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EFFECT OF BROMINATION ON THE OXIDATION RESISTANCE OF PITCH-BASED CARBON FIBERS

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Abstract—Bromination was found to increase the oxidation resistance of Thornel P-100 pitch-based carbon fibers in the temperature range from 675 to 925°C, whereas it decreased the oxidation resistance of P-X-7 pitch-based carbon fibers. The increased oxidation resistance may be due to bromine adsorption or the electron transfer from the graphite to the bromine. However, the pronounced intercalation in brominated P-X-7 (which is more graphitic than P-100) probably causes physical damage which decreases the oxidation resistance.

Key Words—Carbon fibers, oxidation, bromine, intercalation, pitch, oxidation resistance, oxidation protection.

1. INTRODUCTION

The insufficient oxidation resistance of carbon fibers is a serious problem which affects the high temperature applications of carbon fibers and their composites (including carbon-carbon composites). In order to alleviate this problem, ceramic coatings are used[1]. This paper, instead, explores the use of bulk chemical modification of the carbon fibers to improve the oxidation resistance.

Because pitch-based carbon fibers are in general more graphitic than PAN-based carbon fibers, they were chosen for this study. In particular, a type of pitch-based fibers used was Amoco's Thornel P-100. Brominated Thornel P-100 fibers have an electrical resistivity of 50 $\mu\Omega$.cm and are stable in air, vacuum, high humidity and temperatures up to 200°C[2]. Moreover, bromination improves the electromagnetic interferences (EMI) shielding effectiveness of the P-100 fibers[3].

2. EXPERIMENTAL

2.1 *Materials preparation and analysis*

Two types of pitch-based carbon fibers were used. They were Thornel P-100 and P-X-7, both kindly provided by Amoco. Although both types are among the most graphitic kinds of carbon fibers, P-X-7 is even more graphitic than P-100.

Bromination of either type of fibers was carried out by exposure of the fibers (without resin sizing) to bromine vapor in air at room temperature for at least 6 days. After that, the fibers were removed from the bromination vessel and placed under a fume hood, where bromine desorption at room temperature was allowed from the brominated fibers.

The bromine content as a percentage of the weight of the pristine carbon fibers was measured by weighing with a Perkin–Elmer AD-2Z autobalance. Furthermore, the extent of bromine desorption as a function of temperature up to 1000°C was monitored by thermogravimetry, which was performed in air by using the Perkin–Elmer AD-2Z autobalance in conjunction with a Thermcraft resistance tube furnace. The heating rate was 10°C/min. The oxidation of the carbon fibers was negligible in this temperature range and at this heating rate, as confirmed by mass spectroscopic detection of evolved CO_2 as a function of temperature.

Figures 1 and 2 show the thermogravimetric data for brominated P-100 and brominated P-X-7 respectively. The data for brominated P-100 were obtained after five days of room temperature desorption; the data for brominated P-X-7 were obtained after three days of room temperature desorption. Both sets of data show an onset of significant bromine desorption at 100°C, which is the temperature for in-plane melting of graphite intercalated with bromine[4]. However a clearer onset was observed for brominated P-X-7 than brominated P-100.

Electron diffraction using a JEOL-100CX transmission electron microscope was performed to look for the presence of in-plane intercalate ordering at room temperature. The hk0 diffraction pattern characteristic of the superlattice in-plane intercalate ordering of graphite intercalated with bromine[4] was observed in brominated P-X-7, but no in-plane superlattice was observed in brominated P-100.

Differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-2 system was performed to look for the presence of the endothermic (upon heating) peak at 100°C corresponding to the in-plane melting of graphite intercalated with bromine. This peak was indeed observed for brominated P-X-7, but was not observed for brominated P-100.

The above-mentioned analysis of the two types of brominated fibers shows that brominated P-X-7 is definitely intercalated, such that its room tempera-

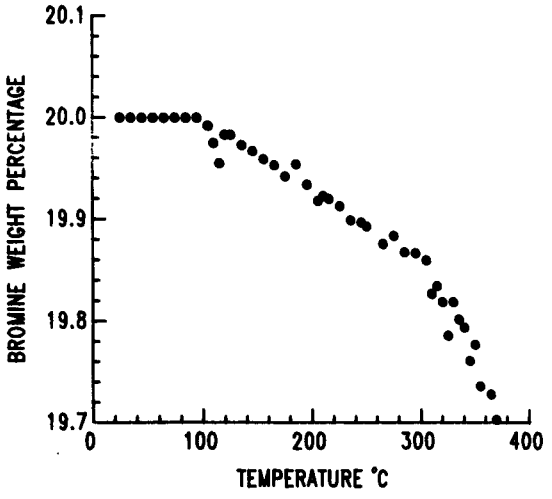

Fig. 1. Thermogravimetric data of brominated P-100 fibers during temperature increase at 10°C/min.

ture structure is similar to that reported for highly oriented pyrolytic graphite (HOPG) intercalated with bromine[4]. However, brominated P-100, whether or not truly intercalated, does not possess at room temperature the usual structure of HOPG intercalated with bromine. The structure of brominated P-100 is the subject of another paper[5].

The electrical resistivity of the fibers was measured at room temperature by applying the four-probe method on single fibers. The electrical contacts were made by using silver paint. The results for pristine (untreated) and brominated fibers of each of the two types are shown in Table 1. The resistivity was decreased by a factor of about 4 by brominating either type of fibers. This indicates the occurrence of electron transfer in both types of brominated fibers and is consistent with previous reports on the decrease of the electrical resistivity by the bromination of carbon fibers[2,3,6,7].

Table 1. Electrical resistivity

Fiber Type	Electrical Resistivity (Ω.cm)	
	Before Bromination	After Bromination
P-100	1.7×10^{-4}	4.3×10^{-5}
P-X-7	9.5×10^{-5}	2.6×10^{-5}

2.2 *Oxidation resistance characterization*

The oxidation resistance of the fibers in air was studied isothermally at various temperatures as well as during temperature scanning.

The isothermal study was made by measuring the weight of a bunch of fibers (typically about 20 mg in weight) after various periods of heating at a chosen temperature. The heating took place in static air in a box furnace with a heated volume of 0.0101 m^3. Due to the large volume of the furnace and the small volume of the fibers, the absence of forced air circulation in the furnace did not affect the quality of the results. The weighing was performed at room temperature using a Perkin–Elmer AD-2Z autobalance, which has a sensitivity of 0.1 μg. Heating of a fiber sample was interrupted at 15 min intervals for the purpose of weighing.

Figure 3 and 4 show the isothermal weight loss data for pristine P-100 and brominated P-100 respectively. Bromination caused a substantial increase of the oxidation resistance at 700 and 750°C, while the effect at 600 and 800°C was small.

Figure 5 and 6 show the isothermal weight loss data for pristine P-X-7 and brominated P-X-7 respectively. Bromination significantly decreased the oxidation resistance at all temperatures.

Comparison of Fig. 3 and 5 shows that the oxidation resistance of pristine P-X-7 is superior to that of pristine P-100. This is expected since P-X-7 is more graphitic than P-100.

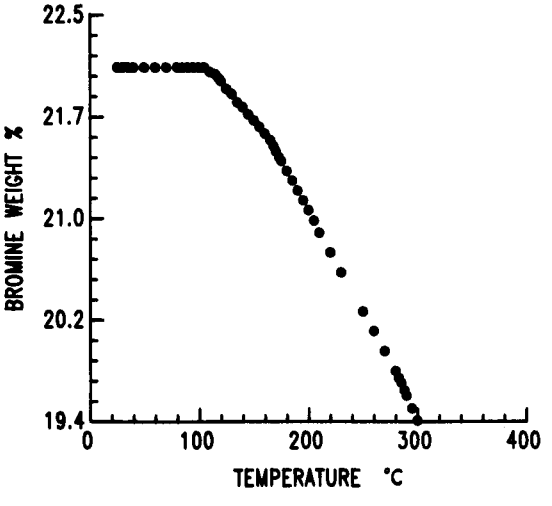

Fig. 2. Thermogravimetric data of brominated P-X-7 fibers during temperature increase at 10°C/min.

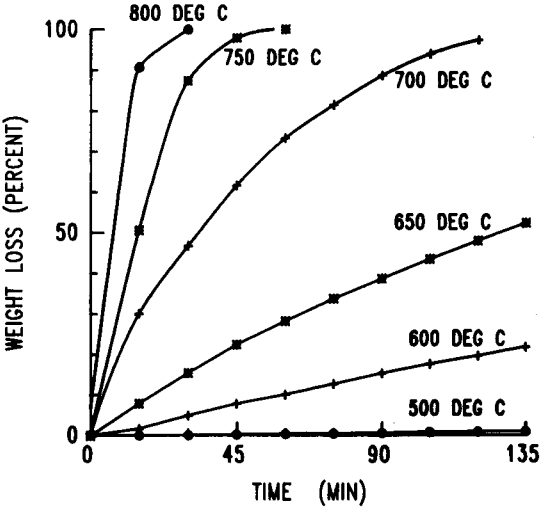

Fig. 3. Isothermal percentage weight loss as a function of time for pristine P-100 fibers.

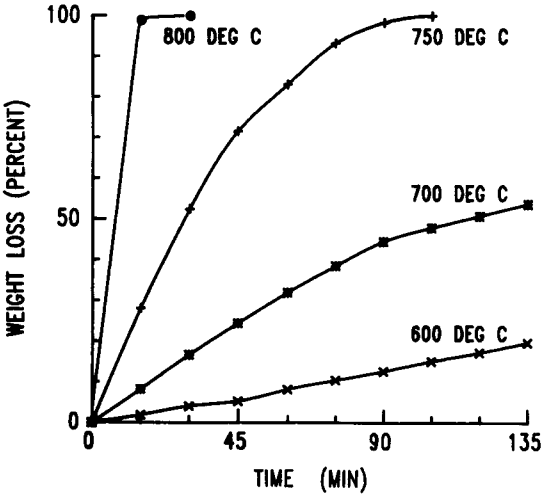

Fig. 4. Isothermal percentage weight loss as a function of time for brominated P-100 fibers.

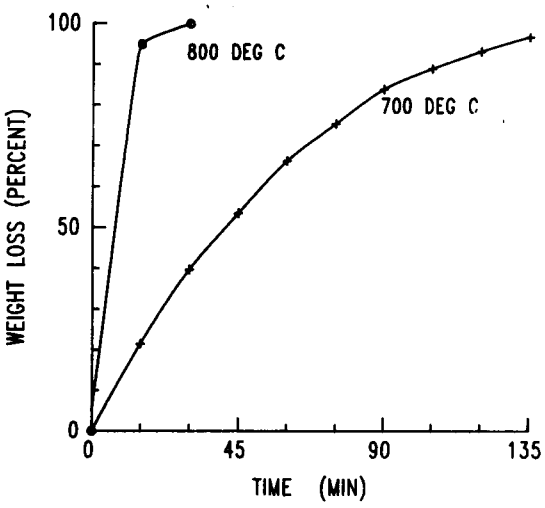

Fig. 6. Isothermal percentage weight loss as a function of time for brominated P-X-7 fibers.

The oxidation resistance of the fibers was also investigated during temperature scanning at a heating rate of 20°C/min. During heating the weight of the fibers was measured in situ using a Perkin–Elmer AD-2Z autobalance and the relative amount of evolved bromine vapor and the relative amount of evolved CO_2 vapor were monitored by using a VG Instruments Inc. 1–300 amu quadrupole mass spectrometer equipped with a glass-lined capillary inlet. Figures 7–9 show such three sets of data obtained from brominated P-100 fibers. The fibers had been desorbed at room temperature for 4 days prior to these measurements. Figure 7 shows the weight loss curve up to 1000°C. As the weight loss has two contributions (one from bromine desorption and the other from the oxidation of the carbon), the mass spectrometric data in Fig. 8 and 9 (circles) are valuable for distinguishing between these two contributions. Figure 8 gives the contribution from bromine desorption (mass number = 160), while Fig. 9 (circles) gives that from carbon oxidation (evolution of CO_2 at a mass number of 44). Figure 8 shows that bromine desorption is important at low temperatures (especially below 400°C), while Fig. 9 (circles) shows that the oxidation of carbon is important at high temperatures (especially above 775°C). Moreover, Fig. 8 shows that bromine desorption is negligible above 900°C, while Fig. 9 (circles) shows that the oxidation of carbon is negligible below 625°C. Thus, the sharp weight loss at about 750°C in Fig. 7 is attributed to the oxidation of carbon.

For studying the oxidation resistance of brominated P-100, Fig. 9 (circles) is most relevant. The corresponding set of data for pristine P-100 is shown by the dashed curve in Fig. 9. Comparison of the two curves in Fig. 9 shows that bromination increases the oxidation resistance most significantly at 675–

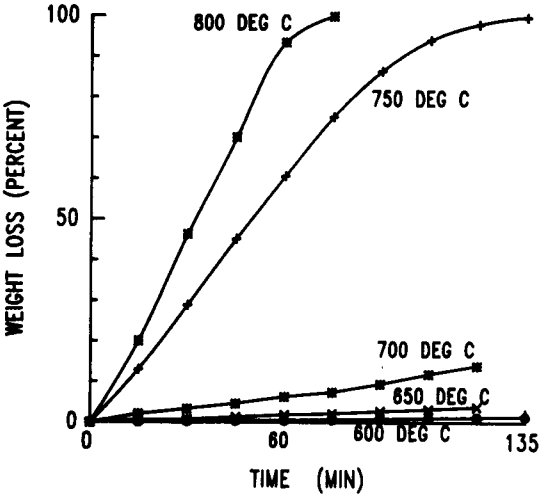

Fig. 5. Isothermal percentage weight loss as a function of time for pristine P-X-7 fibers.

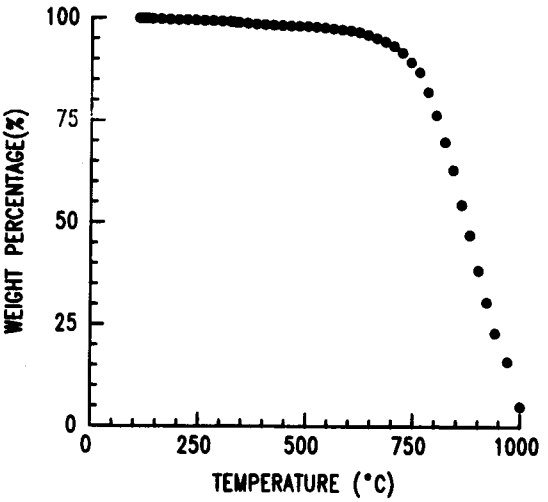

Fig. 7. Thermogravimetric data of brominated P-100 fibers during temperature increase at 20°C/min.

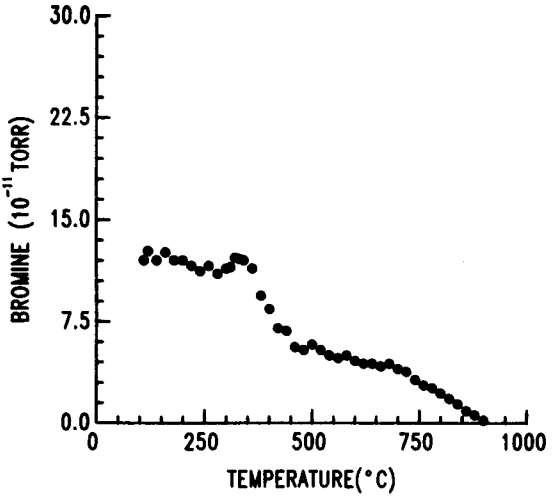

Fig. 8. Relative amount of bromine evolved during temperature increase at 20°C/min for brominated P-100 fibers.

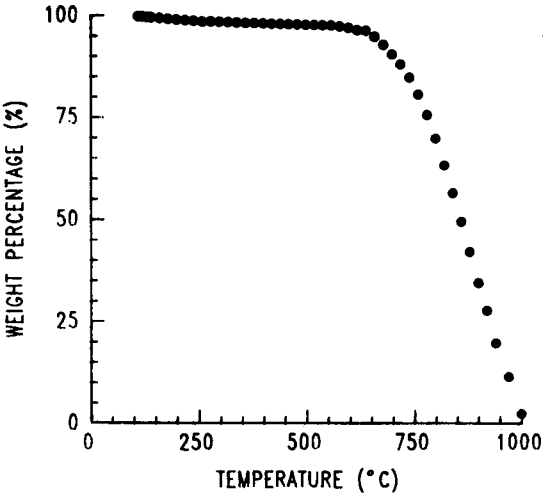

Fig. 10. Thermogravimetric data of brominated P-X-7 fibers during temperature increase at 20°C/min.

800°C, less significantly at 800–925°C and negligibly at other temperatures. This temperature dependence is consistent with the isothermal result in Fig. 3 and 4.

Data corresponding to Fig. 7–9 but for brominated P-X-7 (also desorbed at room temperature for 4 days prior to the measurements) are shown in Fig. 10–12. Figure 11 shows that the bromine desorption occurs mainly below 500°C and is negligible above 900°C. Figure 12 (circles) shows that the oxidation of carbon occurs above 625°C. Data corresponding to Fig. 12 but for pristine P-X-7 is shown by the dashed curve in Fig. 12. Comparison of the two curves in Fig. 12 shows that bromination decreases the oxidation resistance of P-X-7 in the temperature range from 625 to 925°C.

Comparison of Fig. 1 and 2 shows that brominated P-X-7 prior to heating has a slightly higher bromine concentration than brominated P-100 prior to heating. Comparison of Fig. 8 and 11 shows that brominated P-X-7 desorbs bromine more readily than brominated P-100. This suggests that the chemistry of the bromine in P-X-7 is different from that in P-100. This difference is consistent with the difference in structure between the two types of brominated fibers.

3. CONCLUSION

In this work, the oxidation resistance of P-100 carbon fibers was found to be increased by bromination, whereas that of P-X-7 carbon fibers was found to be decreased by bromination. This effect may be due to the bromine adsorption, as adsorbed halogens inhibit carbon oxidation[8]. However, it may also be attributed to the electron transfer from the graphite to the bromine, thereby increasing the

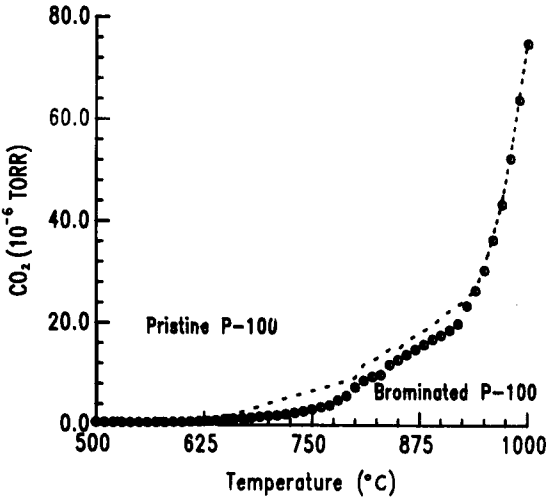

Fig. 9. Relative amount of CO_2 evolved during temperature increase at 20°C/min for brominated P-100 fibers (circles) and pristine P-100 fibers (dashed curve).

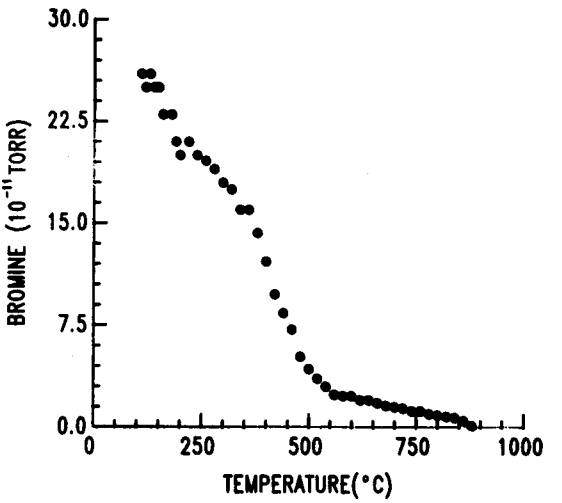

Fig. 11. Relative amount of bromine evolved during temperature increase at 20°C/min for brominated P-X-7 fibers.

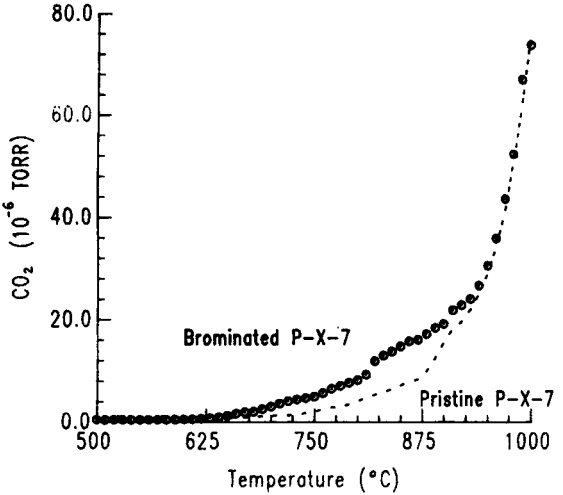

Fig. 12. Relative amount of CO_2 evolved during temperature increase at 20°C/min for brominated P-X-7 fibers (circles) and pristine P-X-7 fibers (dashed curve).

oxidation resistance of P-100. However, for P-X-7, due to its graphitic nature, the bromine intercalation is pronounced and may cause physical damage, which overshadows the bromine adsorption or charge transfer effect and decreases the oxidation resistance of the fibers. Physical damage may be in the form of an increase in the surface area or porosity. It has been observed by scanning electron microscopy in truly intercalated graphite-bromine (not fibers)[4].

The increased oxidation resistance of P-100 fibers only occurs in a limited temperature range, from 675 to 925°C. This effect is partly due to the slow oxidation rate below 675°C. It is probably also due to either the over-abundance of thermal energy for electron removal from the carbon above 925°C (in spite of the depressed Fermi level in the brominated fibers) or the poisoning of the adsorbed bromine above 925°C. Further work is necessary to ascertain the origin of this effect.

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