POSTER

A RAPID TEST FOR MEASURING THE OXIDATION RESISTANCE OF CARBON FIBERS

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INTRODUCTION

The oxidative stability of carbon fibers becomes a concern when the fibers are to be used in composites exposed to the elevated temperatures encountered in aircraft motors or similarly demanding applications. Measurement of weight losses of meaningful magnitude for oxidation resistant carbon fibers at projected service temperatures for polymer matrix composites (up to 400°C) can require excessively long aging times [1,2]. Previously, we reported on an accelerated oxidation resistance test that reduced test time to 16 hours by exposing fibers to oxygen at 430°C [3]. However, there are concerns about using oxygen as the oxidizing agent at some test locations; therefore, a modified test has been devised in which oxygen is replaced by air.

In this study, test conditions are described for the rapid measurement of weight loss for carbon fiber in air at temperatures of 430°C to 470°C. The method has been applied to eight commercially manufactured PAN-based carbon fibers covering a wide range of oxidation resistance. Long-term weight loss in air has been monitored on the same fibers at 316°C (600°F) and 371°C (700°F).

EXPERIMENTAL

Typical carbon fiber properties for the yarns are given in Table 1. Nineteen packages (one pound each) were used to represent each fiber type (T-300, 3K, etc.). Oxidation test samples consisted of three grams of fiber in a continuous length coil. Fibers were supported in Pyrex petri dishes and removed from the dishes for weighing. Finish was removed by heating the fiber in air at 300°C; however, size removal at 400°C has been found to be more efficient. Samples were allowed to cool in desiccators (Drierite) prior to weighing.

A Blue M oven (Model IGF-7780-4) was used for rapid testing with air flows of 0.7 (recommended) or 5.7 m^3/hour. Temperatures were computer monitored at fifteen minute intervals with eight thermocouples. The temperature across the oven was set point ±5°C. The rapid air oxidation test consisted of heating desized yarn for 60 hours at 430°C (207-276 GPa fibers), 450°C (207-345 GPa fibers), and 470°C (345 GPa fibers). Testing at 430°C and 470°C consisted of three samples from each of the 19 packages which comprise a yarn type. Testing at 450°C involved 10 randomly chosen packages (three samples each) from the 19 available for each yarn type.

Long-term oxidation testing was carried out by heating 5-7 samples from a single spool of each yarn type in flowing air at 316°C (Freas Precision oven at 1.7 m^3/hour) and 371°C (Blue M Power-O-Matic 80 oven at 17 m^3/hour). Additional packages of T-650/35 (six) and T-650/42 (five) were sampled (three from each package) and oxidized at 316°C to obtain package statistics. Sample weight was typically monitored at 500 hour intervals.

RESULTS AND DISCUSSION

The 60-hour oxidation test at 430°C or 450°C is a suitable alternative to the faster (16 hour) oxygen-based method reported previously [3]. Weight losses for fibers tested in air at 430, 450, and 470°C are given in Table 2. The 60-hour test of 207-276 Gpa fibers at 430°C resulted in a weight loss of at least five percent, which is an aid in distinguishing between fibers. Increasing the reaction temperature to 450°C produces a two to three times greater weight loss; however, the coefficient of variation also tends to increase. The only yarn tested in multiple tow sizes was T-300, and the greater weight loss for the 3K fiber suggested a tow size effect. To test for a dependence on oven flow rate, 30 samples from the same package of T-300 12K were oxidized at 430°C with air flows of 0.7 and 5.7 m^3/hour. The eightfold increase in air flow resulted in an insignificant difference in average weight loss (0.1%).

The highest test temperature investigated was 470°C, which proved to be too severe in 60-hour testing for 207-276 GPa modulus fibers and barely adequate for 345 GPa yarns. The most oxidation resistant fiber was T-650/50X, which gave a weight loss of only one percent at 470°C. The use of higher temperatures was not pursued because of the possibility of entering a different kinetic regime.

Long-term oxidative weight losses for eight yarns at 316°C are given in Table 3 and plotted in Figure 1. Testing was discontinued at 8000 hours because the low weight losses for the surviving fibers (345 GPa) indicated that a higher temperature (371°C) might be more appropriate. The 345 GPa yarns exhibit exceptional oxidation resistance with weight losses of only 0.5 percent in 8000 hours. Among the 207-276 GPa modulus group, T-650/42 12K is the most stable and T-300 3K is the least stable. The superior oxidation resistance of T-650/42 over T-650/35 at 316°C is also shown in Figure 2, which is a plot of average weight loss from multiple package testing against aging time.

Long-term weight loss after 500 hours in air at 371°C for 207-276 GPa fibers ranged from 31% (T-650/42) to 78% (T-300 3K). In contrast, the 345 GPa modulus fibers were so oxidation resistant at 371°C that monitoring was continued for 21,000 hours (2.4 years). Long-term aging results are given in Tables 4 and 5. Figure 3 shows weight loss as a function of aging time for 345 GPa fibers. Weight loss for T-650/50X after 20,000 hours was only 21.5%.

Weight losses for the 207-276 GPa fibers from rapid air testing at 430°C agree within ± 1% with 1000 hour weight losses at 316°C. Figure 4 is a plot of weight losses from rapid testing at 430°C and 450°C against long-term values after 1000 and 2000 hours. A first order regression fit to the two data sets is linear with a correlation coefficient of 0.99. Therefore, the rapid test method results can be used to approximate the more traditional long-term oxidative weight losses requiring much longer aging times.

CONCLUSIONS

The rapid air oxidation test is convenient for evaluating the oxidative stability of carbon fibers for screening and quality control purposes. Most PAN-based carbon fibers give satisfactory weight losses after 60 hours at 430°C or 450°C, and the results correlate well with long-term aging for 1000 or 2000 hours at 316°C. The 345 GPa fibers exhibited exceptional oxidation resistance; even the more severe rapid test temperature of 470°C gave marginal weight losses while long-term aging at 371°C required thousands of hours to achieve reasonable weight losses.

Table 1. Typical Properties of PAN-based Carbon Fibers Used in This Study

Fiber Type	Carbon Assay (%)	Filament Diameter (microns)	Density (Mg/m3)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Commercial Availability
T-300 3,6,12K	92	7	1.76	3.65	231	Available
T-500 12K	92	7	1.79	4.00	244	Discontinued
T-650/35 3K	94	6.8	1.77	4.55	241	Available
T-650/42 12K	94	5.1	1.78	5.03	290	Available
T-600/50C 12K	96	5.1	1.71	4.14	348	Discontinued
T-650/50X 12K	99	5.1	1.74	4.48	345	Discontinued

Table 2. Rapid Air Oxidation Test Results at Temperatures of 430°C to 470°C

		Percent Weight Loss in Air for 60 Hours					
Fiber	Trace	430°C(1)		450°C(2)		470°C(1)	
Type	No.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
T-300 3K	3L0802	9.86	0.65	28.26	4.41		
T-300 6K	6L1217	6.73	0.68	20.85	3.24		
T-300 12K	12L1008	7.70	0.98	21.03	3.19		
T-500 12K	12J0528	5.54	0.98	16.16	3.87		
T-650/35 3K	B3L0906	5.44	0.42	13.41	1.85		
T-650/42 12K	B12L0450	4.89	0.16	10.90	1.23		
T-650/50C 12K	B12L0803					1.66	0.21
T-650/50X 12K	B12L0802			0.28	0.059	0.96	0.31
(1) 19 packages per yarn type; test 3 samples each package							
(2) 10 packages per yarn type; test 3 samples each package							

Table 3. Long-Term Weight Losses for Carbon Fibers Oxidized in Air at 316°C

	Average Percent Weight Loss for Fiber*							
Exposure Time (Hours)	T-300 3K	T-300 6K	T-300 12K	T-650/35 3K	T-500 12K	T-650/42 12K	T-600/50C 12K	T-650/50X 12K
235	0.74	0.68	0.76	0.58	0.82	0.53	0.005	0.033
500	2.42	1.94	2.05	1.42	1.53	1.33	0.041	0.038
800	6.27	4.50	4.47	3.05	2.98	2.62	0.052	
1000	10.96	7.51	7.61	4.81	4.67	3.90	0.053	0.055
1250	17.96	12.44	12.20	7.80	7.50	5.78	0.095	
1500	24.92	17.25	16.95	11.06	10.41	7.56	0.10	0.10
2000	37.84	27.76	26.94	19.09	17.49	11.35	0.10	0.18
2500	52.20	41.83	39.85	30.83	27.32	17.04	0.13	0.21
3000	64.22	54.37	52.00	43.09	38.81	23.83	0.17	0.20
3500				53.82	49.09	31.17	0.25	0.24
4000				62.84	57.76	37.91	0.23	0.28
4500						45.71	0.27	
5000						54.00	0.30	
5500						62.03	0.33	0.31
6000							0.37	0.34
7000							0.41	0.37
8000							0.52	0.46
*One spool each fiber type with 5 to 7 samples per spool								

Table 4. Long-Term Weight Loss for 207-276 GPa Modulus Fibers in Air at 371°C

Fiber	Weight Loss (%) After 500 Hours	
Type	Average	Std. Dev.
T-300 3K	77.78	3.95
T-300 6K	65.55	6.04
T-300 12K	66.41	6.74
T-650/35 12K	58.08	4.60
T-500 12K	49.40	6.37
T-650/42 12K	30.69	4.43

Table 5. Long-Term Weight Losses for 345 GPa Modulus Fibers in Air at 371°C

Exposure Time (Hours)	Weight Loss (%) For: T-600/50C	T-650/50X
500	0.62	0.44
1000	1.29	0.79
2000	2.57	1.58
4000	5.34	3.45
6000	8.05	5.32
8000	10.73	7.37
10000	12.85	9.02
12000	16.88	12.05
14000	20.16	14.52
16000	23.53	16.87
18000	26.80	19.19
20000	30.16	21.54
21000	31.86	

ACKNOWLEDGMENTS

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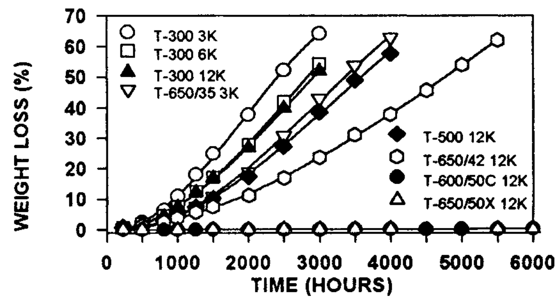

Figure 1. Weight losses for carbon fibers in air at 316°C.

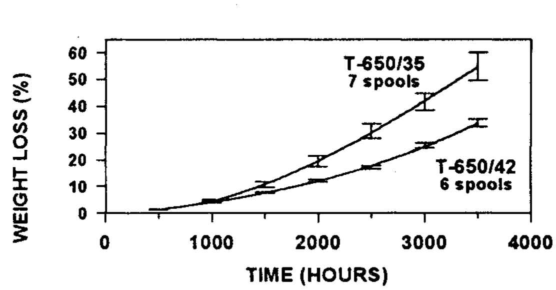

Figure 2. Weight Losses of 241 and 290 GPa fibers in air at 316°C. Error bars show one standard deviation.

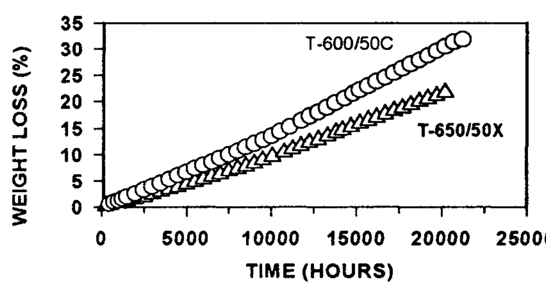

Figure 3. Weight losses of 345 GPa fibers in air at 371°C.

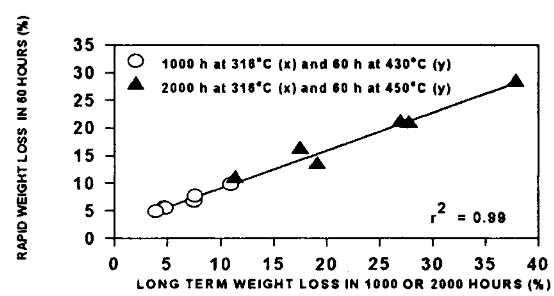

Figure 4. Correlation of rapid and long term weight loss.