THE RATE OF OXIDATION OF CARBON FIBERS IN AIR

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Introduction

Most earlier work on the oxidation of carbon fibers was aimed at modifying the fibers' surfaces to improve interfacial bonding. There are also TGAs and oxidation studies at temperatures where carbon fibers are oxidized fairly rapidly. This paper provides information on the long term isothermal oxidation of carbon fibers based on polyacrylonitrile, rayon, and mesophase pitch between 230 and 315°C.

Materials and Methods

The yarns and cloths studied, all products of Union Carbide, are shown in Table I. The first three items are derived from PAN, items 4-10 are based on rayon; the rest are made from mesophase pitch. Analyses were made because it was expected that the rate of oxidation would be affected by the carbon content of the samples, and because alkali and alkaline earth metals are oxidation catalysts for carbon materials, especially at low temperatures. The densities were obtained in a density gradient column. The metallic elements were determined by atomic absorption.

For the oxidation measurements, duplicate 3 gram samples of each test item were suspended in a Freas Oven with an air flow of about 3 cfm. The nominal temperatures of 230, 290, and 315°C were maintained to ±2°C. The samples were weighed on a 1 mg balance except for the 230°C items where a balance with 0.1 mg sensitivity was used. The samples were weighed initially as received, after 4 hrs. at temperature, after 24 and 72 hrs. at temperature, and approximately at 3 or 4 day intervals thereafter until 1000 hrs. of exposure had been exceeded. The results are summarized in Table II and some typical curves are shown in Figure 1.

The materials used contain different amounts of finishes, have different surface areas, and may, therefore, sorb different amounts of atmospheric gases, etc. To eliminate these variables and obtain a measure of the weight loss due to the isothermal oxidation of the carbon, a weight loss vs. time curve was plotted for each sample. Usually, there was a rapid initial weight loss, then a levelling off. The more nearly level portion of this curve was extrapolated back to time 0, and the intercept was used as the starting weight. Table II lists an initial (4 hrs.) weight loss, and then weight losses to 100, 300, and 1000 hrs. These latter three are calculated from the intercepts; to obtain the actual weight loss at those times, the initial weight loss needs to be added.

Another element of arbitrariness: It was assumed, considering the low weights and heat capacities of the samples, that they would reach the oven temperature in 10 minutes, and that they would cool to room temperature in 5 minutes. Hence, the samples were allowed to sit in the room air for about 5 minutes before being weighed. They gradually gained weight at room temperature due to the resorption of atmospheric gases, but this weight increase was almost negligible in this short time.

Discussion of Results

The first item in Table II is commercial "Thornel"*-300; the second item is the same, finish free. The materials are of comparable purity and show no substantial differences in their oxidation behavior except for the higher initial weight loss for item 1, due to loss of the finish. Neither yarn survived 1000 hrs. at 315°C. However, the third item, a higher modulus version derived from the same precursor, shows a higher carbon content, greater purity, and a weight loss of well under 1% after 1000 hrs. at 315°C.

Among the rayon-based carbon fibers, there is one anomaly: WYB yarn, produced by carbonization under stress-free conditions, showed no weight loss except at 315°C. Both samples behaved similarly, and this behavior is being investigated further. The WCA cloth, also produced in a stress-free condition, showed only very low weight losses, less than .25%. The remaining yarns in this group, which achieve their strengths and elastic moduli (25, 50, and 75 Mpsi, resp.) by hot stretching, seem to show increasing sensitivity to oxidation with increasing orientation, but the numbers are too close to be considered conclusive.

The pitch-based carbon fibers exhibit oxidation rates comparable to the rayon-based fibers of comparable moduli. They have much better oxidation resistance than the PAN-based fibers. Grade VSA-11, a commercial material with modulus of 55 Mpsi, shows good oxidation resistance, but not as good as the experimental grade VS-0031, with a modulus of only about 35 Mpsi and again, presumably, a smaller degree of crystallite orientation. Among the cloths, grade VC-0150 is similar to the VS-0031 in filament properties and shows similar oxidation behavior. The VC-0149 has lower modulus, but is also somewhat less pure and oxidized more rapidly.

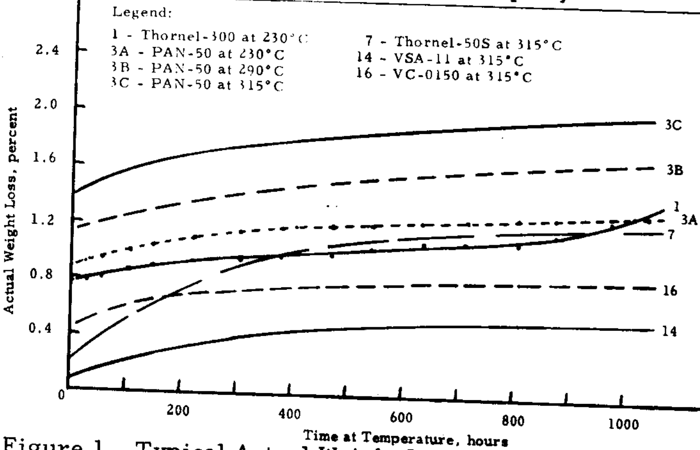

Figure 1. Typical Actual Weight Loss Curves

*"Thornel" is a registered trademark of Union Carbide Corporation.

Table I

Description of the Carbon Fibers Studied

Item	Material	Density Mg/m³	Nominal Filament Diameter μm	Analyses: Carbon %	Hydrogen %	Ash %	Li, ppm	Na, ppm	K ppm	Mg, ppm	Ca, ppm	Ba, ppm
1	Thornel 300, WYP, UC-309	1.76	6.9	93.3	0.38	0.566	0.27	2020.0	49.8	3.1	7.0	1.1
2	Thornel 300, WYP, No finish	1.76	6.9	93.4	0.41	0.638	0.27	2160.0	52.0	5.7	5.8	0.3
3	PAN-50, WYR, UC-309	1.82	6.6	99.6	0.20	0.025	0.20	58.9	5.0	8.3	28.1	0.6
4	WYB	1.31	8.9	99.9	----	0.075	0.003	43.2	14.1	0.3	23.7	1.7
5	Thornel-25, WYD, UC-304	1.42	7.4	99.9	----	0.147	0.01	104.0	12.1	11.3	57.4	0.9
6	Thornel-50, WYG, UC-304	1.66	6.6	99.9	----	0.026	0.01	32.2	4.1	0.5	5.3	0.4
7	Thornel-50S, WYH, UC-307	1.66	6.6	99.9	----	0.074	0.003	37.3	18.2	7.2	44.4	1.6
8	Thornel-50S, WYH, No finish	1.68	6.6	99.9	----	0.009	negligible	0.8	0.5	0.3	0.5	0.5
9	Thornel-75, WYJ, UC-307	1.80	6.0	99.9	----	0.014	0.002	4.0	2.3	0.3	0.5	0.3
10	WCA Carbon Cloth	1.40	8.1	99.9	----	0.002	0.002	6.7	1.6	0.8	1.8	0.2
11	VS-0031, No shear treatment	1.91	13.0	98.8	----	0.236	0.10	13.5	15.3	26.4	7.2	11.0
12	VS-0031, Shear treated	1.91	13.0	98.8	----	0.141	0.09	14.4	9.0	23.2	15.4	6.8
13	VSA-11, UC-304	2.02	13.0	99.0	----	0.009	0.002	12.3	1.9	0.8	4.1	2.5
14	VSA-11, No finish	2.06	13.0	99.0	----	0.017	0.009	14.0	1.4	0.4	17.2	3.3
15	VC-0149 cloth	1.84	13.0	98.6	----	0.167	0.14	230.0	10.2	4.1	74.7	3.8
16	VC-0150 cloth	2.06	13.0	99.0	----	0.134	0.006	5.3	0.7	0.7	61.7	4.0

Table II

Percent Weight Loss of Carbon Fibers in Air

		At 230°C				At 290°C				At 315°C			
Item	Fiber	Initial 4 hrs. *	100 hrs.	300 hrs.	1000 hrs.	Initial 4 hrs. *	100 hrs.	300 hrs.	1000 hrs.	Initial 4 hrs. *	100 hrs.	300 hrs.	1000 hrs.
1	Thornel 300, WYP, UC-309	.76	.07	.20	.69	.88	.10	1.80	21.1	1.08	3.66	18.5	**
2	Thornel 300, WYP, No finish	.04	0.00	.03	.20	.04	.08	2.76	19.9	0.04	4.81	21.30	***
3	PAN-50, WYR	.88	.10	.24	.44	1.13	.09	.28	.55	1.38	.21	.40	.64
4	WYB	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	.68	6.30
5	Thornel-25, WYD	.32	.03	.06	.14	.07	0.00	.18	.42	.36	.37	.66	.69
6	Thornel-50, WYG	.47	.05	.13	.07	0.00	.05	.15	.53	.33	.35	.78	1.27
7	Thornel-50S, WYH	.28	.03	.08	.24	.40	0.00	.12	.40	.22	.31	.71	.89
8	Thornel-50S, WYH, No finish	.20	.32	.49	.56	.18	.35	.45	.45	.56	.40	.66	1.20
9	Thornel-75, WYJ, UC-307	.32	.13	.26	.44	.32	.04	.14	.96	.30	.20	.57	1.12
10	WCA Carbon Cloth	.02	0.00	.02	.23	.04	0.00	.03	.05	.08	.04	.12	.20
11	VS-0031, No shear treatment	0.00	0.00	0.00	0.00	.12	.08	.16	.22	.25	.07	.15	.36
12	VS-0031, Shear treated	.03	0.00	.01	.04	0.00	0.00	0.00	.18	.04	.06	.14	.19
13	VSA-11, UC-304	.80	.15	.40	.80	1.76	.19	.43	.59	1.00	.40	.95	1.90
14	VSA-11, No finish	.01	.02	.05	.14	.10	.18	.15	.22	.08	.13	.32	.46
15	VC-0149 cloth	.07	.11	.41	1.55	.04	.19	.55	1.42	.59	.90	1.84	6.00
16	VC-0150 cloth	.04	.02	.04	.08	.05	.15	.37	1.21	.42	.19	.29	.39

* To obtain the true weight loss at 100, 300, or 1000 hours, add the "initial" weight loss to the reading given (see text).
** 92% total weight loss at 875 hours.
*** 88% total weight loss at 875 hours.