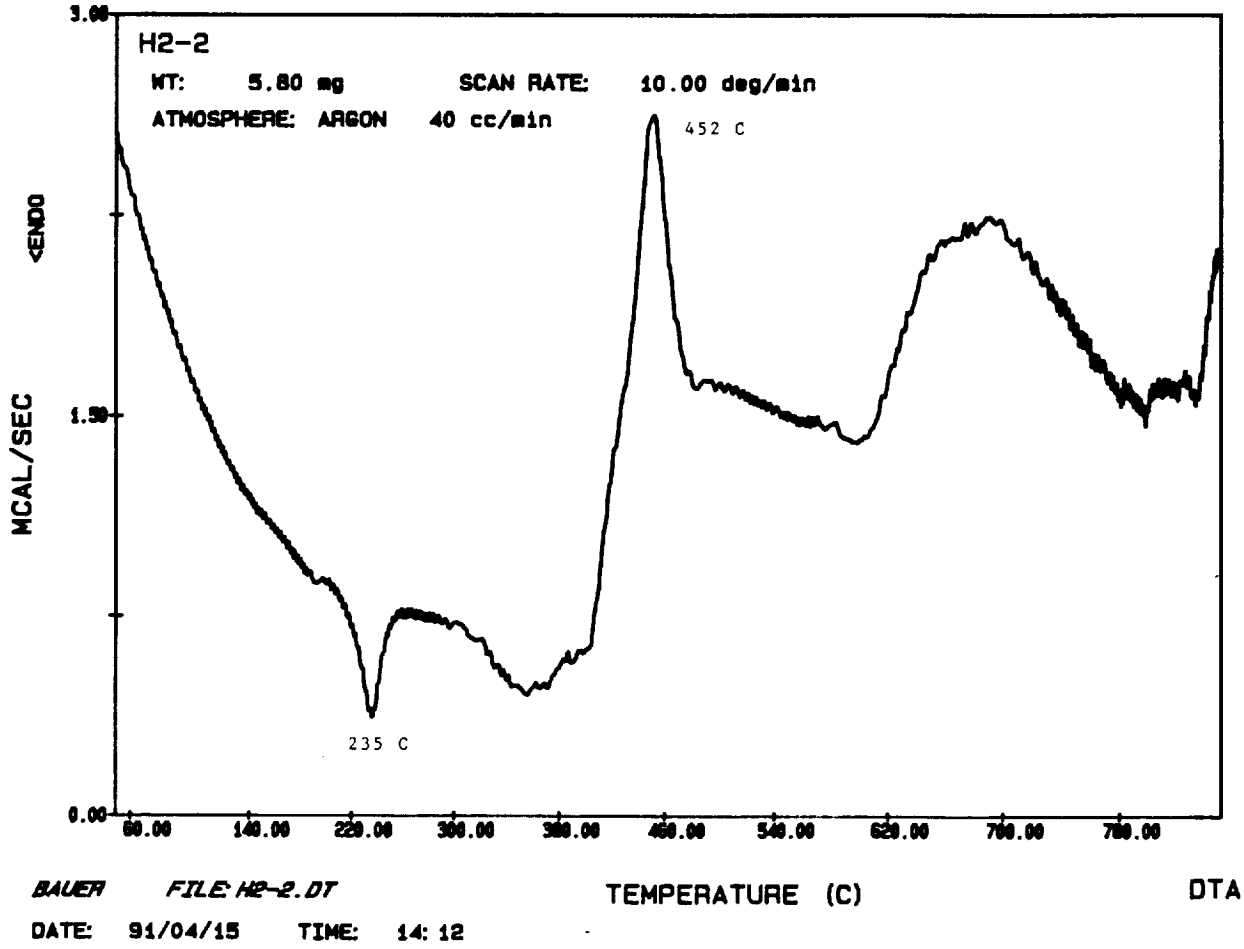

Figure 10 DSC Plot for the Second Section of the Halar Control Sample Showing a Strong Endotherm at 235° C and a Strong Exotherm at 452° C

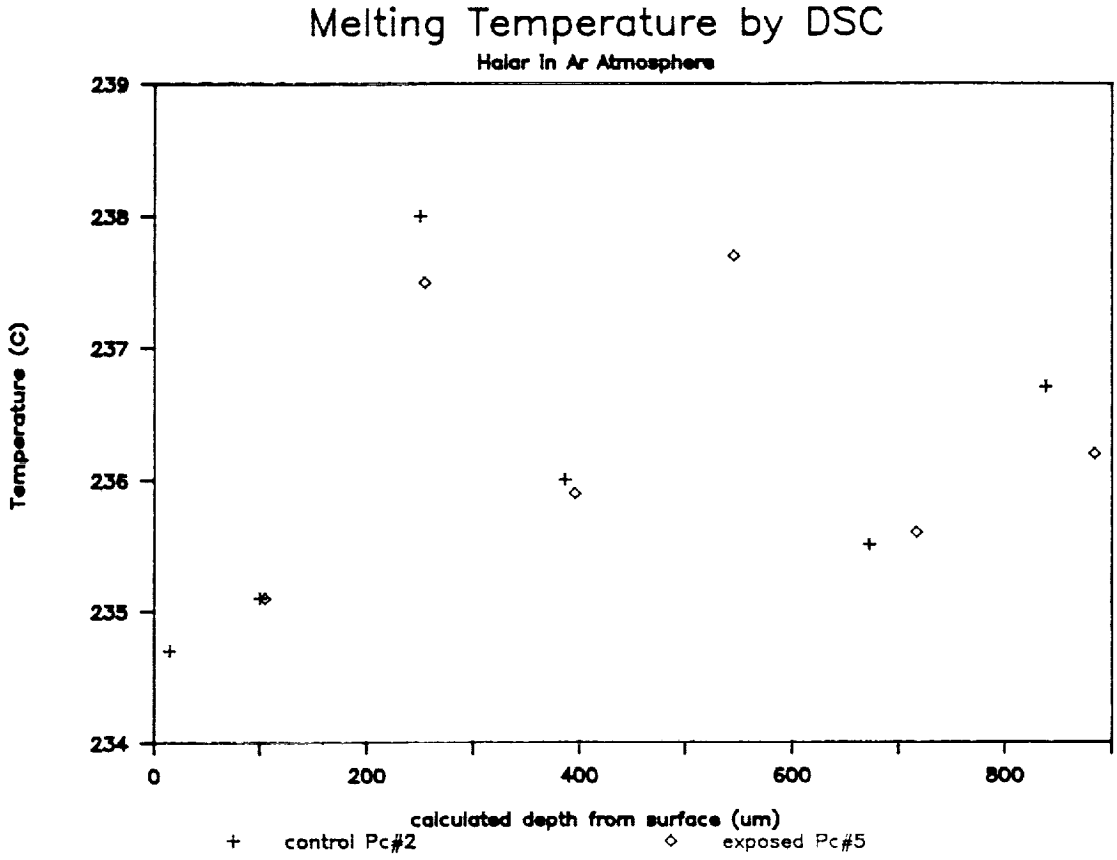

Figure 11 DSC Melting Endotherm Temperature as a Function of Section Depth for Halar LDEF and Control Samples

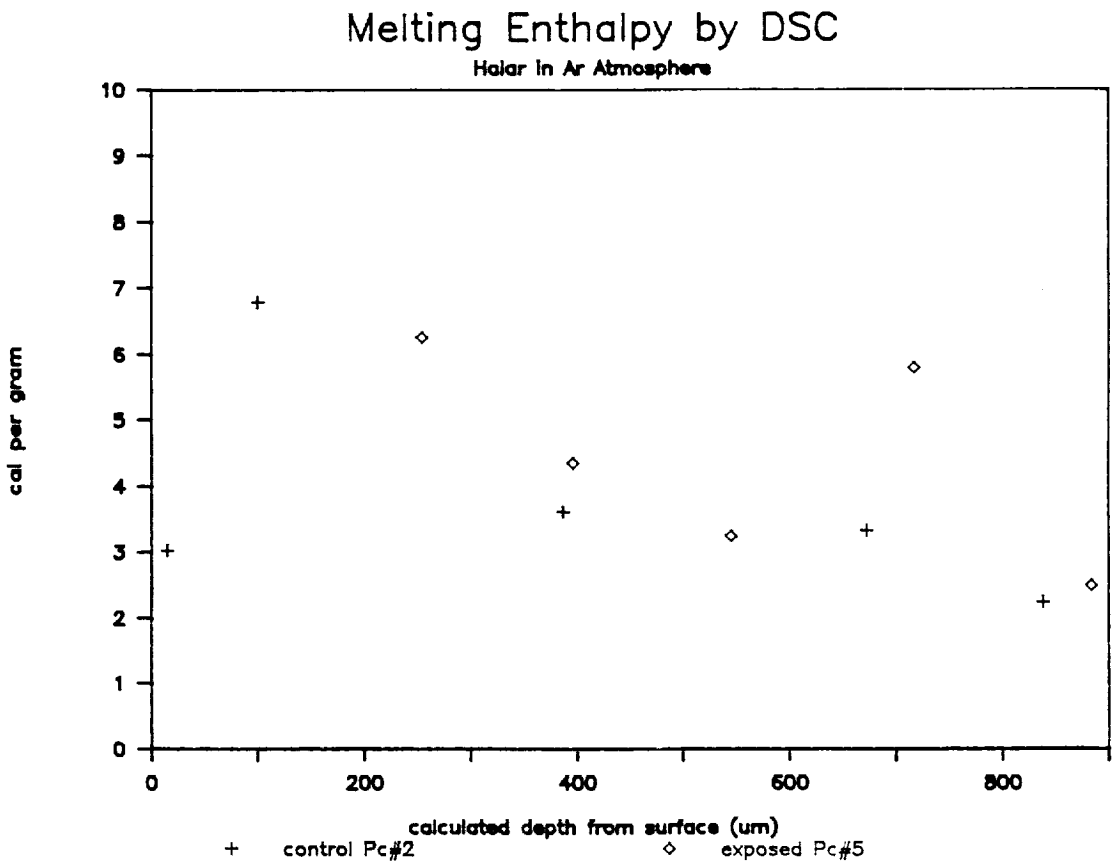

Figure 12 DSC Melting Enthalpy as a Function of Section Depth for Halar LDEF and Control Samples