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BROMINATION OF GRAPHITIC PITCH-BASED CARBON FIBERS

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Abstract—Bromination of the du Pont E-130 pitch-based carbon fibers was found to degrade the tensile strength, tensile modulus and oxidation resistance. This degradation was greater when bromination was carried out by exposure to bromine vapor than by the electrochemical method, and is attributed to the physical damage of bromination. This degradation is in contrast to the beneficial effect of bromination of less graphitic fibers, such as Amoco's Thornel P-100. However, bromination decreased the electrical resistivity by up to a factor of 5. This effect is due to the intercalation of bromine, as indicated by the in-plane intercalate superlattice order at room temperature and up to 100°C, at which temperature in-plane melting occurred for fibers brominated by either method. A sharp intercalate Raman peak was observed at 240 cm^{-1}, in contrast to the large breadth of this peak in Thornel P-100 fibers.

Key Words—Carbon fibers, bromine, intercalation, oxidation, Raman, melting.

1. INTRODUCTION

In the last few years, there has been much research work on brominated pitch-based carbon fibers[1–12]. Most of this work was focused on brominated Thornel P-100 pitch-based carbon fibers of Amoco Corp. (formerly Union Carbide Corp.)[1–9], because the bromination of P-100 fibers essentially did not affect the mechanical properties[5], while the oxidation resistance was enhanced[2,3] and the electrical resistivity was decreased to values as low as 50 μΩ.cm (comparable to the value for stainless steel)[4,5]. One of the main applications is in electromagnetic interference (EMI) shielding[5].

The effect of bromination on electrical resistivity was less pronounced in Thornel P-75 fibers than Thornel P-100 fibers. The resistivity of P-75 fibers was decreased by a factor of 4 ± 1 by bromination, whereas that of P-100 fibers was decreased by a factor of 5 ± 1[6]. This effect is related to the less graphitic nature of P-75 fibers compared to P-100 fibers, as indicated by the lower tensile modulus of P-75 fibers. The modulus is 520 GPa for P-75 fibers and is 724 GPa for P-100 fibers. The effect of bromination on electrical resistivity was about the same in Thornel P-100 and P-120 fibers, even though P-120 fibers are more graphitic than P-100 fibers[6]. The tensile modulus of P-120 fibers is 827 GPa, compared to a value of 724 GPa for P-100 fibers. Bromination decreased the tensile modulus of P-120 fibers by 23% and decreased the strength of P-120 fibers by 38%[11]. This suggests that bromination induced flaws in P-120 fibers[11].

Differential scanning calorimetry (DSC) showed an endothermic peak at around 100°C upon heating in vapor brominated, vapor grown, carbon fibers that had been heat treated at 2550°C or above, but no DSC peak was observed in vapor brominated P-100 or P-120 fibers[6]. The fact that in-plane melting of the bromine intercalate superlattice occurs at 100°C in highly oriented pyrolytic graphite (HOPG) intercalated with bromine, as shown by diffraction[13,14] and DSC[15], suggests that in-plane superlattice ordering of the bromine occurs in the vapor grown carbon fibers below around 100°C, but not in P-100 or P-120 fibers below 100°C. Hence, there is a substantial difference in structure between brominated P-100 or P-120 fibers and brominated, vapor grown, carbon fibers that were all brominated by exposure to bromine vapor.

The graphite layers of P-120 fibers are parallel to the fiber axis, such that they are oriented like the PAN-AM logo. The graphite layers of the vapor grown carbon fibers are parallel to the fiber axis, such that they are oriented in the form of concentric cylinders. Either type of microstructure, together with the high degree of graphitization, facilitates flaw propagation. It would be of interest to see how bromination affects graphitic fibers with graphite layers parallel to the fiber axis, such that they are oriented randomly. Such pitch-based fibers have recently become available from E. I. du Pont de Nemours & Co., Inc., which labeled them as E-130. The bromination of these fibers is therefore the subject of this paper.

Table 1 shows the properties of the du Pont E-130 fibers compared with those of the P-75, P-100 and P-120 fibers. The tensile strength, tensile modulus, and elongation at break of the du Pont fibers are all greater than those of the P-75, P-100, and P-120 fibers. The superior mechanical properties of the du Pont fibers make these fibers practically important. Therefore, bromination of the du Pont fibers deserves investigation.

In this paper, we brominated the du Pont E-130 carbon fibers by the vapor method as well as the

Table 1. Properties of pristine pitch-based carbon fibers*

	Amoco			Du Pont
	P-75	P-100	P-120	E-130
Tensile strength (GPa)	1.9	2.2	2.2	3.8
Tensile modulus (GPa)	520	724	827	897
Elongation at break (%)	0.4	0.31	0.27	0.5
Density (g/cm^3)	2.0	2.15	2.18	2.19
Electrical resistivity (μΩ.cm)	700	250	220	300
Diameter (μm)	10	10	10	10

*All data were provided by the fiber manufacturers.

Table 3. Tensile properties of du Pont E-130 fibers

Fiber type	Modulus (GPa)	Strength (GPa)	Ductility (%)
Pristine	886 ± 29	3.79 ± 0.36	0.51 ± 0.04
Type II	770 ± 26	3.18 ± 0.28	0.49 ± 0.06
Type I	735 ± 39	2.48 ± 0.32	0.49 ± 0.03

electrochemical method. In the case of P-100 fibers, the two methods of bromination gave brominated fibers that are different in structure[2]. Fibers brominated by the vapor method are called Type I; fibers brominated by the electrochemical method are called Type II. For brominated P-100 fibers, Type I and Type II differ in structure in the following ways[2].

1. Type I exhibits in-plane disorder at room temperature; Type II exhibits in-plane superlattice order at room temperature.
2. Type I undergoes in-plane melting at −2°C (271 K); Type II undergoes in-plane melting at 100°C (373 K).
3. Intercalation is more homogeneous in Type II than Type I.
4. The chemical state of the intercalated bromine is more uniform in Type II than Type I.

Although P-100 fibers had been brominated by both vapor and electrochemical methods[2], P-120 and the vapor grown carbon fibers had only been brominated by the vapor method[6]. However, DSC results[2,6] suggest that Type II P-100 fibers and Type I vapor grown carbon fibers are similar in structure, both exhibiting in-plane superlattice order up to about 100°C, at which point in-plane melting occurs. This paper provides a systematic comparative investigation of Type I and Type II du Pont E-130 fibers.

2. EXPERIMENTAL

2.1 *Sample preparation*

The carbon fibers used were continuous, pitch-based, and kindly provided by du Pont. They are labeled E-130. Bromination of the carbon fibers was carried out using two methods.

Table 2. Electrical resistivity of du Pont E-130 fibers

	Resistivity (μΩ.cm)
Pristine	287 ± 16
Type II	104 ± 7
Type I	62 ± 3

Method 1 involved exposure of the fibers to bromine vapor in air at room temperature for seven days. After that, the carbon fibers were removed from the bromination vessel and placed under a fume hood, where bromine desorption at room temperature was allowed from the brominated carbon fibers for three days. Fibers prepared using this method are labeled Type I.

Method 2 involved anodic oxidation of the carbon fibers in an electrolyte, which was a saturated aqueous potassium bromide solution. The fibers were suspended in the electrolyte by a platinum wire and basket, which served as the anode. Electrical contact between the fibers and the platinum basket was rendered by pressure. Another platinum wire served as the cathode. Anodic oxidation was performed at a constant current of 0.5 mA for 72 h. The set-up was the same as that of ref. 2. The curve of potential versus time during the anodic oxidation was smooth, exhibiting no step. This implies the absence of pure stages. The fibers prepared by using this method are labeled Type II.

The fractional weight increase relative to the weight of pristine fibers was about 22.8% for Type I and 16.2% for Type II, as measured with a Perkin-Elmer AD-2Z autobalance. The weight increase for Type II includes the weight of the small amount of KBr crystals that remained on the surface of the fibers after drying.

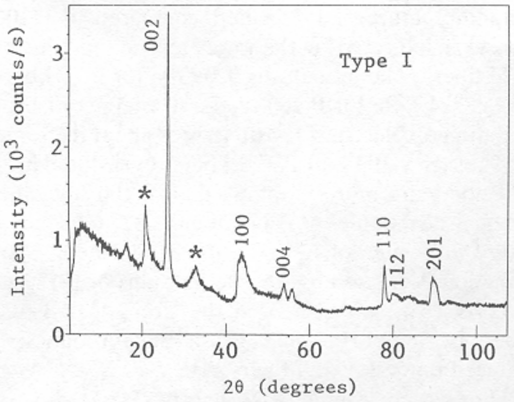


Fig. 1. X-ray diffraction pattern of Type I du Pont E-130 fibers at room temperature. The Miller indices correspond to graphite. The in-plane intercalate superlattice peaks are labeled by *.

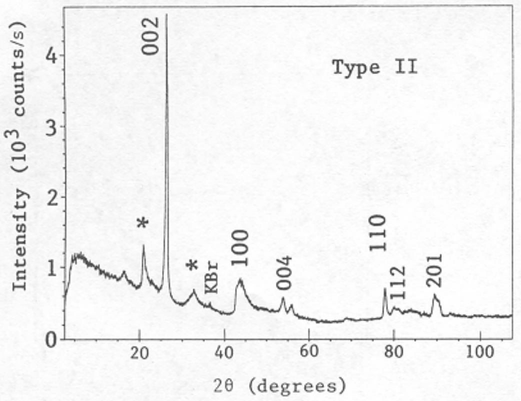


Fig. 2. X-ray diffraction pattern of Type II du Pont E-130 fibers at room temperature. The Miller indices correspond to graphite. The in-plane intercalate superlattice peaks are labeled by *.

2.2 *Electrical resistivity*

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 fiber diameters were measured by scanning electron microscopy (SEM) of the tips of about 11 fibers of each type. Bromination increased the fiber diameter from an average of 10.15 ± 0.19 μm to an average of 11.2 ± 0.26 μm. The average diameter values were used in calculating the resistivity. The results for pristine (untreated) Type I and Type II fibers are shown in Table 2. The resistivity was decreased by a factor of about 5 by Method 1 and a factor of about 3 by Method 2.

The percentage decrease in resistivity was much greater for Type I than Type II. This is consistent with the much larger weight uptake for Type I than Type II.

2.3 *Mechanical properties*

Tensile tests were performed on untreated fibers, Type I, and Type II fibers. The tests were carried out using an Instron Model 1000 tensile tester. Individual fibers of each type were attached to card stock "picture frame" mounts (gage length 0.5 ≤ L ≤ 2.5 cm) with epoxy cement. Fiber diameters were measured as described in section 2.2.

Table 3 shows the tensile modulus, tensile strength, and tensile ductility (elongation) for the untreated, Type I, and Type II fibers. The modulus was decreased by 17% with Method 1 and by 13% with Method 2. The strength was decreased by 35% with Method 1 and by 16% with Method 2. The ductility was decreased slightly by both methods. The decreases in modulus and strength are more than what the fiber cross-sectional area increase (10%) can account for.

2.4 *Structure*

X-ray diffraction was performed at room temperature in the transmission mode with the diffraction

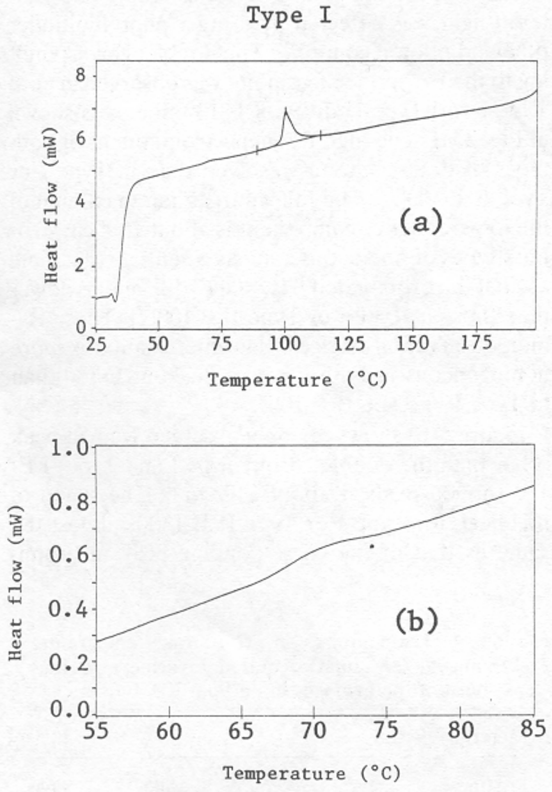


Fig. 3. DSC thermogram of Type I du Pont E-130 fibers during heating. (b) shows part of (a) in enlarged scale.

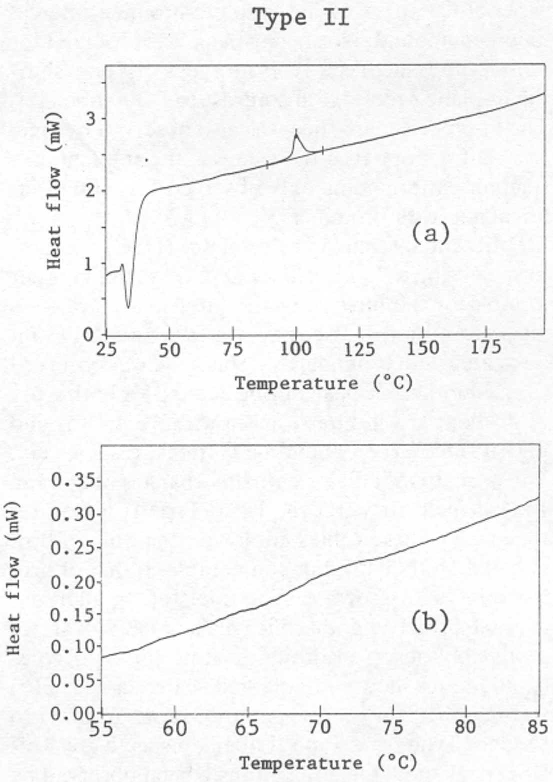
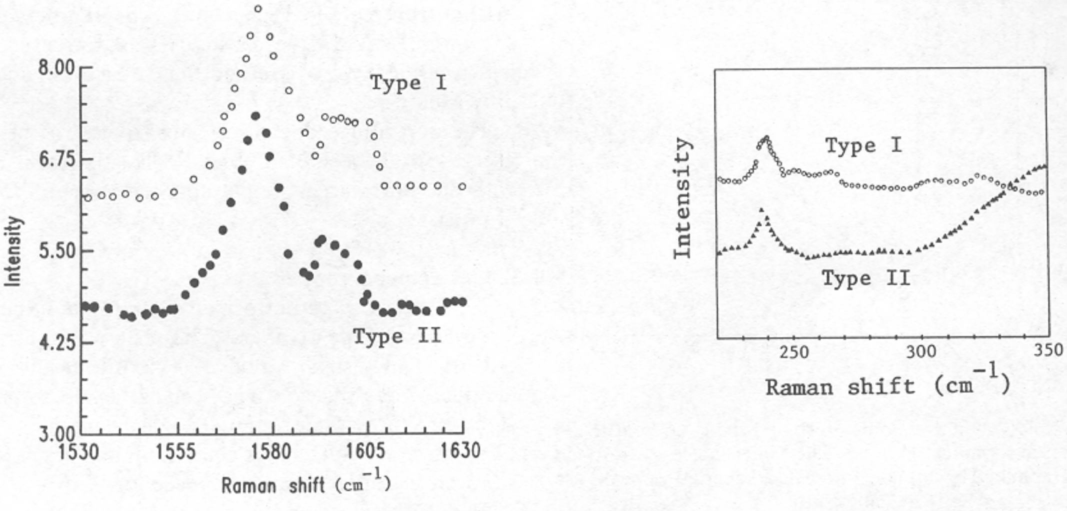


Fig. 4. DSC thermogram of Type II du Pont E-130 fibers during heating. (b) shows part of (a) in enlarged scale.



(a) (b)

Fig. 5. Raman spectra of Type I and Type II du Pont E-130 fibers during heating. (a) shows the doublet corresponding to the E_{2g_2} mode of graphite. (b) shows the intercalate peak.

plane perpendicular to the fiber axis. A Stoe X-ray diffractometer system was used, with CuKα radiation and a 41° curved position sensitive detector. Figures 1 and 2 show diffraction patterns obtained on Type I and Type II du Pont E-130 samples, each weighing about 4.1 mg. Most of the peaks in the diffraction pattern were labeled with the Miller indices of graphite or labeled with * for the in-plane superlattice peaks of the graphite-bromine intercalation compound. No staging peak was observed for both Type I and Type II. Both types of fibers show the in-plane ordering, in contrast to P-100 fibers[2]. The in-plane superlattice was also observed by electron diffraction. It is the same as the in-plane diffraction pattern commonly observed for HOPG intercalated with bromine[13].

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 system in order to look for the melting of the intercalate layers—a phase transition that occurs at 100°C in HOPG intercalated with bromine[15]. This peak was observed as an endothermic peak during heating for both types of du Pont E-130 fibers, as shown in Fig. 3(a) and Fig. 4(a) for Type I and Type II fibers, respectively. The peak areas indicate enthalpy changes of 151 and 106 cal/mole Br_2 for Type I and Type II fibers, respectively. These values are lower than that of brominated HOPG[15], but comparable to that of brominated vapor-grown carbon fibers[6]. In addition, a small broad endothermic peak at 68°C was reproducibly observed during heating for both types of fibers, as shown in enlarged scales in Fig. 3(b) and Fig. 4(b) for the temperature range from 55 to 85°C for Type I and Type II fibers, respectively. This DSC peak at 68°C had previously been observed by Jaworske et al.[6] for brominated graphitized vapor-grown carbon fibers. It may be due to the commensurate-incommensurate phase transition observed in stage 4 graphite-bromine at 69°C (342 K)[14,16]. No peak was observed at 271°K, which was the in-plane intercalate melting transition temperature of Type I P-100 fibers.

Raman scattering was performed in the 180°C backscattering geometry using the 5145 Å line of an argon ion laser operating at a power of 250 mW. The scattered light was detected by using a photomultiplier tube and photon counting. The doublet corresponding to the E_{2g_2} mode of graphite was observed in both Type I and Type II du Pont E-130 fibers, as shown in Fig. 5(a). The high frequency component of both types of fibers is better resolved than in Type I or Type II P-100[2]. The full width at half maximum of the low frequency component is about 15.4 cm^{-1} for both types of fibers; this value is essentially the same as that in brominated HOPG[17,18] and is lower than those in Type I or Type II P-100[2]. These Raman observations suggest that intercalation is more homogeneous in both types of du Pont E-130 than in Type I or Type II P-100.

Figure 5(b) shows the only observed Raman peak other than the doublet. Both Type I and Type II E-130 show a peak at about 240 cm^{-1}. The shape of this peak for Type I or Type II E-130 is almost the same as that of the corresponding peak in bromi-

Table 4. Temperatures in °C (during temperature scanning at 20°C/min) required to achieve various burn-off percentages in du Pont E-130 fibers

Material	5%	15%	25%	40%
Pristine	694	760	806	864
Type II	642	713	741	806
Type I	631	692	729	795

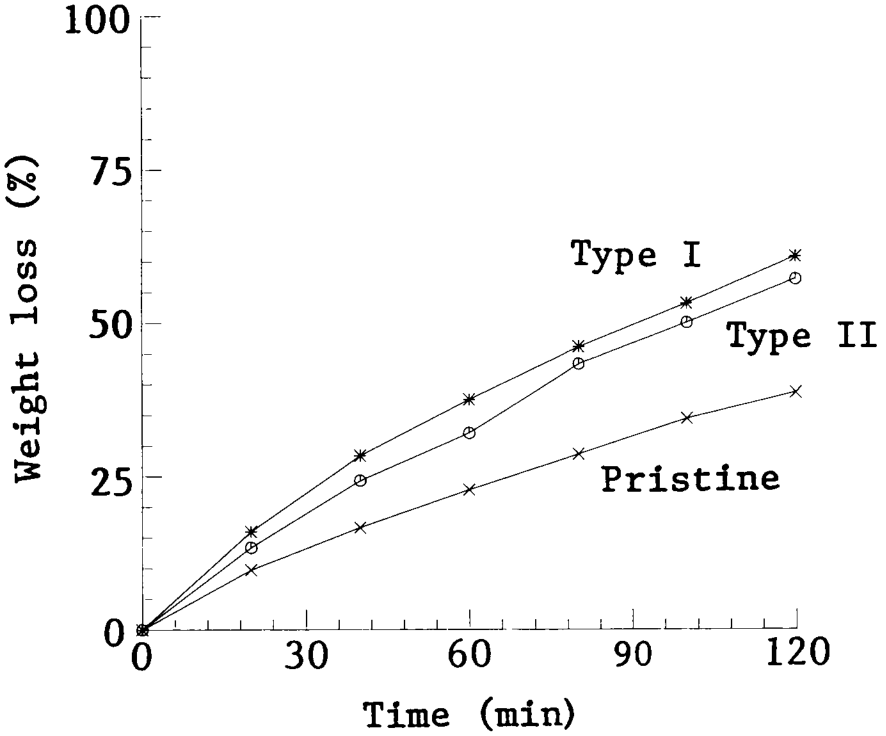


Fig. 6. Weight loss as a function of time at 650°C for du Pont E-130 pristine, Type II, and Type I fibers.

nated HOPG[17,18], and is much sharper than that of Type I or Type II P-100 fibers. This result suggests that the chemical state of bromine in both types of E-130 fibers is more uniform than that in Type I or Type II P-100 fibers, and the chemical state of bromine in both types of E-130 fibers is similar to that of brominated HOPG.

2.5 *Oxidation resistance*

The oxidation resistance of the fibers was studied 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. Table 4 shows the temperatures required to achieve 5, 15, 25, and 40% burn-off in air for pristine, Type I, and Type II du Pont E-130 fibers. The oxidation resistance thus clearly follows the trend: pristine > Type II > Type I.

The isothermal study was carried out 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. Because of the large volume of the furnace and the small volume of fibers, the absence of forced air circulation in the furnace did not affect the quality of the results. The heating of a fiber sample was interrupted at 20 min intervals for the purpose of weighing.

The weight loss of the three types of du Pont E-130 fibers as a function of time at 650°C is shown in Fig. 6. The oxidation resistance of the fibers is again seen to follow the trend: pristine > Type II > Type I.

Table 5 shows the oxidation rate at 25% weight loss (determined from the slope of isothermal weight loss curves, such as Fig. 6, at 25% weight loss) for pristine, Type I, and Type II fibers at 650, 700 and 750°C. The oxidation rate at each temperature again shows that the bromination decreased the oxidation resistance, such that the oxidation resistance follows the trend: pristine > Type II > Type I.

2.6 *Microstructure*

The effect of bromination on the microstructure of the fibers was studied by SEM. Bromination by either Method 1 or 2 had no effect on the cross-sectional morphology. Shown in Fig. 7 is an SEM photograph of the cross-section of a Type I du Pont E-130 fiber. The random orientation of the graphite layers is seen in this photograph.

Bromination by either Method 1 or Method 2 caused physical damage to the du Pont E-130 fibers in the form of cracks mainly along the fiber axis, as shown

Table 5. Oxidation rate measured at 25% burn-off

	Oxidation rate (min^{-1})		
Material	650°C	700°C	750°C
Pristine	0.34	0.92	1.63
Type II	0.61	1.51	2.90
Type I	0.71	1.84	3.70

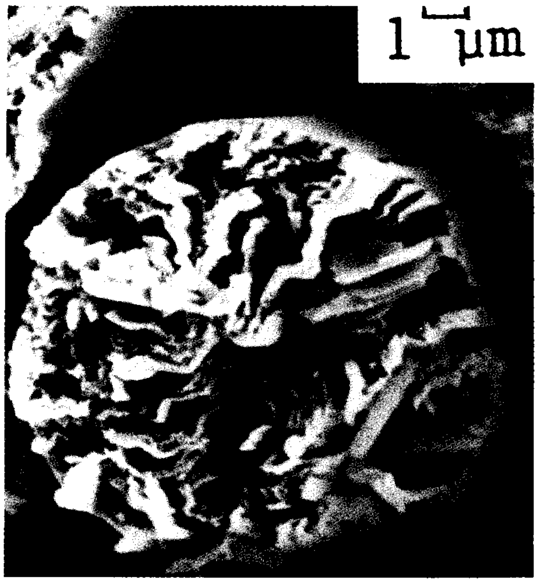


Fig. 7. SEM photograph of a Type I du Pont E-130 fiber, showing the cross-sectional view.

in Fig. 8, which is the side view of a Type I E-130 fiber. The fraction of damaged fibers in a given sample was higher for Type I fibers than for Type II fibers.

2.7 *Comparison with Amoco P-X-7 carbon fibers*

We have also performed similar studies on Type I Amoco P-X-7 carbon fibers. The P-X-7 fibers are pitch-based and are experimental in nature, but they are even more graphitic than the P-120 fibers. The results obtained on the brominated P-X-7 fibers are essentially the same as those obtained on the brominated du Pont E-130 fibers. In other words, for the brominated P-X-7 fibers, in-plane intercalate superlattice order occurred at room temperature and up to 100°C, at which point in-plane melting occurred. In addition, bromination caused physical damage and decreased the oxidation resistance of the P-X-7 fibers.

The similarity between brominated Amoco P-X-7 fibers and brominated du Pont E-130 fibers suggests that a high degree of graphitization rather than certain processing parameters is mainly responsible for the observed behavior in the du Pont E-130 fibers.

3. CONCLUSION

Bromination of du Pont E-130 carbon fibers by either Method 1 (vapor) or Method 2 (electrochemical) degraded the tensile strength and modulus, as well as the oxidation resistance, such that Method 1 caused more degradation than Method 2. This degradation is due to the physical damage caused by the bromination. However, the extent of degradation is less than that of P-120 fibers[11].

Bromination of du Pont E-130 fibers by either Method 1 or Method 2 decreased the electrical resistivity, such that the decrease was larger for Method 1 than Method 2. The abovementioned difference between Type I (Method 1) and Type II (Method 2) du Pont E-130 fibers is due to the larger bromine uptake in Type I than Type II.

Both Type I and Type II du Pont E-130 fibers exhibited in-plane intercalate ordering at room temperature and up to 100°C, at which temperature in-plane melting occurred. The chemical state of the bromine was as homogeneous as that of bromine in HOPG, as shown by Raman scattering. This homogeneity of Type I or Type II E-130 fibers was superior to that of Type I or Type II P-100 fibers. These results are due to the fact that pristine E-130 fibers are more graphitic than pristine P-100 fibers.

The structures of Type I and Type II E-130 fibers are similar, whereas those of Type I and Type II P-100 fibers are quite different. This is due to the dependence of the ease of intercalation on the degree of graphitization, and this dependence is different in vapor phase intercalation (Method 1) and electrochemical intercalation (Method 2). For Method 1, the ease of intercalation increases with increasing degree of graphitization[19]; easier intercalation is associated with the development of the in-plane intercalate superlattice order, which is present in Type I E-130 fibers (this work) and absent in Type I P-100 fibers[2]. For Method 2, the dependence of the ease of intercalation on the degree of graphitization is not a simple one, as Method 2 fails to intercalate

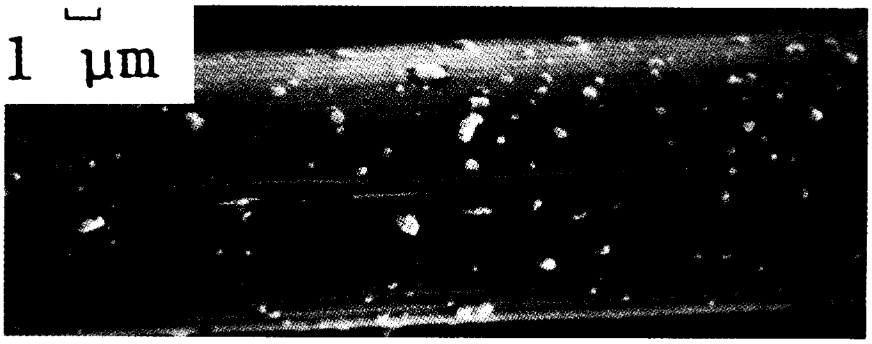


Fig. 8. SEM photograph of a Type I du Pont E-130 fiber, showing the side view.

HOPG[2], which is more graphitic than the du Pont E-130 fibers.

Bromination decreased the oxidation resistance of the du Pont E-130 fibers, whereas it increased the oxidation resistance of the P-100 fibers. This difference is due to the physical damage that bromination caused in the E-130 fibers. The damage overshadows the role of bromine adsorption and charge transfer in increasing the oxidation resistance.

Vapor brominated du Pont E-130 fibers, Amoco P-X-7 fibers, vapor grown carbon fibers, and HOPG exhibit in-plane intercalate superlattice order at room temperature and up to around 100°C. On the other hand, vapor brominated Amoco P-120 and P-100 fibers exhibit in-plane intercalate disorder at room temperature. The difference between these two groups of carbon materials lies mainly in the degree of graphitization. A high degree of graphitization is needed for the development of in-plane intercalate superlattice order. Accompanying the ready and extensive intercalation is the physical damage, which caused degradation in the mechanical properties and decrease of the oxidation resistance.

Although du Pont E-130 fibers, Amoco P-X-7 fibers, vapor grown carbon fibers, and HOPG are very different in crystallographic texture, they all belong to the first group of carbon materials mentioned above. This means that the crystallographic texture is not important compared to the degree of graphitization in determining the readiness and extent of intercalation.

Vapor-phase bromination degrades the tensile properties of E-130 [this work] and P-120 fibers[11] by similar percentages. The decrease in tensile modulus is 17% for E-130 and 23% for P-120; the decrease in tensile strength is 35% for E-130 and 38% for P-120. This similarity is in contrast to the difference in intercalate structure, which makes them belong to two different groups of carbon materials, as classified above. That the P-120 fibers have a large degradation in mechanical properties is attributed to the more oriented carbon layers in P-120. The orientation facilitates flaw propagation. On the other hand, the E-130 fibers have carbon layers that are random in the lateral orientation. This randomness probably hinders flaw propagation, so that the degradation in mechanical properties is smaller than what is expected for a highly graphitic material after bromination.

In spite of the well-developed intercalate structure in brominated E-130 fibers and the superior mechanical properties of pristine E-130 fibers, these brominated fibers suffer from degradation in mechanical properties and oxidation resistance due to bromination. Amoco's Thornel P-100 carbon fibers remain the most suitable kind of fibers for property improvement by bromination.

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