Effects of Sequential Treatment With Fluorine and Bromine on Graphite Fibers

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ABSTRACT

Three pitch based graphite fibers with different degrees of graphitization and one polyacryonitrile (PAN) based carbon fiber from Amoco Corporation were treated with 1 atm, room temperature fluorine gas for 90 hr each. Fluorination resulted in higher electrical conductivity for all pitch fibers. Further bromination after ambient condition defluorination resulted in further increases in electrical conductivity for less graphitized, less structurally ordered pitch fibers (P-55) which contain about 3 percent fluorine by weight before bromination. This product can be stable in 200 °C air, or 100 percent humidity at 60 °C. Due to its low cost, this less graphitized fiber may be useful for industrial application, such as airfoil deicer material. The same bromination process, however, resulted in conductivity decreases for fluorine rich, more graphitized, structurally ordered pitch fibers (P-100 and P-75). Such decreases in electrical conductivity were partially reversed by heating the fibers at 185 °C in air. Differential scanning calorimetric (DSC) data indicated that the more graphitized fibers (P-100) contained BrF_3, whereas the less graphitized fibers (P-55) did not. DSC data also showed that some exothermic reactions, presumably the reaction between carbon and fluorine to form covalent bonds, start at 120 °C for less graphitized fibers (P-55). The weight data suggests the fluorine to carbon atom ratio was 3 for more graphitized fibers (P-100),

and 1 or 2 for less graphitized fibers (P-55). Fluorination reduces the electrical conductivity of PAN based carbon fibers (T-300). Under high temperature vacuum heating, this fluorinated PAN fibers returned to the mass and conductivity of their pristine values.

INTRODUCTION

Bromination of Amoco P-100 graphite fibers results in a 5-fold increase in electrical conductivity (Refs. 1 and 2). The brominated fibers are potentially useful in fabricating materials for electromagnetic interference shielding, aircraft lightening strike protection, and aircraft deicing (Ref. 1). Halogenation of graphite fibers by other than bromine is not well understood. However, highly graphitized graphite materials can also be intercalated with fluorine in the presence of metal fluorides at room temperature, with up to a factor of 11 increase in conductivity (Refs. 3 to 6).

In order to determine if fluorine intercalated fibers are better than brominated fibers in terms of conductivity increase and environmental stability, the fluorination of three pitch fibers with different degrees of graphitization and one PAN fiber in the presence of CuF_2 was studied. Subsequent bromination of the fluorinated products was also studied to determine how further bromination effects the conductivity and stability of the fluorine intercalated fibers. The potential benefits of using these new products in the applications described above were also discussed.

EXPERIMENTAL METHODS

The fibers used in this work were Amoco P-100, P-75, P-55, and T-300 fibers. The P-100 and P-75 are highly graphitized, structurally ordered pitch fibers. The P-55 is a less graphitized, less structurally ordered pitch fiber. The T-300 is a PAN based carbon fiber.

One gram of anhydrous cupric fluoride (CuF_2) powder was spread along the bottom of a 33 cm long copper boat. The fibers described above were also

placed on the boat. One type of fiber was fluorinated in a run. The boat was then placed in a 2.54 by 45.72 cm nickel tube reactor. The fibers were fluorinated by flowing 1 atm fluorine gas through the nickel tube at room temperature for 90 hr.

The samples were then transferred to the ambient conditions for defluorination. After the sample weight indicated the completion of room temperature defluorination, every fluorinated pitch fiber sample (P-100, P-75, and P-55) was divided into three parts. One sample was left in ambient conditions until further bromination. The other two were respectively heated to 185 °C for 3 days in air, and 420 °C for 3 hr followed by 520 °C for 3 hr in vacuum. The heating temperature 185 °C was chosen to determine if the fluorinated pitch fibers could be used to fabricate composite materials with epoxy which cures at this temperature. The resulting data can also be used to compare the thermal stability of fluorinated pitch fibers and brominated P-100 fibers, which are stable to 200 °C in air (Ref. 1). The high temperature vacuum heating histogram was chosen to avoid the complication of overshoot of fiber temperature to much higher than 500 °C during the initial heating period.

All pitch fiber samples were then placed in saturated bromine vapor at room temperature and pressure for 7 days. The samples were then transferred to the ambient condition for debromination. After sample weight indicated completion of room temperature debromination, every brominated fiber sample was divided into two parts. One was left in ambient conditions, the other was heated to 185 °C in air for 3 days.

In addition to the vaporous bromination described above, liquid bromination of fluorinated P-55 was also conducted. This liquid bromination process and the resulting fibers are potentially useful for industrial application because P-55 fibers are much less expensive than P-75 and P-100 fibers, and liquid bromine was speculated to react faster with the fibers than

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vaporous bromine because of its higher bromine concentration. Fluorinated P-55 was immersed in liquid bromine for 3 days at room temperature. The samples were then transferred to the ambient conditions for debromination. After sample weight indicated the completion of room temperature debromination, the fibers were divided into three parts, they were, respectively, left in ambient conditions, heated to 185 °C in air for 3 days, and heated to 300 °C in air for 6 days. The resulting fibers were also tested for stability at 200 °C and 100 percent humidity at 60 °C.

The P-100 and P-55 fiber samples were also examined after treated with 1 atm fluorine at room temperature for 90 hr without adding CuF_2 to the nickel reactor. Data from this experiment were used to tell the significance of CuF_2 in the fluorination reaction. Although a 1 in. section of cooper tube near the inlet of the fluorine gas stream might react with fluorine to form CuF_2 in the gas stream, the quantity of the CuF_2 thus formed was believed to be too small to be significant in this experiment.

The fluorinated PAN fibers (T-300) were treated differently because fluorination affected them differently. After the sample weight indicated the completion of room temperature defluorination, the fluorinated fiber sample was divided into six parts. These were, respectively, left in the ambient conditions, heated overnight in air at 50, 100, 150, and 200 °C, and heated for 3 hr in vacuum at 420 °C followed by 3 hr in vacuum at 520 °C.

Differential scanning calorimetry (DSC) data on four selected samples were studied. The samples were fluorinated T-300 (PAN) fibers, fluorine and saturated vaporous bromine treated P-100 (highly graphitized pitch) fibers, fluorine and saturated vaporous bromine treated P-55 fibers, and fluorine and liquid bromine treated P-55 fibers. Each sample was scanned twice during heating. From these data, evaporation from the sample and chemical reaction in the sample during the first scan were detected.

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The electrical conductivity and mass of each sample before and after each of the processes described above were measured.

RESULTS AND DISCUSSION

In the DSC data (Figs. 1 to 3), the vertical distance between the two heating scans resulted from both evaporation from the sample and chemical reaction in the sample during the first heating scan. For fluorine and vaporous bromine treated P-100 fibers (Fig. 1), this vertical distance reaches a maximum value near 135 °C, the boiling point of BrF_3. But for fluorinated P-55 fibers, which were subsequently brominated by vaporous (Fig. 2) or liquid (Fig. 3) bromine, no such maximum value can be observed, suggesting that very little BrF_3 was in these fibers. Instead, it shows an exothermic reaction starting at about 120 °C. It is speculated that the formation of carbon-fluorine covalent bonds is responsible for this exothermic peak. The exothermic reaction for fibers brominated by liquid bromine is much slower than that brominated by vaporous bromine. Based on this result and the weight data, fibers with high bromine concentration were found to have a slower exothermic reaction than those with low bromine concentration. Therefore, bromine is not likely to be a reactant of this reaction.

All mass and electrical resistivity values P-100, P-75, and P-55 fibers after each treatment described in this report are summarized in Table I. The resistivity values of pristine and bromine treated fibers are also included in this table for comparison.

Comparing the weight data in Table I to that obtained by Nakajima et al., the products described in this report are stage 1, 2, and 3 mix-stage compounds for P-100 and P-75 fibers, and stage 6 or higher for P-55 fibers.

Table I also shows that, during fluorination, P-100 fibers gained more weight in the nickel environment than in the CuF_2 environment. But P-55 gained less weight in the nickel environment than in the CuF_2 environment.

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More work is needed to determine the reason for such differences and the role of CuF_2 and nickel during the fluorination reaction.

From Table I, the atomic ratio values of all unheated, fluorine and bromine treated fibers were calculated. From these atomic ratio values, the empirical formulas of the intercalated fibers were obtained. The suggested empirical formulas and the atom ratio values are summarized in Table II. These empirical formulas suggest that, after fluorination and bromination, one bromine atom and one or two fluorine atoms formed stable compounds with P-55 fibers, while one bromine atom and three fluorine atoms formed stable compounds with P-75 or P-100 fibers. The DSC data confirmed that BrF_3 was present in P-100 fibers but was absent in P-55 fibers.

The fluorine to carbon atom ratio in fluorine intercalated P-100 and P-75 fibers (0.053 to 0.077, respectively) are twice and three times of the bromine to carbon atom ratio in brominated P-100 and P-75 fibers (0.026 in both cases, (Refs. 1 and 7)). However, the effect of fluorination on electrical conductivity of these fibers (about three fold increase) is less than that caused by bromination (about five fold increase). This suggests that either the number of intercalant atoms per charge transfer or carrier mobility of fluorine intercalated fibers is different from that of brominated fibers.

The halogen to carbon atom ratios for the three particular fibers described in the last paragraph are 1, 2, and 3 times 0.026. It is not clear whether this is a result of different stage numbers for these three fibers, different intercalant concentrations between the carbon layers for these three fibers or coincidence.

Bromination of fluorinated fibers increases the fiber electrical conductivity if the fluorine content in the fiber is low and the fiber structure is not orderly (e.g., fluorinated P-55 fibers). However, at high fluorine concentration in ordered fiber structure (e.g., fluorinated P-75 and

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P-100 fibers deintercalated at room temperature), bromine reacts with fluorine, forms BrF_3, reduces the amount of charge transfer between carbon and halogen, and therefore decreases the fiber electrical conductivity (Table I).

Bromine does not react with P-55 fibers. However, fluorine in the presence of copper fluoride does react with P-55. Furthermore, after fluorine intercalation, which produces $C_{52}F$ fibers, the fluorinated P-55 fibers can react with bromine and produce fibers with electrical conductivity about three times the pristine value. This result is in parallel with a previous report showing iodine does not intercalate with pristine graphite, but can intercalate with the residue compound of bromine intercalated graphite (Ref. 8).

Bromination of fluorine intercalated P-55 fibers by liquid bromine produced fibers with slightly higher electrical conductivity, and much higher bromine concentration and thermal stability than those produced by vaporous bromine. Electrical resistance of fibers produced by liquid bromine increased 2 percent after 3 days of exposure to 100 percent humidity and 60 °C. At 200 °C in air, the electrical resistivity of this fiber kept increasing for more than 7 days and appeared to approach a certain value asymptotically. Seven days of 200 °C air heating caused a 3.7 percent increase in the average fiber resistivity. For industrial application of this fiber, the fiber needs to be stable at 200 °C for fabricating composite materials, and the processing time needs to be short. Therefore, heat treating the fibers to temperatures above 200 °C for a short time before composite fabrication is suggested. It was observed that after 3 days at 300 °C in air, the resistivity of these fibers increased 7.3 percent ± 1 percent. Further heating at 200 °C for 2 weeks caused additional 1 percent resistivity increase.

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Similar to the DSC data of the fluorine and bromine treated P-55 (Figs. 2 and 3), the DSC data of the fluorinated PAN fibers (T-300) showed the same exothermic reaction during the first heating scan, but to a much less extent (Fig. 4). Except during this exothermic reaction at 120 to 180 °C, the difference of these two scans increases with temperature, with the first scan at higher vertical position than the second scan. This suggests that evaporation from fluorinated T-300 fibers occured during the two heating scans.

Figure 5 shows the electrical resistivity and fluorine concentration data for all fluorinated T-300 fibers. Fluorination increases the electrical resistivity of these fibers. High temperature treatment of the fluorinated T-300 fibers reduces their electrical resistivity. Heating these fibers in vacuum at 420 °C for 3 hr and then 520 °C for 3 hr reduces the fiber weight to 99 percent of the carbon weight in the unheated fibers. It also decreases the fiber elctrical resistivity to the pristine value. This phenomenon was not observed by Nakashima in their work on more graphitized PAN fibers (Ref. 3). It is therefore believed to be resulting from the degree of graphitization, not from the type of the fibers. These data agree with the DSC data described in the last paragraph. They suggest that fluorine was not intercalated with, but absorbed by, the T-300 fibers during fluorination.

CONCLUSION

Fluorination of a PAN fiber (T-300) at room temperature resulted in decrease in fiber conductivity by a factor of 2. Vacuum heating at 520 °C on fluorinated PAN (T-300) fibers reversed its conductivity and mass to the original pristine values.

Fluorination of three different pitch fibers (P-100, P-75, and P-55) at room temperature in the presence of CuF_2 resulted in an increase in fiber conductivity by a factor of 4, 4, and 2, respectively. Vacuum heating cannot reverse their conductivity and mass to the original pristine values.

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Bromination of fluorinated highly graphitized pitch fibers (P-100) resulted in fibers containing BrF_3. This bromination process caused a decrease in fiber electrical conductivity.

Less graphitized pitch fibers (P-55) do not react with bromine. However, the fibers do react with fluorine in the presence of CuF_2. Bromination of this less graphitized fluorinated pitch fiber results in fibers containing fluorine and bromine atoms with fluorine to bromine atomic ratios being 1 or 2. According to DSC data, this fiber did not contain BrF_3. Unlike fluorinated P-100 or P-75, bromination of fluorinated P-55 results in increasing electrical conductivity.

If liquid bromine was used for brominating fluorinated P-55, the brominated product has electrical conductivity three times of the pristine value, and is stable at 200 °C air and 100 percent humidity at 60 °C, making it suitable for industrial application environments.

ACKNOWLEDGMENT

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TABLE I. - ELECTRICAL RESISTIVITY AND HALOGEN CONTENT OF PITCH BASED
FIBERS THROUGHOUT THE PROCESS OF FLUORINATION, HEATING,
BROMINATION, AND FURTHER HEATING

Fiber type		P-100			P-75			P-55			
Pristine resistivity Brominated resistivity, $\mu\Omega$-cm		250 50			500 100			900 900			
First step treatment[a]		F	FH	FHH	F	FH	FHH	F	FH	FHH	L
Second step treatment[b]											
Resistivity, $\mu\Omega$-cm	None	84 c130	148	402	125	188	729	574 c635	746	687	574
	B	111	106	344	189	118	535	379	758	722	315
	BH	215	206	332	279	310	555	845	746	696	325
Total halogen to carbon weight ratio x 100	None	8.5 c27	4.2	5.8	12	8.1	7.1	3.0 c1.4	1.8	1.2	3.0
	B	20.0	18.1	10.6	27.7	24.2	15.6	9.8	6.2	6.0	14.9
	BH	9.2	10.2	8.4	14.9	14.5	12.6	7.9	5.2	2.2	14.0

[a]The first step halogenation
 F:Fluorination
 FH:Fluorination followed by 185 °C heating in air for 3 days
 FHH:Fluorination followed by vacuum heating at 420 °C for 3 hr and then 520 °C for 3 hr
 L:Identical to F, except in the subsequent bromination, liquid bromine was used for 3 days. All other bromination use vaporous bromine for 7 days.
[b]The second step halogenation
 B:Bromination for 7 days
 BH:Bromination for 7 days followed by heating at 185 °C air for 3 days.
[c]These data were from the fluorination experiment without copper fluoride added to the reactor. All other data were from fluorination experiments with copper fluoride added to the reactor

TABLE II. – ATOMIC RATIO AND EMPIRICAL
FORMULAS FOR FLUORINE AND BROMINE
TREATED, UNHEATED PITCH
BASED FIBERS

	F/Br	C/F	C/Br	Suggested empirical formula
P-100	3.1	19	59	$C_{60}BrF_3$
P-75	3.2	13	42	$C_{40}BrF_3$
P-55[a]	1.9	52	99	$C_{100}BrF_2$
P-55[b]	0.94	52	49	$C_{50}BrF$

[a]From vaporous bromine reaction.
[b]From liquid bromine reaction.

FIGURE 1. – DIFFERENTIAL SCANNING CALORIMETRY
DATA ON HIGHLY GRAPHITIZED PITCH FIBERS (P-100)
WHICH WAS FLUORINATED AND THEN BROMINATED BY
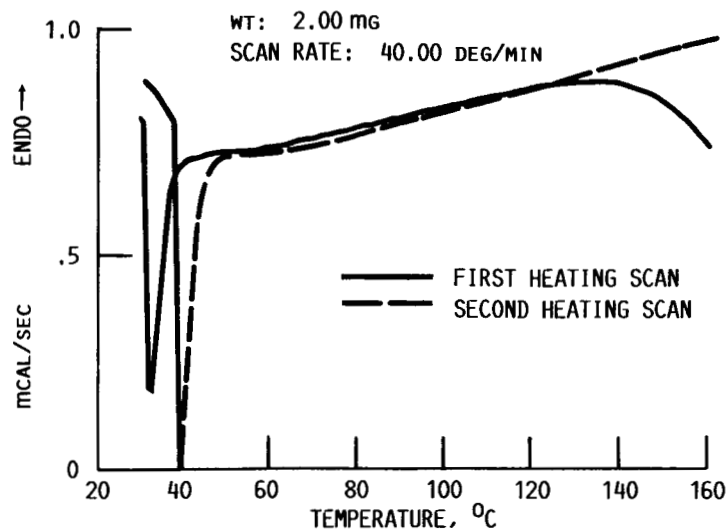SATURATED BROMINE VAPOR.

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WT: 2.00 mg
SCAN RATE: 40.00 DEG/MIN

FIRST HEATING SCAN
SECOND HEATING SCAN

ENDO →

mCAL/SEC

TEMPERATURE, °C

FIGURE 2. - DIFFERENTIAL SCANNING CALORIMETRY DATA
ON ORDINARY PITCH FIBERS (P-55) WHICH WAS FLUORI-
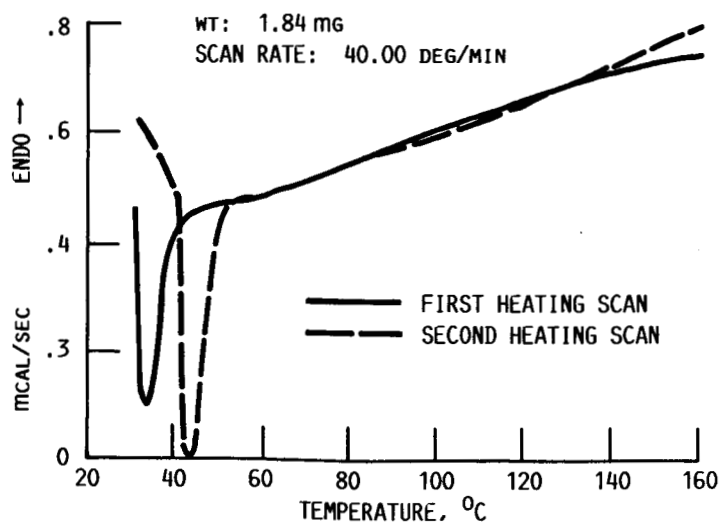NATED AND THEN BROMINATED BY SATURATED BROMINE
VAPOR.

WT: 1.84 mg
SCAN RATE: 40.00 DEG/MIN

FIRST HEATING SCAN
SECOND HEATING SCAN

ENDO →

mCAL/SEC

TEMPERATURE, °C

FIGURE 3. - DIFFERENTIAL SCANNING CALORIMETRY DATA
ON ORDINARY PITCH FIBERS (P-55) WHICH WAS FLUORI-
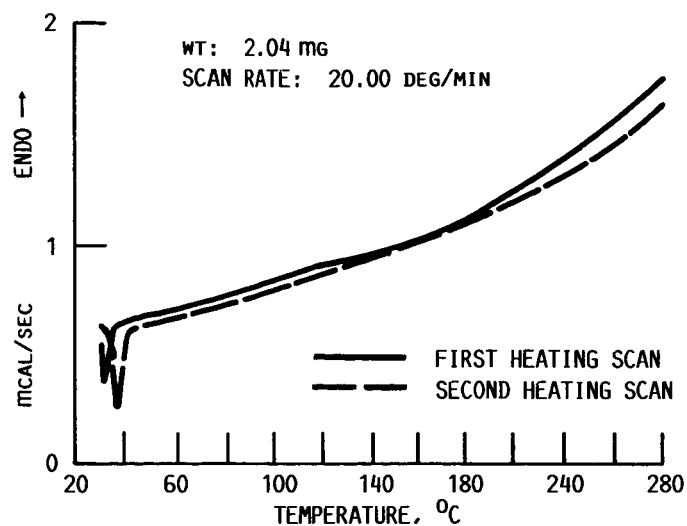NATED AND THEN BROMINATED BY LIQUID BROMINE.

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FIGURE 4. - DIFFERENTIAL SCANNING CALORIMETRY DATA
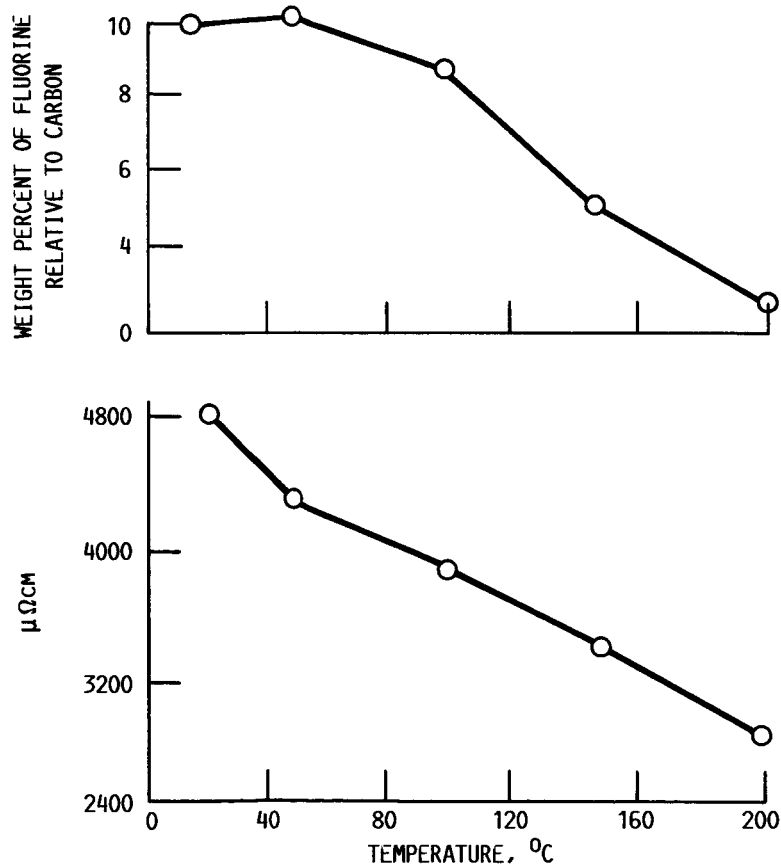ON FLUORINATED POLYACRYONIYRILE (PAN) FIBERS
(T-300).

FIGURE 5. - COMPOSITION AND ELECTRICAL RESISTIVITY
OF FLUORINATED T-300 FIBERS AFTER 16 HOURS OF
HEATING.

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16. Abstract

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