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Diamagnetic characterization of carbon fibres from pitch mesophase, pitch and polyacrylonitrile

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The room temperature diamagnetic characteristics of carbon fibres from pitch mesophase (PM) have been determined and compared with those of fibres from isotropic pitch (P) and polyacrylonitrile (PAN) both in the as-processed condition and as a function of heat-treatment temperature over the approximate range 1000 to 3000° C. These fibre types show quite different magnetic behaviours indicative of different graphitizabilities which may be ranked PM, PAN, P in decreasing order. Microstructural and X-ray diffraction observations are also consistent with this ranking. Magnetic measurements provide a useful tool for characterization of fibre type and/or processing history.

1. Introduction

1.1. Fibre types and structure

Carbon fibres [1, 2] are made commercially from several different precursors: rayon (R), "isotropic" pitch (P), polyacrylonitrile (PAN), and anisotropic pitch mesophase (PM). Fibres from PAN are presently the most common; and fibre production from pitch mesophase (an aromatic liquid-crystal intermediate that forms during pyrolysis of thermoplastic precursors) is the most recent development [3–6]. Although similar ranges of tensile modulus and strength may be obtained from the different precursors, the required processing and the detailed fibre characteristics differ because of differences in carbonization chemistry and microstructure. Graphitizability and layer plane orientation texture are important microstructural aspects. Because the primary-bonding configuration in graphitic carbons is laminar, high intrinsic stiffness and strength are available only parallel to the layers. For fibres from PAN and PM, molecular alignment parallel to the fibre axis, generated in the precursor, evolves during carbonization into axial layer alignment which increases spontaneously with increasing heat-treatment temperature (HTT), resulting in increased modulus. For fibres from R or P, plastic hot-stretching at ⩾2500° C is required to develop high alignment and modulus. The very large interlaminar shear compliance characteristic of crystalline graphite is deleterious to the realization of good mechanical properties, especially when layer alignment is imperfect. Structural imperfections that inhibit interlaminar shear (cross-link bonds, microstructural constraints resulting from tangled or intertwined ribbon layer morphologies, etc.) facilitate the realization of high mechanical property levels with imperfect fibre orientation textures. Such imperfections also contribute to layer stacking disorder and small apparent layer sizes, L_a; and when stable at high temperatures, they effectively inhibit the development of graphitic crystallinity during processing. Structural disorder and poor graphitizability are common characteristics of the most common carbon fibre types; however, fibres from PM might be expected to be quite graphitizable, like other mesophase carbons such as petroleum and pitch cokes.

1.2. Magnetic characteristics

Information on both the average degree of layer plane orientation and the graphitization behaviour of carbon materials may be obtained from magnetic measurements. Carbons are diamagnetic and the

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diamagnetism is anisotropic and structure-dependent, sensitive to both layer development and layer stacking order [7]. The parallel-to-layer principal susceptibility results from the ion cores and is very small, $\chi_a \simeq 0.3$ in units of -10^{-6} emu g^{-1} used throughout this paper. Most of the diamagnetism is contributed by the perpendicular-to-layer principal susceptibility, χ_c, which results from conduction carriers in the layers and is structure-sensitive. At room temperature, $\sim 1.5 \leqslant \chi_c \leqslant 34$, increasing with increasing layer size and perfection and with increasing deviations from hexagonal stacking order; for single crystal graphite, $\chi_c \simeq 21.4$ and the tensor trace susceptibility $\chi_T = 2\chi_a + \chi_c \simeq 22$.

The magnetic characteristics of as-processed fibres from P, R and PAN have been discussed in detail elsewhere [8]; and preliminary observations on heat-treated fibres from PAN have also been reported [9]. This paper describes the results of an initial study of the magnetic behaviour of the new fibres from PM, as-processed and as a function of treatment temperature; and comparison of the characteristics of this new fibre type with those of fibres from P and PAN.

2. Procedure

Information on the fibres investigated is given in Table 1. The three developmental grades, PM-A, B, C were from the same or similar spinning lots and differed in modulus because of different processing temperatures. They had no surface treatment or coating. Samples of two earlier developmental lots, PM-D, E were also examined in the as-processed state. All of the PM fibres were produced by Union Carbide Corp. The fibres from PAN (Union Carbide T-400) and P (Kreha KCF-100) were from commercial production lots.

Bundles of parallel fibres, about 1 cm long, 1 to 3 mm diameter and weighing from 7 to 30 mg were tied with cotton thread. Mass susceptibilities, χ, were measured at room temperature in dry air with the fibre bundle axes aligned parallel (χ_A) and perpendicular (χ_R) to the magnetic field using the Faraday method and apparatus and techniques described earlier [8, 9]. Tied bundles were heat-treated isochronally (30 min residence time) in graphite crucibles in argon in a graphite resistance furnace at 1250 to $\sim 3000^\circ$ C. The thread ties remained intact despite pyrolysis during the heat-treatment. However, the carbonized ties were quite fragile, so the bundles were usually retied with cotton after heat-treatment. The contribution of the ties to the susceptibility was negligible; but a correction was necessary for the mass of the cotton. Tensor trace (total) susceptibilities, $\chi_T = 2\chi_R + \chi_A$, and anisotropy ratios, An.R. $= \chi_R/\chi_A$, were computed and used to characterize the fibres. For all of the fibre grades, the susceptibilites were independent of magnetic field strength over the range 0.4 to 0.7 Torr accessible with the apparatus.

3. Results and discussion

3.1. Microstructure

It has been reported [4, 5] that the microstructures of PM fibres may be classified, according to the layer orientation in the transverse cross-section, as circumferential, random or radial, the latter two being the most common. Moreover, the development of electronic properties with heat-treatment temperature (HTT) was found to depend on structure types, the radial configuration being the most graphitic [6]. Scanning electron micrographs of fracture cross-sections of some of the PM fibres investigated here are shown in Fig. 1. For PM-A, B, C the cross-sections are generally circular and 9 to 11 μm diameter; but some fibres are twice that size, with hollow cores (not shown). The fracture surfaces are rough and the microstructures are clearly laminar, graphitic and coarsely fibrillar

TABLE I Some characteristics of the fibres studied.

Type	Source	Precursor	Processing temperature (° C)	Modulus E (GPa)	Strength (GPa)
PM-A	Union Carbide	Pitch Mesophase	~ 1650*	184	1.1
B	Union Carbide	Pitch Mesophase	~ 1800*	260	1.3
C	Union Carbide	Pitch Mesophase	~ 2000*	365	1.3
D	Union Carbide	Pitch Mesophase	≈ 2100*	200	–
E	Union Carbide	Pitch Mesophase	≈ 2150*	365	–
T-400	Union Carbide	PAN	≈ 1000	220	3.0
KCF 100	Kreha	Pitch	≈ 1000	70	1.1

*Inferred from response to heat-treatment.

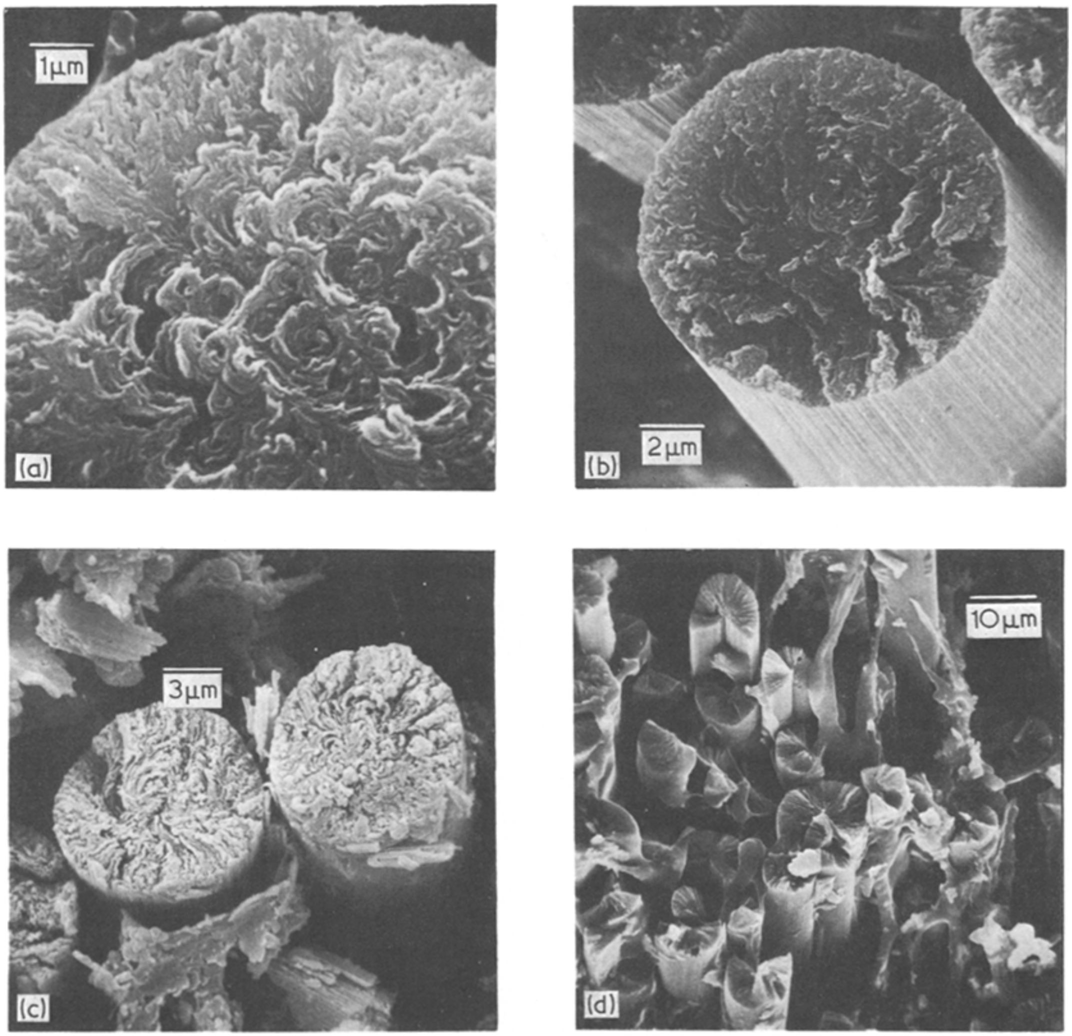

Figure 1 Scanning electron micrographs of fracture cross-sections of pitch mesophase fibres: (a) PM-A, as-received; (b) PM-C, as-received; (c) PM-C, 2700° C; (d) PM-D, as-received.

(Fig. 1a and b). The smallest substructure unit resolvable in the SEM consists of irregularly crinkled or curved layer packets $\leqslant 0.1\,\mu$m thick and $\geqslant 0.5\,\mu$m wide running parallel to the fibre axis. Near the periphery, the orientation textures are predominantly (but imperfectly) radial, and there is continuity between the laminar fracture features and the longitudinal surface striations; in the fibre interiors, the textures are complex, but predominantly circular, scalloped or spiral. After high temperature treatment (Fig. 1c) the laminar substructure is more pronounced, but there is little apparent change in the overall texture. PM-D (Fig. 1d) is strongly radial with the "missing wedge" cross-section characteristic of this type (some PM-B fibres also have small wedge gaps on the periphery). The structureless webbing between the PM-D fibres probably resulted from precursor pitch that melted prior to carbonization, due to insufficient cross-linking [10]. PM-E (not shown) also has some inter-fibre webbing, and a tendency toward longitudinal splitting when fractured; but the microstructure is generally similar to those of A, B, C. The T-400 (PAN) fibres have slightly elliptical or bean-shaped cross-sections, about 5 μm by 7 μm; the KCF-100 (P) fibres are circular, $\sim 10\,\mu$m diameter. For carbonized PAN, P (and R) fibres the fracture surfaces are usually glass-like with little or no substructure; after processing to high temperatures, these fibres typically show a fine ($\sim 0.1\,\mu$m) granular substructure but no strongly laminar characteristics in SEM micrographs.

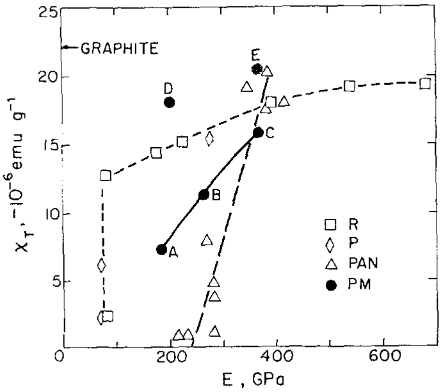

Figure 2 Trace diamagnetic susceptibility as a function of elastic modulus for as-processed carbon fibres from rayon (R), pitch (P), polyacrylonitrile (PAN) and pitch mesophase (PM).

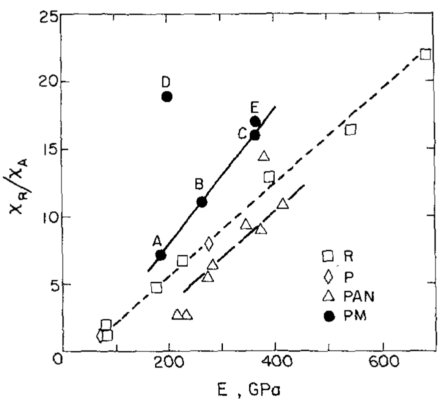

Figure 3 Susceptibility anisotropy ratio as a function of elastic modulus for as-processed fibres.

3.2. Magnetic properties of as-processed fibres

The trace susceptibility and anisotropy ratio values of the as-received PM fibres are compared with those of as-processed fibres from PAN, P and R [8] as a function of tensile elastic modulus in Figs. 2 and 3. The An.R. values for the PM fibres (especially the radial PM-D) are appreciably larger than those of the other fibre types. The trace susceptibilities of the PM-A, B, C series increase regularly with modulus along a trajectory that is intermediate between the PAN and the hot-stretched R and P values at moderate moduli, but roughly comparable to those of the other fibre types at higher moduli. The values for PM-D, E are somewhat larger.

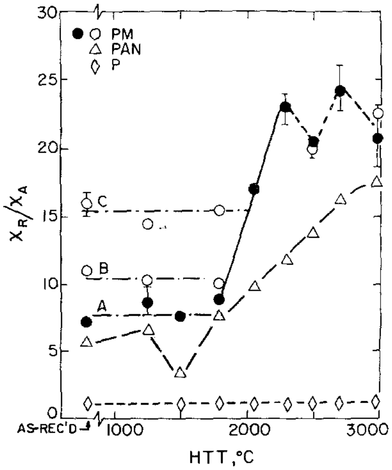

Figure 4 Trace susceptibility as a function of isochronal (30 min) heat-treatment temperature for fibres from pitch mesophase, pitch and polyacrylonitrile.

3.3. Magnetic properties of heat-treated fibres

The significance of the as-processed fibre parameters may be further elucidated by examining the influence of heat-treatment temperatures (HTT) on the magnetic characteristics. The results are shown in Fig. 4 for χ_T and in Fig. 5 for An.R. The error bars indicate the range of observed values where it exceeds the symbol size. Although the fibres from PM and PAN achieve similar χ_T values for HTT $\simeq 3000^\circ$ C, the paths followed and the associated An.R. values are quite different; and the behaviour of the low-modulus (unstretched) fibres from P is different from either.

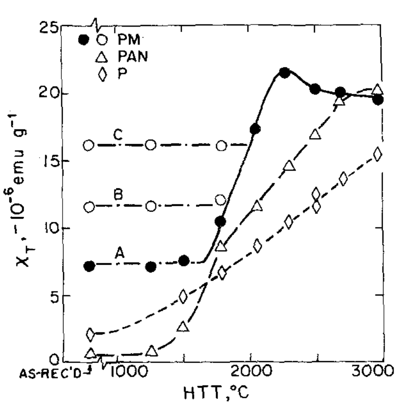

Figure 5 Susceptibility anisotropy ratio as a function of isochronal heat-treatment temperature for fibres from various percursors.

3.3.1. Fibres from pitch mesophase

For the PM fibres, χ_T increases rapidly with HTT $\geqslant 1800^\circ$ C to a maximum of about 22 at $\sim 2300^\circ$ C; then decreases to ~ 19.5 at 3000° C. Approximate processing temperatures for the as-received fibres may be inferred from the Fig. 3 results and are listed in Table I. The temperatures for PM-A, B, C are consistent with information reported in the literature [5]. The values for PM-D, E are based on the risky assumption that χ_T is insensitive to microstructure type, since no heat-treatment data were obtained for these fibres. It is possible that the properties of PM-D, in particular owe more to the radial structure than to a higher processing temperature. For fibres from PAN with similar moduli the corresponding temperatures are ~ 1000, 1500 to 1800 and 2500 to 2800° C. The χ_T versus HTT curve of the PM fibres is very similar to those of synthetic graphites made from petroleum coke and coal-tar pitch [7, 11], which also carbonize via the mesophase process; and of graphitizable low deposition temperature pyrolytic carbons [12, 13]. The changes in χ_T result from changes in the principal susceptibility χ_c. In the HTT range below the χ_T maximum, χ_c is increasing due to increasing structural perfection and effective size of the layers. At higher HTT, developing layer stacking order, which reduces χ_c, dominates the magnetic behaviour. Finite layer size and residual structural defects such as crystallite boundaries keep χ_T of the graphitized fibres below the single crystal value of 22.

The anisotropy ratio (Fig. 5) of the PM fibres increases rapidly to ~ 23 at HTT $\sim 2300^\circ$ C and fluctuates thereafter. These changes in An.R. also result from several factors [8]: the intrinsic crystallite anisotropy χ_c/χ_a follows the change in χ_c (and χ_T). This alone can account for a doubling of the observed An.R. between 1800 and 2300° C, and the more graphitic structure of the PM fibres appears to be the primary reason for their higher magnetic anisotropies. A higher degree of axial orientation may also be necessary to realize the same modulus value in PM fibres because the effective interlayer shear compliance tends to be larger in more graphitic structures. Improvement in the axial alignment of the layers increases the An.R.:

$$\frac{\chi_R}{\chi_A} = \frac{[1 + (\chi_c/\chi_a - 1)R_z/2]}{[R_z + (\chi_c/\chi_a)(1 - R)]}$$

where $R_z = \langle \sin^2 \phi \rangle$, the mean square sine of the angle ϕ between the layer normals and the fibre axis.

In the limit of an ideal fibre texture ($R_z = 1$) the ratio has a maximum value of $(\chi_c + \chi_a)/2\chi_a$. Taking $\chi_c = \chi_T - 2\chi_a$ and $\chi_a = 0.32$ (the graphite single crystal value), the ideal-texture maximum An.R. increases from ~ 16 for HTT = 1800° C to ~ 33 for 2300° C, then falls to ~ 30 for 3000° C for the PM fibres. Tensile moduli up to 90% of the single crystal value, corresponding to a very high degree of preferred orientation, have been reported for graphitized PM fibres [5], so the fibre An.R. might be expected to approach the limiting value of 30 at high HTT. The highest value observed for the bundle samples was about 26 and mean values are somewhat lower. When the anisotropy is large, the measured An.R. values are quite sensitive to fibre misorientation in the bundle, misalignment of the bundle in the magnetic field, and measurement errors in the small χ_A values. The large fluctuations and relatively low mean values of An.R. after high HTT can be reasonably attributed to these factors. In particular, it was difficult to maintain good fibre alignment in the bundles of fibres with high HTT.

3.3.2. Fibres from PAN

The as-received (HTT $\sim 1000^\circ$ C) T-400 fibres from PAN are only weakly diamagnetic ($\chi_T \leqslant 0.5$). Electron spin resonance measurements on carbonized PAN fibres [14] indicated a paramagnetic contribution of about 0.5, so that the total diamagnetism is about 1, corresponding to just the ion core contribution ($3\chi_a$) in graphite. These magnetic properties are associated with the presence of several percent residual nitrogen in the material [15, 16]. With increasing HTT this nitrogen is evolved and χ_T increases rapidly in the 1300 to 1800° C HTT range to a value comparable to that of the lowest modulus PM fibre. Thereafter, χ_T increases regularly toward a limiting value of ~ 20 at HTT $\simeq 3000^\circ$ C. The dominant process above 1800° C is again development of the layer structure, but this is evidently less extensive than in the PM fibres. Some incipient stacking influence may contribute to determining the saturation value at the highest HTT, but the stacking order is not sufficient to make χ_T decrease.

The PAN An.R. values in the HTT range below 1800° C are subject to large uncertainties due to the very small χ_A values ($\leqslant 0.3$), and the interpretation is uncertain because of lack of information about anisotropy of the paramagnetic contribution and the effects of the nitrogen impurity on the principal susceptibilities. However, it is interesting that even these very small net diamagnetic susceptibilities are quite anisotropic. The An.R. increases approximately linearly with HTT above 1800° C, but is less than that of the PM fibres, even in the 2700 to 3000° C range where the χ_T values are comparable. In studies [9] on other ex-PAN fibres from various sources, the χ_T behaviour was always similar to that found here, but the An.R. development varied appreciably among different grades (due probably to differences in precursor and processing). The values observed here lie in the middle of the range.

3.3.3. Fibres from pitch

The low modulus fibres from isotropic pitch remain isotropic throughout the entire HTT range, and χ_T increases only to ~ 15 for HTT ≃ 3000° C. This behaviour is similar to those of difficult-to-graphitize isotropic pyrocarbon coatings (⩽ 100 μm) deposited in a fluidized bed [12, 13] and bulk (3 mm thick) glassy carbons [17, 18]. It seems to be characteristic of carbons in which layer development is inhibited due to an intrinsic narrow-ribbon substructure and the constraints of a complex, "tangled" microstructural morphology. Low modulus fibres from rayon (not shown) exhibit a similar χ_T behaviour, but develop an An.R. ≃ 2 after high HTT, indicative of a small amount of axial preferred orientation. When the tensile moduli of fibres from P or R are increased above ~ 100 GPa by hot-stretching (Fig. 2), the An.R. and χ_T values also increase. The resulting anisotropy ratios are intermediate between those of unstretched fibres from PM and PAN, but the χ_T values remain less than those for PAN with HTT ⩾ 2700° C. For hot-stretched fibres ex-rayon with 500 ⩽ E ⩽ 700 GPa, 16 ⩽ An.R. ⩽ 22 but χ_T ≃ 19. Thus, even large amounts of high temperature deformation do not produce very graphitic structures in these fibres.

3.4. Graphitizability

Based on the influence of HTT on the magnetic parameters, the graphitizability of carbon fibres may be ranked as follows: pitch mesophase, fairly good; PAN, moderate; isotropic pitch or rayon, poor. This is consistent with Debye – Scherrer X-ray diffraction information. For high HTT fibres from PAN and hot-stretched fibres from rayon, the mean interlayer spacing, d (determined from the (0 0 4) line) is ~0.340 nm compared with 0.335 nm for crystalline graphite, and there is no evidence of layer stacking order. For the as-received PM fibres there is no stacking order and d ≃ 0.342 to 0.343 nm; but after HTT ⩾ 2700° C, d ≃ 0.338 nm and there is evidence of some stacking regularity (the (1 1 0) and (1 1 2) lines are clearly resolved, although there is no obvious modulation of the two-dimensional (1 0) line.

4. Conclusions

Diamagnetic susceptibility measurements may be used to characterize carbon fibres from various precursors in terms of average layer-plane preferred orientation and graphitizability, and to infer approximate maximum processing temperatures of as-received fibres. The new fibres from pitch mesophase with complex, coarsely laminar microstructures are much more graphitizable and have higher magnetic anisotropies than fibres from polyacrylonitrile and the latter graphitize more than fibres from rayon or isotropic pitch.

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