

## STRUCTURE OF BROMINATED THORNEL P-100 CARBON FIBERS

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**Abstract**—Brominated Thornel P-100 carbon fibers are found to be intercalated, as shown by Raman scattering. X-ray diffraction and electron diffraction show that the bromine layers in the fibers are disordered at room temperature, even though all previously reported graphite-bromine phases exhibit inplane superlattice ordering at room temperature. A new phase transition at 271 K was observed by differential scanning calorimetry, electron diffraction, and the variation of the electrical resistivity with temperature; it corresponds to the reversible change between inplane disorder above 271 K to inplane superlattice order below 271 K. The  $240\text{ cm}^{-1}$  intercalate Raman peak at room temperature is much broader than that of previously reported graphite-bromine, indicating more nonuniformity in intercalate structure in the fibers. The chemical interaction between bromine and the fibers is similar to that between bromine and graphite, as shown by the increase of the bromine desorption rate at  $100^\circ\text{C}$  upon heating for both fibers and graphite and the decrease of the electrical resistivity by bromination in fibers as well as graphite. No evidence for bulk bromine in the fibers was obtained.

**Key Words**—Carbon, fiber, bromine, carbon fiber, structure, Raman, diffraction.

### 1. INTRODUCTION

Although much attention has been given to improving the mechanical properties of carbon fibers, relatively little work has been done to improve the electrical conductivity of carbon fibers. A high electrical conductivity is desirable for making airframe composite materials that can better withstand lightning strikes. Moreover, a high electrical conductivity enables better shielding of electromagnetic interference (EMI), whether the interference is from radar signals, infrared signals (for defense), or electronics.

In the recent few years, considerable research work has taken place in the Lewis Research Center of NASA to improve the electrical conductivity of carbon fibers for the above-mentioned applications[1]. It was thus found that brominated pitch-based carbon fibers (namely brominated Thornel P-100 carbon fibers of Amoco, formerly Union Carbide) have an electrical resistivity of  $50\ \mu\Omega\text{ cm}$  (comparable to the value for stainless steel) and are stable in air, vacuum, high humidity, and temperatures up to  $200^\circ\text{C}$ [2]. Moreover, the EMI shielding effectiveness is greatly improved by the bromination[1]. Even though the mechanical properties of the fibers themselves are not affected by bromination, the interlaminar shear strength of the brominated fiber-epoxy composite is 18% greater than its pristine counterpart[1].

In spite of the high potential for technological applications of brominated pitch-based carbon fibers, very little work has been done to understand the chemical and physical nature of the bromine in the fibers. Based on the lowering of the electrical resistivity by bromination, previous workers reported that the bromination was an intercalation process.

However, one should take a more objective view in considering all the possible ways of bromine incorporation in the fibers, as listed below:

1. Bromine is intercalated in the graphite lattice, i.e. it is in the form of layers between the carbon layers.
2. Bromine is in solid solution (mainly interstitial) in the graphite or carbon lattice.
3. Bromine is in the form of clusters (or precipitates) located along the grain boundaries of the graphite or carbon.
4. Bromine is in the form of clusters (or precipitates) inside the grains of the graphite or carbon.
5. Bromine is trapped at defects, such as dislocations and stacking faults, of the graphite or carbon.
6. Bromine is physisorbed on the surface of the fiber.
7. Bromine is chemisorbed on the surface of the fiber.
8. Bromine is trapped in the pores of the fiber.

In this article, X-ray and electron diffraction, Raman scattering, differential scanning calorimetry, and thermogravimetric analysis were used to study the structure of brominated Thornel P-100 fibers.

### 2. TESTS FOR INTERCALATION

"Intercalation" refers to the insertion of the intercalate layers among carbon layers. This means that the intercalate is in the form of layers and is not simply trapped at defects.

Ideally the intercalate layers and the carbon layers are periodically stacked. The number of carbon lay-

ers between nearest intercalate layers is known as the "stage" of the intercalation compound. The lower the stage, the higher the intercalate concentration. The "staging" phenomenon is clearest in intercalation compounds with stage  $\approx 4$ . As the intercalate concentration decreases, the tendency for mixed staging (i.e. coexistence of more than one stage) increases. For example, it is rare to have a pure stage 7. Furthermore, as the intercalate concentration decreases, the intercalate layers become farther apart and the tendency for staging decreases. For example, it is inconceivable to have a stage 20! Therefore, in dilute compounds, staging is unclear and hence cannot be used as a test for the occurrence of intercalation.

In concentrated compounds (which require the host material to be sufficiently graphitic), staging is clear and can be used as the test for intercalation. For probing the staging, X-ray diffraction is most commonly used. The  $00l$  diffraction pattern includes (1) strong lines that are close to (but shifted from) the graphite 002, 004, 006, etc., lines; and (2) weaker lines between the nearest strong lines. For example, in stage 2, there are two weak lines between the nearest strong lines. The observation of shifted 002, 004, and 006 graphite lines is a necessary but not sufficient test for staging. Rather, the observation of the superlattice lines is a sufficient test for staging.

Below the intercalate inplane melting temperature (which is different from the intercalate bulk melting temperature), the intercalate is ordered within an intercalate layer, forming a superlattice perpendicular to the *c*-axis. This inplane ordering is clear even when the intercalate concentration is low and staging is unclear. It has been shown that inplane ordering exists in residue graphite-bromine with an intercalate concentration of only 0.2 mole %  $\text{Br}_2$  (3 wt %)[3]. The observation of inplane intercalate ordering implies the presence of intercalate layers. Therefore, inplane intercalate ordering implies the presence of intercalate layers and thus can be used as a test for intercalation, provided that the test is made below the intercalate inplane melting temperature (which is 100°C for graphite-bromine intercalation compounds[3]). Inplane ordering can be observed by either X-ray diffraction or electron diffraction. The  $hk0$  diffraction pattern includes (1) strong graphite lines and (2) weaker superlattice lines.

Since the intercalate inplane melting temperature is a well-defined temperature that is different from the intercalate bulk melting temperature and is specific to the intercalate species, the observation of a phase transition at the appropriate intercalate inplane melting temperature is an indication of the existence of inplane intercalate ordering and thus can be used as a test for intercalation. Other phase transitions of the intercalation compound may also be used for this purpose. However, since melting is usually the dominant and most well-known phase transition, it can be observed most easily. The tran-

sition temperature may be conveniently determined by using differential scanning calorimetry (DSC) or differential thermal analysis (DTA).

A consequence of intercalation is the appearance of a Raman peak which is typically about  $20\text{ cm}^{-1}$  upshifted from the  $1580\text{ cm}^{-1}$  Raman peak of graphite ( $E_{2g_2}$ ) mode[4,5]. The upshifted Raman peak has been attributed to the graphite layers bounding the intercalate layers, whereas the Raman peak at  $1580\text{ cm}^{-1}$  has been attributed to the graphite layers not immediately adjacent to the intercalate layers[4,5]. In addition, Raman scattering can probe the intercalate modes, thus giving information on the structure of the intercalate itself. For example, graphite intercalated with bromine gives an intercalate mode at  $240\text{ cm}^{-1}$ [4,5]. Thus, Raman scattering is a good test for the occurrence of intercalation. Since the Raman effect is a near surface effect, it provides complementary information to the electrical resistivity, which is a bulk effect.

Due to the charge transfer between the intercalate and the carbon, intercalation decreases the inplane electrical resistivity of the carbon[6]. However, a decrease in the electrical resistivity does not necessarily mean that intercalation has taken place, since adsorption, for instance, might involve charge transfer and also might lead to a change in the electrical resistivity. For example, the adsorption of bromine in anthracite decreases the electrical resistivity by a factor of 3.7[7] and intercalation cannot possibly take place in anthracite (not graphitic). Therefore, a change in the electrical resistivity cannot be used as a self-sufficient test for intercalation.

Intercalation gives rise to an increase in weight of the carbon sample. However, an increase in weight does not necessarily mean that intercalation has taken place, since absorption of any kind may cause an increase in weight. Therefore, weight uptake cannot be used as a test for the occurrence of intercalation.

The ease of intercalation decreases tremendously with decreasing degree of graphitization of the carbon[8]. Under this situation, staging is not a good test for intercalation, but inplane ordering is, as explained above. As previously mentioned, X-ray diffraction or electron diffraction may be used for probing the inplane ordering. Alternatively, DSC or DTA may be used for determining the intercalate inplane melting temperature. In addition, Raman scattering is valuable for testing for intercalation and probing the structure of the bromine.

Previous authors used bromine intercalation into pyrolytic graphite, graphite flakes, or other nonfibrous graphite materials as a reference so that the resistivity technique became the main characterization tool for the intercalation of bromine into P-100 fibers. The present authors questioned this characterization technique[9] and performed a series of experiments that confirmed that intercalation had occurred, providing a more quantitative basis for the characterization of these samples.

### 3. PREVIOUS WORK

The bromination of pitch-based carbon fibers (Union Carbide's experimental Thornel Type P) was shown by Dowell[8] to cause true intercalation, as revealed by X-ray diffraction of sealed capillaries containing the powdered fibers and Br<sub>2</sub>. This was the first study of brominated pitch-based carbon fibers and turned out to be the only work that provided firm evidence for intercalation of brominated pitch-based carbon fibers.

The bromination of pitch-based carbon fibers (F54-3000°) was shown by Hooley and Deitz[10] to cause a residual bromine uptake of 1.5 moles of Br<sub>2</sub> for every 100 moles of carbon (i.e. 20% weight increase). The bromination was performed by exposing the fibers at 20°C to the saturated vapor of Br<sub>2</sub> or to a solution of Br<sub>2</sub> in nitromethane and subsequently allowing most of the absorbed bromine to desorb in a vacuum or in air at 20°C or higher. Moreover, Hooley and Deitz observed with X-ray diffraction that the interplanar spacing increased from 3.375 Å to 3.396 Å at 20°C after bromination. However, no superlattice diffraction peak was reported so there was no diffraction evidence for intercalation. In addition, Hooley and Deitz observed that the emission of Br<sub>2</sub> from its residue brominated fibers occurred mostly at about 380°C upon first heating. In contrast, truly intercalated residue graphite-bromine (flakes or pyrolytic graphite) showed a sudden onset of Br<sub>2</sub> emission at about 100°C upon first heating due to the intercalate bromine inplane melting transition at 100°C[10,11]. Thus, although the emission temperatures observed in the brominated pitch-based carbon fibers are interesting, they do not provide any evidence for intercalation. It should also be mentioned that the boiling point of bulk bromine is 58°C. The lack of Br<sub>2</sub> emission from the fibers at 58°C suggests that the bromine in the fibers is probably not in the form of bulk bromine trapped in pores or other defects.

The bromination of pitch-based carbon fibers (Union Carbide TP 4104B) had also been investigated by Dominguez *et al.* of the Naval Research Laboratory[12]. The bromination was performed by exposing the carbon fibers to Br<sub>2</sub> vapor at room temperature for approximately 24 h and subsequently bromine desorption was allowed to occur at room temperature in a fume hood until the change in weight leveled off to a constant value, which was about 10% greater than the initial weight. Again no evidence for intercalation was provided. On the other hand, the electrical resistivity, as measured by the two-point probe technique, decreased from 220 to 50 μΩ cm after both bromination and desorption, and Dominguez *et al.* interpreted this as intercalation.

The bromination of pitch-based carbon fibers (Union Carbide, 3000°C HTT) had also been investigated by Natarajan and Woollam[13], who also performed the intercalation in bromine vapor. The

electrical resistivity, as determined by the four-probe technique, was decreased by the bromination from 190 to 38.4 μΩ cm for one sample and from 190 to 56.3 μΩ cm for another sample[13], and they interpreted this as intercalation.

Most recently, the bromination of pitch-based carbon fibers (Union Carbide Thornel P-100) was extensively investigated by Gaier *et al.* of NASA[1,2]. Bromination was again performed by exposing the fibers to Br<sub>2</sub> vapor at room temperature for about 24 h[14]. The electrical resistivity, as measured by the four-point probe technique, decreased from 250 to 18 μΩ cm after bromination (before desorption) and then increased to about 50 μΩ cm after subsequent desorption in air at room temperature to an environmentally stable condition[1]. Bromination by immersion of the fibers in liquid bromine yielded similar results[15]. They interpreted this as intercalation.

DSC showed the absence of a peak at 58°C[16], suggesting the absence of bulk bromine in the NASA fibers. It also showed the absence of a peak at 100°C, suggesting the absence of in-plane order in the bromine in these fibers[16]. On the other hand, the effect of bromination on the electrical resistivity and the occurrence of slight shoulders in the curve of electrical resistivity vs. time during the desorption of the NASA fibers were used as support for the occurrence of true intercalation[17].

After bromination and desorption, the NASA fibers weighed 17%–20% more than the pristine counterpart[18]. After subsequent heating at 200°C in air for three days, the fibers then weighed 17%–18% more than the pristine counterpart; after heating at 260°C for six days, the fibers then weighed 14.5%–18% more than the pristine counterpart. Energy-dispersive X-ray spectroscopic determination of the bromine concentration profile across the diameter of a single brominated and desorbed (room temperature) fiber showed that there was less bromine near the edges than at the center of the fiber cross section[15,19]. Furthermore, scanning Auger microscopy showed no detectable bromine in the surface 30 Å layer of such a fiber[15], though the removal of the bromine by the vacuum in the microscope and by the electron beam heating cannot be ruled out.

### 4. EXPERIMENTAL

The pitch-based carbon fibers used were Thornel P-100 fibers. X-ray diffraction on this batch of pristine fibers had been previously reported[20]. The 112 graphite diffraction line was observed as a diffuse ring in the transmission Laue photograph. The same transmission Laue method was used to probe the brominated Thornel P-100 carbon fibers. In this method, MoKα radiation and a specimen-to-film distance of 6 cm were used.

We exposed Thornel P-100 fibers to bromine liquid or vapor at saturated vapor pressures at room

temperature and above to try to intercalate them. Subsequent X-ray diffraction showed no evidence for intercalation under any bromination condition, even when the fibers were sealed in glass capillaries containing liquid bromine. Exposure of the P-100 fibers to  $\text{ICl}$  vapor at room temperature again failed to yield any diffraction evidence for intercalation. However, by raising the  $\text{ICl}$  temperature to  $95^\circ\text{C}$  (as  $\text{ICl}$  boils at  $97.4^\circ\text{C}$ ), intercalation occurred, as evidenced by both staging and inplane superlattice diffraction lines[20]. Bromine and  $\text{ICl}$  are both acceptor intercalates in graphite, but  $\text{ICl}$  has a higher tendency for intercalation due to its higher reactivity. Even for  $\text{ICl}$ , true intercalation was not evidenced by X-ray diffraction at room temperature. For bromine, true intercalation was not evidenced by X-ray diffraction at any temperature. This seemingly inconsistent result compared to Dowell's result[8] is attributed to the fact that Dowell did not use P-100 fibers.

Shown in Fig. 1 is the bromine weight uptake of the P-100 fibers (after exposure to bromine vapor for seven days) as a function of time after removal of the fibers from the bromine vapor. Both bromination and desorption took place in air at room temperature. It can be seen from Fig. 1 that the bromine weight uptake in the desorbed fibers was 20%.

Because electron diffraction is sensitive to small local regions that might exhibit the inplane intercalate ordering, we used electron diffraction as a further test for the intercalation of the P-100 fibers with bromine. However, this test could only be applied to the desorbed fibers. Only graphite diffraction spots were observed. Neither diffraction spots of the intercalation compound nor those of bulk bromine were observed.

Hooley and Deitz[10] reported that bromine emission from brominated P-100 fibers occurred at about  $380^\circ\text{C}$  upon first heating. This emission temperature is high compared to that of truly intercalated graphite-bromine, which starts emitting bromine significantly at about  $100^\circ\text{C}$ [10,11]. We have thus performed thermogravimetric analysis(TGA) in air in the temperature range from 25 to  $380^\circ\text{C}$ , and at a heating rate of  $5^\circ\text{C}/\text{min}$ . The sample was P-100 fibers that had been brominated in  $\text{Br}_2$  vapor at room temperature for seven days and subsequently desorbed in air at room temperature for five days. During heating, appreciable weight loss began at about  $100^\circ\text{C}$ , as shown in Fig. 2. Hence, our TGA results are not consistent with the bromine emission result of Hooley and Deitz[10]. However, the observed weight loss onset at  $100^\circ\text{C}$  shows that the affinity of bromine with the graphite in the fibers is similar to that of bromine with highly oriented pyrolytic graphite (HOPG). The weight loss onset at  $100^\circ\text{C}$  cannot be due to adsorbed water because of the small surface area of the fibers[21].

Raman scattering was performed in the  $180^\circ$  back-scattering geometry using the  $5145 \text{ \AA}$  line of an argon ion laser operating at a power of 250 mW. The scat-

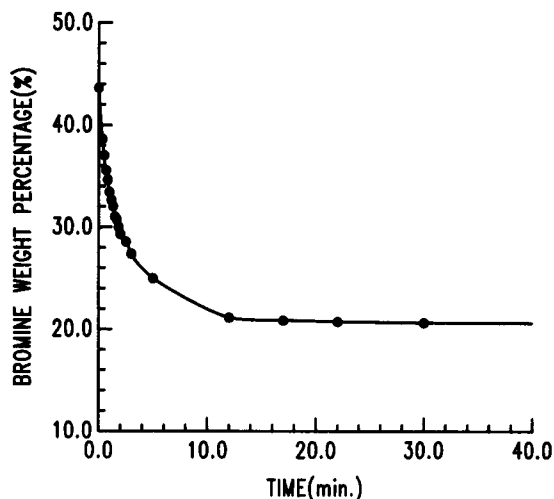


Fig. 1. Bromine weight uptake in the brominated Thornel P-100 carbon fibers after removal from the bromine vapor.

tered light was detected by using a photomultiplier tube and photon counting. The brominated P-100 fibers had been desorbed at room temperature for three days prior to Raman measurement. Figure 3 shows the doublet corresponding to the  $E_{2g2}$  mode of graphite, as previously observed in HOPG intercalated with bromine[4,5]. The intensity ratio of the high-frequency component to the lower-frequency component is 0.42. According to Fig. 7 of ref. [4], this intensity ratio corresponds to a residue compound containing 1.4 mole %  $\text{Br}_2$  (18.6 wt %  $\text{Br}_2$ )—a bromine concentration close to the value of 20 wt % determined by weight measurement. This provides evidence for true intercalation of the P-100 fibers. However, the full width at half maximum of the low-frequency component is  $25 \text{ cm}^{-1}$ , which is much larger than the  $15 \text{ cm}^{-1}$  width observed in HOPG intercalated with bromine[4]. Moreover, the high-frequency component (due to the graphite lay-

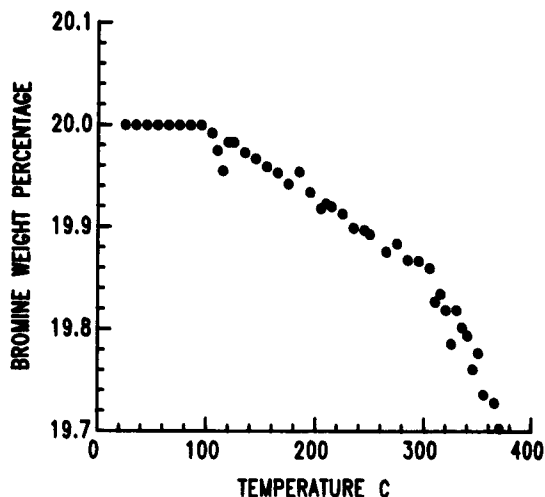


Fig. 2. Bromine weight uptake in the brominated Thornel P-100 carbon fibers during heating in air.

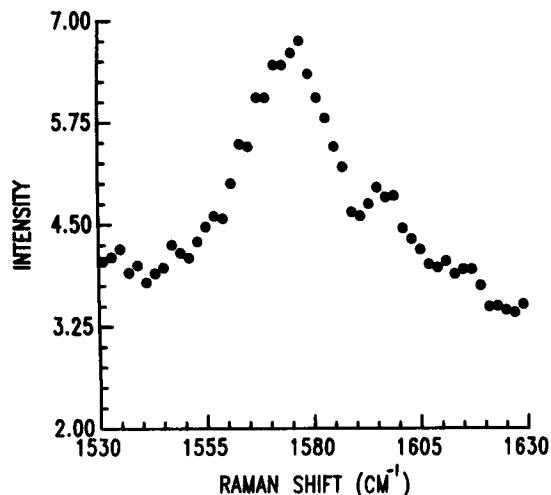


Fig. 3. Raman spectrum of brominated Thornel P-100 carbon fibers in the frequency range showing the  $E_{2g2}$  graphite mode.

ers bounding the intercalate layers) is not well resolved, in contrast to the clearly resolved doublet for HOPG intercalated with bromine[4]. These Raman observations suggest the occurrence of inhomogeneous intercalation. Figure 4 shows the only observed Raman peak other than the doublet. It is at about  $240\text{ cm}^{-1}$ . Though this peak occurs at the same frequency as the intercalate mode previously observed in HOPG intercalated with bromine[4,5], it is much broader than the HOPG counterpart. No Raman peak was observed around  $1360\text{ cm}^{-1}$  (due to the crystallite boundaries[22]) or around  $323\text{ cm}^{-1}$  (the vibration frequency of a free bromine molecule). Raman peaks quite close to  $240\text{ cm}^{-1}$  also exist for  $\text{Br}_3^-$  and  $\text{Br}_5^-$  ions[23]. Thus, the observation of the  $240\text{ cm}^{-1}$  line in the fibers does not provide clear

evidence for intercalation, but shows that at least the short-range structure of the bromine in the fibers resembles that of truly intercalated bromine in HOPG. The large breadth of the  $240\text{ cm}^{-1}$  in brominated P-100 compared to brominated HOPG further suggests that the chemical state of the bromine in P-100 is far less uniform compared to that of bromine in HOPG.

DSC was performed using a Perkin-Elmer DSC-2 system to look for the known phase transitions of intercalated bromine (melting temperature =  $100^\circ\text{C}$ ) or bulk bromine (boiling temperature =  $58^\circ\text{C}$ ). The sample was P-100 fibers that had been brominated in  $\text{Br}_2$  vapor at room temperature for seven days and subsequently desorbed in air at room temperature for four min. No DSC peak was observed for the brominated fibers in the temperature range from 25 to  $227^\circ\text{C}$  (Fig. 5b), but an endothermic peak was observed at  $-2^\circ\text{C}$  (271 K) during heating (Fig. 5a). This endothermic peak could only be observed during heating if the sample had been equilibrated for at least two min in the calorimeter at 230 K prior to heating. It was not observed during subsequent cooling. Upon second heating, it was only faintly observed. This peak is attributed to a new phase transition, which is probably the melting of the intercalated bromine in P-100 fibers. It should be noted that no phase transition at this temperature had been previously reported in graphite intercalated with bromine. The necessity of low temperature equilibration for observing the peak during subsequent heating and the absence of an exothermic peak during subsequent cooling are consistent with the sluggishness of ordering at such low temperatures.

Low temperature electron diffraction was performed using a JEOL 200 transmission electron mi-

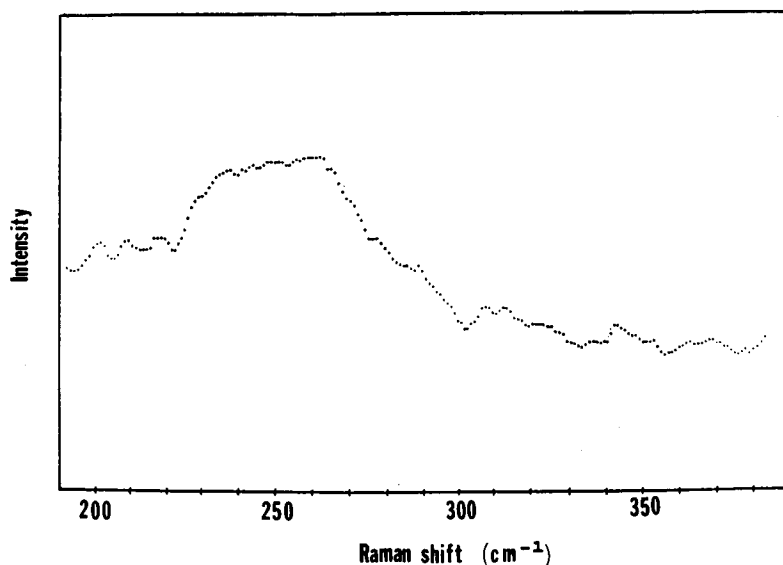


Fig. 4. Raman spectrum of brominated Thornel P-100 carbon fibers in the frequency range showing the intercalate mode.

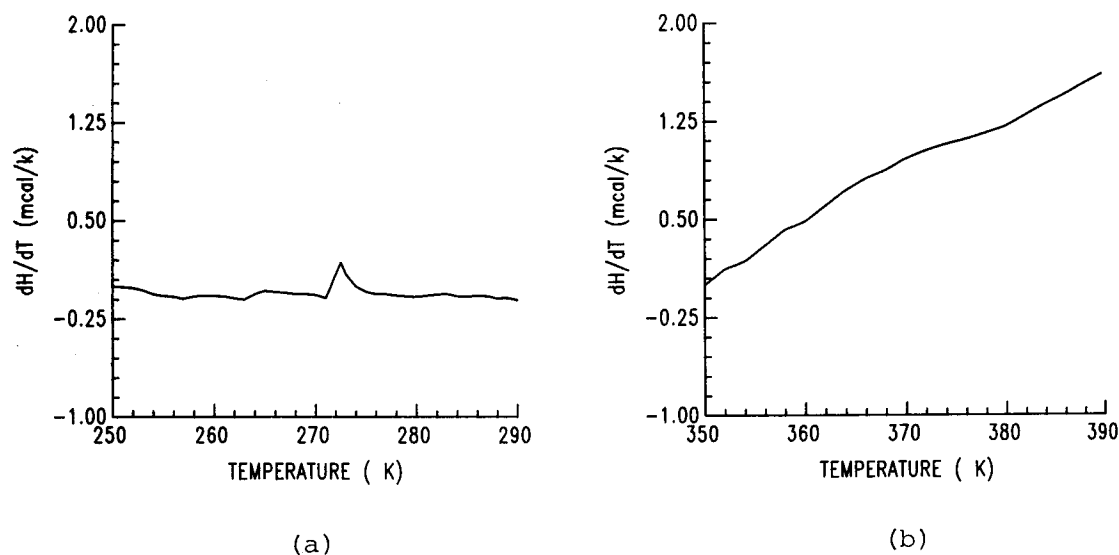


Fig. 5. Differential scanning calorimetry data of brominated Thornel P-100 carbon fibers during (a) heating at 10 K/min. and (b) cooling at 10 K/min.

microscope at Cornell University. A phase transition from the graphitic inplane diffraction pattern at room temperature to a superlattice inplane diffraction pattern at low temperature was indeed observed reversibly at about 270 K. This observation confirms that brominated P-100 fibers do not exhibit inplane bromine ordering at room temperature, but the ordering takes place at 270 K or below.

The electrical resistivity of single fibers was measured as a function of temperature, using the four-probe method, to obtain more evidence for a phase transition at 271 K. A step increase in the electrical resistivity was indeed observed at 271 K upon heating at 10 K/min, as shown in Fig. 6.

The absence of DSC peaks at 100°C and 58°C are consistent with the result of Jaworske *et al.*[16]. In particular, the absence of a DSC peak at 100°C supports the diffraction evidence for the absence of inplane bromine ordering at room temperature.

### 5. CONCLUSION

This work has shown that brominated P-100 fibers are intercalated, but the intercalate layers lack inplane long-range superlattice ordering at room temperature, even though such ordering exists at room temperature in HOPG intercalated with bromine. However, the chemistry of the bromine is similar for fibers and HOPG as hosts, as indicated by TGA (bromine desorption temperature) and Raman (240  $\text{cm}^{-1}$  line) results. This chemical similarity is consistent with

1. the similar residual bromine content in both after room temperature desorption,
2. the similar bromine desorption onset temperature of 100°C for both, and
3. the significant decrease in electrical resistivity in both by bromination.

3. the significant decrease in electrical resistivity in both by bromination.

The observed lack of inplane superlattice ordering at room temperature in the brominated fibers is probably not due to the relatively small  $L_a$  value of the host P-100 fibers as inplane superlattice ordering was observed in P-100 fibers intercalated with IC1[19] (though  $L_a$  depends on both the host material and the intercalate species). This result is probably due to the thermodynamics and it adds to the complexity of the phase equilibria in graphite-bromine[24]. In contrast, brominated P-X-7 (Amoco, pitch-based, more graphitic than P-100) exhibits at room temperature the same inplane superlattice as brominated HOPG.

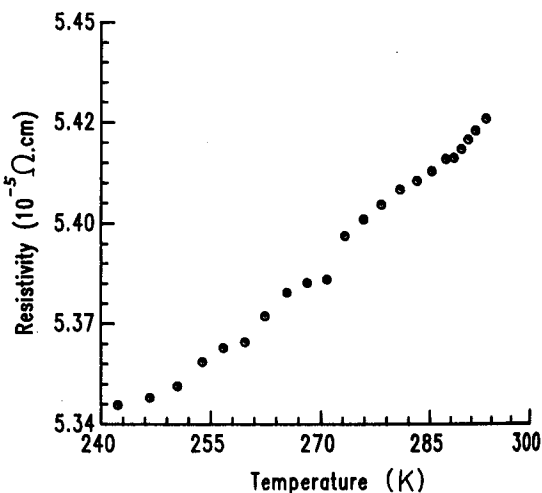


Fig. 6. Electrical resistivity of brominated Thornel P-100 carbon fibers as a function of temperature during heating at 10 K/min.

Upon cooling below room temperature, brominated P-100 fibers change from inplane disorder to inplane superlattice order, as observed reversibly by electron diffraction at about 270 K. This new phase transition is further supported by DSC observation of an endothermic peak during heating at 271 K, though this peak could only be observed if the sample had been equilibrated for at least 2 min in the calorimeter at 230 K prior to heating. This DSC peak was not observed during cooling. Hence, the ordering process is sluggish. Additional support for this transition was provided by a step increase of the electrical resistivity at 271 K upon heating.

The absence of a DSC peak at 58°C (boiling point of bulk bromine) and the absence of a Raman peak at about 323  $\text{cm}^{-1}$  in brominated P-100 show the essential lack of bulk bromine in the brominated P-100 fibers.

Section 1 lists eight possible ways of bromine incorporation. The second cannot be important because of the very low solid solubility of bromine in graphite. Numbers 3, 4, and 8 are not significant based on the last paragraph. Numbers 5, 6, and 7 are bound to apply, but they cannot account for large amounts of bromine. In particular, numbers 6 and 7 must be insignificant because of the small pore volume of these fibers[17,21]. Thus, we conclude that number 1 is predominant.

The structure of intercalated bromine in P-100 fibers differs from that in HOPG at room temperature in at least two ways. First, the former is in the form of disordered layers. Second, the former exhibits a much broader 240  $\text{cm}^{-1}$  Raman peak, suggesting a more nonuniform state of short-range order and/or a more nonuniform chemical state. Such nonuniformity is related to the inhomogeneous structure of the fibers. However, the chemical interaction between bromine and graphite is basically similar for P-100 fibers and HOPG.

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