

Conversion of acrylonitrile-based precursors to carbon fibres

Part 3 *Thermooxidative stabilization and continuous, low temperature carbonization*

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The effects of stabilization conditions on the formation of a consolidated carbon fibre structure from two acrylonitrile-based precursor fibres, one containing itaconic acid as comonomer and the other a commercial precursor, have been studied. The progression of changes in elemental composition and properties such as sonic modulus, electrical resistance and density in a continuous, low temperature (1200°C) carbonization process are reported for the first time. A criterion based on attaining a composition dependent critical density in stabilization is proposed for avoiding the formation of a hollow core in carbon fibres processed continuously at reasonably rapid rates. Aspects related to the development of open and closed micropores in the carbon fibre structure and the possible mechanisms for the formation of a hollow core in carbonization are also discussed.

1. Introduction

Manufacture of carbon fibres from acrylonitrile-based precursor copolymers involves

(a) formation of oriented fibres, usually through solution spinning and a combination of drawing in the gel state and plastic deformation of dried fibre,

(b) low temperature (200–350°C) thermooxidative stabilization of the oriented precursor fibre to yield a structure that can maintain its cohesion during subsequent carbonization,

(c) carbonizing heat treatment (800–1600°C) in an inert atmosphere to drive off non-carbon elements, and

(d) an optional high temperature (> 2000°C) treatment to improve the mechanical properties, especially the stiffness of the fibres.

The nature of the fibres at every stage in the formation of carbon fibres depends on the conditions of processing at that stage as well as the chemical composition and the geometrical and morphological features of the material produced at the previous stage. As described in our review of the literature on the production of carbon fibres [1], numerous studies of isolated aspects have yielded extensive empirical knowledge but only a partial understanding of this complex process. We have undertaken a comprehensive experimental study in our laboratories to help expand our knowledge of the material and process contributions to the properties of the ultimate carbon fibres. The results from experiments in precursor fibre formation and batch stabilization, and from an extensive study of the rearrangements in continuous ther-

mooxidative stabilization have been reported earlier [2, 3]. We report here additional results from continuous stabilization and initial experiments on the evolution of properties in low temperature (1200°C) continuous carbonization. The progression of carbonization was monitored through measurements of density, linear density, elemental composition, electrical resistance and sonic modulus.

2. Experimental details

2.1. Precursor fibres

Detailed descriptions of the experimental procedures are given in [3]. Two acrylic precursor fibres, II and III, were used in this study. Precursor III is a commercial precursor for carbon fibres. Precursor II fibres were produced in our laboratories from a 17.5% (w/w) solution of a copolymer of acrylonitrile (AN) and itaconic acid (IA) in the weight ratio of 97/3 (average molecular weight = 131 000 g mol⁻¹, estimated from intrinsic viscosity). The spinning conditions for precursor II, established to produce fibres of good quality, are given in Table I. The jet stretch and the draw ratio were changed to obtain fibres having different orientations. High-temperature drawing of some of the precursor fibres was performed in order to produce fibres with high orientation and morphological parameters different from those produced by drawing in boiling water. Two types of post-spinning high temperature drawing processes, i.e. over a hot godet and through a hot oven, were performed on the hot water (partially) drawn fibres. In the former type of drawing, precursor fibres were drawn directly from the heated feed-godet, whereas

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TABLE I Conditions of formation of precursor II fibres

Precursor II			
<i>Polymer solution:</i>			
Solution concentration, % (w/w)	17.5		
Solution viscosity, poise	140		
<i>Coagulation bath</i>			
Coagulation bath composition, % DMF	60		
Coagulation bath temp., °C	14		
<i>Drawing conditions:</i>			
Jet Stretch	0.7	1.2	0.7
Draw Ratio, in boiling water	2.5	3	5
Denier/filament (dpf)	3.9	2.2	2.2

in the latter type the fibres were first annealed at a relatively low temperature (115 to 130°C) on the feed-godet and then drawn through an oven. Details of the drawing conditions are given in Table II. The first letter in the sample identification code refers to the precursor type. The second and the third terms represent the jet-stretch and the draw-ratio (in boiling water), respectively. The last three terms signify the post-spinning, high temperature plastic drawing conditions, such as type of heater (oven or godet), temperature and draw-ratio, respectively. The temperatures employed in the hot-oven drawing were the maximum possible for a smooth drawing operation without filament breakages. The mechanical properties and morphological parameters of the precursor fibres are given in Table III. It can be seen clearly that a broad range of precursor fibre properties has been achieved through the different drawing processes.

2.2. Continuous stabilization and carbonization

The fibres were stabilized in air in a continuous process with an 18-ft long linear, tubular oven. The furnace was divided into three, 6-ft zones, with each zone controlled by individual temperature controllers. Various ascending temperature profiles (Table III) were used in this process. Precursor II was processed at an input and output linear velocity of 1 inch min⁻¹. When processed at constant input and output velocities, precursor III fibres developed excessive shrinkage forces, leading to breakage of filaments and so these were run with the minimum net shrinkage (9%)

TABLE II Precursor II drawing conditions

Sample	Draw-ratio			Drawing godet/oven temp. (°C)	Annealing godet temp. (°C)	Denier/filament
	B.W.*	H.T.†	Total			
II-1.2-3	3.0	—	3.0	—	—	2.3
II-0.7-5	5.0	—	5.0	—	—	2.2
II-0.7-2.5-O-228-1.8	2.5	1.8	4.5	228, oven	115	2.2
II-0.7-2.5-G-160-1.8	2.5	1.8	4.5	160, godet	160	2.2
II-0.7-2.5-O-224-2.5	2.5	2.5	6.2	224, oven	118	1.6
II-0.7-2.5-G-190-2.7	2.5	2.7	6.7	190, godet‡	190	1.5

*Draw-ratio in boiling water.

†High-temperature draw-ratio.

‡The drawn fibres were yellowish due to partial degradation/stabilization.

Sample notation: Precursor type-jet stretch-hot water draw ratio-oven/godet drawing-drawing temperature-draw ratio. e.g., II-0.7-2.5-O-228-1.8 refers to a sample with precursor II, jet stretch = 0.7, hot water draw ratio = 2.5, drawing through the oven at 228°C with draw ratio of 1.8.

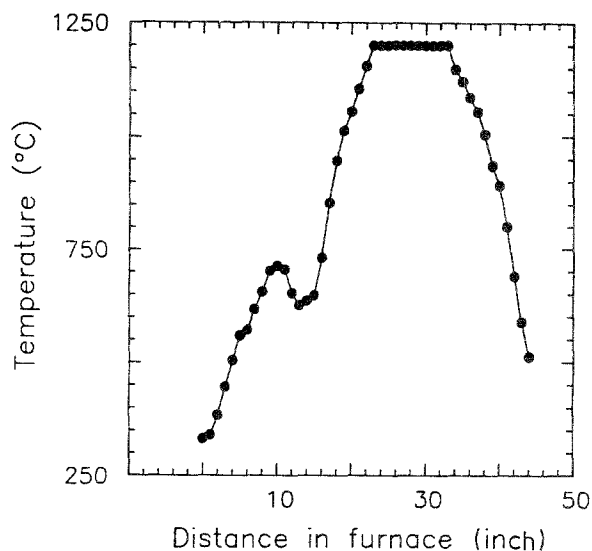


Figure 1 Temperature profile in carbonization.

required for good processing. The finer filaments in this precursor required lower residence times for stabilization when compared with Precursor II fibres and so these were processed at input and output velocities of 2.75 and 2.5 inch min⁻¹, respectively.

Carbonization of the stabilized fibres was carried out by passing them through a Lindberg furnace at 1200°C. To avoid thermal shock and allow for a gradual increase in the temperature of the filaments, two heaters were installed at the entrance to the furnace which provided two 6-inch precarbonization zones of 500 and 700°C. The temperature profile obtained in this set-up is shown in Fig. 1. The dip in the temperature profile is caused by the separation between the second preheater and the heater in the Lindberg furnace. Nitrogen was passed through both ends of the furnace to maintain an inert atmosphere.

Samples for studies of the progression of carbonization in a steady state process were obtained by cutting the fibre bundle at the delivery end and rapidly winding it on a spool at the feed end.

2.3. Properties of fibres

Measurement of velocity of sonic pulse propagation through the fibre samples was made with the sonic modulus tester PPM-5 with a refractory mount,

TABLE III Mechanical properties and morphological parameters of precursor fibres.

Sample	Denier/ filament	Tenacity (g denier ⁻¹)	Elong. (%)	Young's modulus (g denier ⁻¹)	Sonic modulus (g denier ⁻¹)	Orientn. function f_c	Crystal size (nm)
<i>Boiling water drawn fibres</i>							
II-1.2-3	2.2	2.1	11.1	78	95	0.67	7.3
II-0.7-5	2.2	3.1	11.8	90	149	0.78	7.5
II-0.7-2.5	3.9	1.8	11.4	64	105	0.61	6.5
<i>High temperature drawn fibres</i>							
II-0.7-2.5-O-228-1.8	2.2	3.4	9.7	114	150	0.83	11.3
II-0.7-2.5-G-160-1.8	2.2	3.5	8.6	117	147	0.77	8.8
II-0.7-2.5-O-224-2.5	1.6	4.4	8.7	132	182	0.87	11.0
II-0.7-2.5-G-190-2.7	1.5	4.4	7.6	144	207	0.84	12.8
<i>Precursor III</i>	0.9	5.3	8.8	127	143	0.87	

Sample notation: Precursor fibre-jet stretch-hot water draw ratio-oven/godet drawing-high temperature draw temperature-high temperature draw ratio.

(H. M. Morgan Co.). The measurement on precursor and stabilized fibres using the scanner mount is described elsewhere [3, 4]. The measurements corresponding to changes in sonic modulus with position along the carbonization line were difficult because of the drastic increase in the modulus of the fibres over a short distance in the carbonization process. The sonic modulus increases 10-fold over a distance of 15 to 20 inches. For this measurement on the filament bundle removed from the carbonization line, the transmitter was moved in 3-inch steps and the time for propagation was measured, starting with the stabilized length over lengths of 1, (1 + 3), (1 + 6) inches, etc. The average sonic velocity of each 3-inch section was obtained from the difference between the propagation times for the corresponding two successive steps.

The densities of stabilized or carbonized fibres were measured by the flotation technique. Solutions of various densities were made for this purpose by mixing the required quantities of carbon tetrachloride (1.585 g cm⁻³) with either toluene (0.866 g cm⁻³) or tetrabromoethane (2.964 g cm⁻³), depending on the density range required.

Moisture contents of fibres were obtained from their dried and conditioned weights. A 2-m length of fibre bundle was weighed accurately after conditioning for 24 h at standard temperature (20°C) and humidity (65% r.h.) conditions. The sample was then dried in an air circulated oven at 110°C for 8 h. The dried sample was allowed to cool in a desiccator and weighed again.

Mechanical properties of the carbon fibres were tested as a bundle after impregnation with – and curing – an epoxy resin system. These measurements were carried out with an Instron (model 1130) at an elongation rate of 0.2 inch min⁻¹ and a 12-inch gauge length.

A mini SEM by International Scientific Instruments was used to examine the surface and cross-section of the carbon fibres after coating with a thin layer of gold.

Electrical resistance measurements on the carbon fibre bundles, and on the filament bundles removed from the carbonization line, were made using two instruments, HP3456A Digital Multimeter and HP4329A High Resistance Meter, to cover the entire

range of resistances of the stabilized and carbonized fibres. The fibre sample was enclosed inside a shielded metal box. The contact resistance at the point of contact between the measuring probe and the fibre bundle was minimized with silver paint.

3. Results and discussion

3.1. A criterion for sufficient stabilization

Table IV lists the various temperature profiles employed in the stabilization process for different precursor fibres. The stabilized fibres were characterized by measuring the density and moisture content which are also listed in Table IV. The densities of precursor fibres increase significantly during stabilization due to the structural rearrangements associated with stabilization reactions and the incorporation of oxygen. The stabilized fibre densities range from 1.455 to 1.535 g cm⁻³ depending on the precursor draw ratio and the temperature profile employed for its stabilization. As expected, the densities obtained for a given precursor were higher when a higher temperature profile was employed. The fibres which were drawn to a combined draw ratio of 6.7 (II-0.7-2.5-G-190-2.7) had turned yellowish during the drawing process and show high density values (1.52 g cm⁻³ and higher) upon stabilization even when low temperature profiles were employed, suggesting a high rate of stabilization in these fibres. Moisture content of stabilized fibres do not show any specific trends with either the draw ratio or the temperature profile. The majority of values, however, fall in the narrow range of 9 to 10%.

One of the consequences of insufficient stabilization in a diffusion controlled stabilization process is the development of a hole in the centre of such fibres during carbonization. The holes form as a result of the incompletely stabilized core of the precursor fibres being burned off during carbonization. All the stabilized fibres listed in Table IV were carbonized with a residence time of 1 min at the maximum temperature of 1200°C and their cross-sections were examined under a scanning electron microscope. Whether a hollow core is observed to be present or not in these carbon fibres is also specified in Table IV. It appears that the stabilization of precursor II fibres is indeed a diffusion controlled process under the conditions employed for stabilization. With increasing

TABLE IV Properties of stabilized precursor II fibres

Precursor	Stabilization temperatures (T_1 - T_2 - T_3)*	Denier/filament	Density (g cm^{-3})	Moisture (%)	Hollow core in carbon fibres
II-1.2-3		2.25	1.180	2.0	–
	225-250-275	2.42	1.455	9.3	Yes
	250-275-275	2.39	1.475	9.3	Yes
	250-275-300	2.38	1.495	9.6	Yes
	250-275-325	2.25	1.515	9.3	Yes
	275-300-325	2.29	1.525	10.6	No
II-0.7-5		2.16	1.175	2.0	–
	250-275-275	2.34	1.515	9.2	Yes
	250-275-300	2.29	1.525	8.9	No
	250-275-325	2.25	1.535	9.7	No
II-0.7-2.5		3.86	1.180	1.9	–
II-0.7-2.5-O-228-1.8		2.22	1.175	1.8	–
	250-275-275	2.23	1.480	8.8	Yes
	250-275-300	2.19	1.495	8.9	Yes
	275-300-325	2.24	1.515	9.4	Rare
	275-300-350	2.24	1.530	9.2	No
II-0.7-2.5-G-160-1.8		2.17	1.175	1.7	–
	250-275-275	2.14	1.475	8.7	Yes
	250-300-350	2.00	1.510	9.5	Yes
	275-300-350	1.93	1.535	9.8	No
II-0.7-O-224-2.5		1.61	1.180	2.1	–
	225-250-275	1.70	1.475	8.5	Yes
	250-275-275	1.63	1.500	9.0	Yes
	250-275-300	1.66	1.515	9.6	Rare
	250-275-325	1.63	1.535	9.8	No
II-0.7-2.5-G-190-2.7		1.55	1.185	1.6	–
	250-275-275	1.62	1.525	9.4	No
	250-275-300	1.57	1.535	9.5	No

* T_1 - T_2 - T_3 refer to the temperatures in zones 1, 2 and 3, respectively, in the stabilization unit.

stabilization temperatures, the rate of diffusion increases, causing insufficient stabilization of the material closer to the centre of the fibre. An important observation from the data in Table IV is that when the stabilized fibres possessed a density of 1.52 g cm^{-3} or higher, the carbonized fibres did not show holes due to core blow out, irrespective of the precursor fibre forming conditions and the temperature profile employed in stabilization. The fact that narrow density ranges are required for optimum stabilization has been disclosed in the patent literature [5]. It should be mentioned here that under conditions of carbonization different from those mentioned above, holes in the core of carbonized fibres can result even with apparently well stabilized fibres. This aspect is discussed further in the following sections.

3.2. Progression of carbonization

Progression of carbonization using stabilized precursor II fibres (stabilized under conditions that would prevent core blow out) was followed with density, $[\text{H}]/[\text{C}]$ and $[\text{N}]/[\text{C}]$ ratios, electrical resistance and sonic modulus measurements. The scatter in the sonic modulus values in the high modulus range (Fig. 2) is the result of experimental limitations. As mentioned earlier, the sonic modulus values were obtained from discrete measurements of pulse propagation times. At the high modulus end, the time taken by the sonic pulse to travel three inches is only 6 to 8 μsec , and significant errors can be incurred in

reading this value from the output on a chart. When the plots in Fig. 2 are compared with the temperature profile in the carbonization furnace (Fig. 1), a sharp increase in sonic modulus during heating from 700 to 1200°C can be observed. Once the fibre temperature reaches 1200°C, a much slower asymptotic increase in sonic modulus occurs with time at this temperature. The sonic moduli of the carbon fibres after 1200°C carbonization are higher with precursor fibres of higher draw ratios. Also, the carbon fibres from the high temperature drawn fibres show an increase to a higher sonic modulus compared to those from boiling water drawn fibres. The development of modulus is determined by the degree of graphitic order and the orientational order in the basal planes achieved during carbonization. The rate and the extent to which this ordering process occurs should increase with initial order in the precursor fibres.

The results from elemental analysis on samples removed from the carbonization furnace are plotted in Fig. 3. The $[\text{H}]/[\text{C}]$ and the $[\text{N}]/[\text{C}]$ ratios also change sharply during heating between the temperatures 700 and 1200°C, showing that both aromatization and basal plane formation occur rapidly in this temperature range. The requirement that a certain degree of aromatization has to precede the formation of basal planes is reflected clearly in the more rapid change in the $[\text{H}]/[\text{C}]$ ratio in the early stages when compared with the $[\text{N}]/[\text{C}]$ ratio. The progression of changes in electrical resistance through carbonization follows the

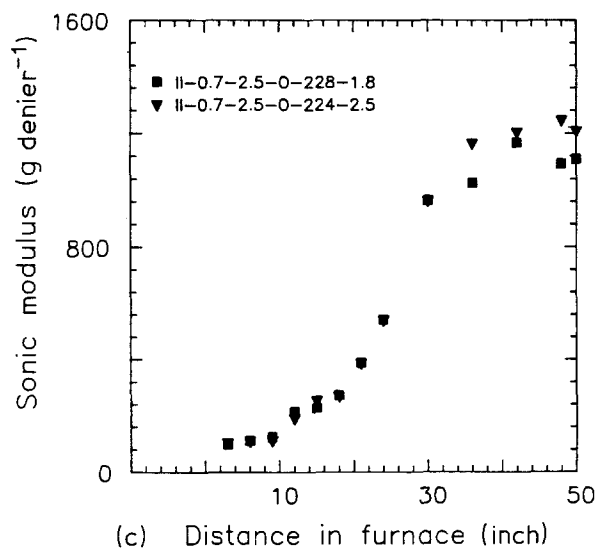
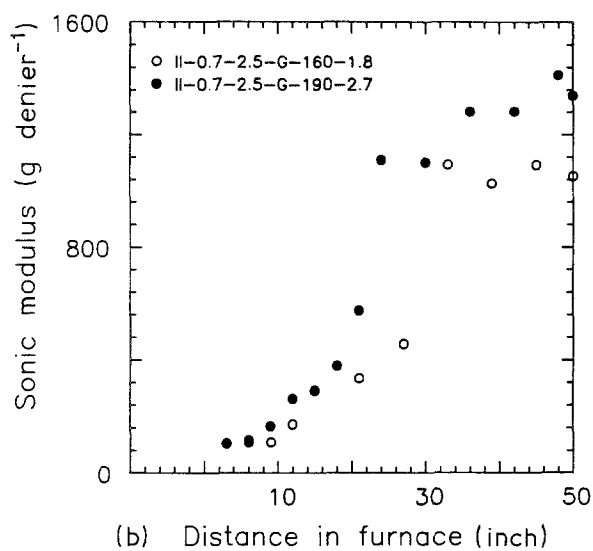
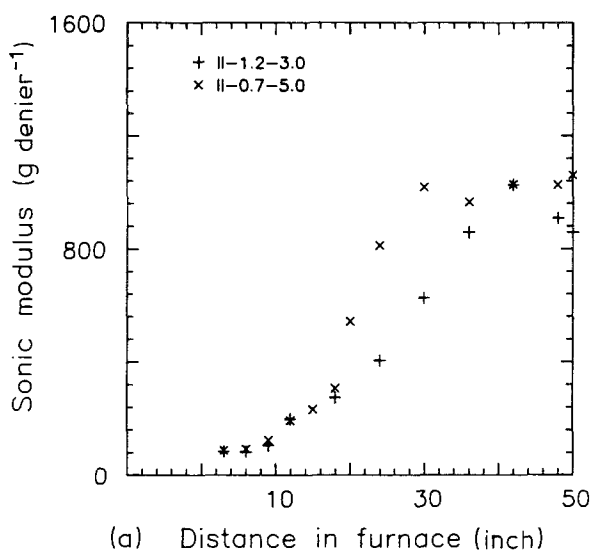


Figure 2 Change in sonic modulus during carbonization of precursor II. The fibres are drawn in (a) hot water; (b) hot water and over a hot godet; (c) hot water and through a hot oven. (The conditions of formation of the precursor fibres are given in the sample designations.)

same trend of rapid change in the 700 to 1200°C zone (Fig. 4). The resistance falls from about $10^{14} \Omega \text{ cm}^{-1}$ to less than $10 \Omega \text{ cm}^{-1}$ when the temperature is raised to its maximum of 1200°C, after which it remains constant upon continued heating at this temperature.

The progression of density changes is plotted as a function of distance in the furnace in Fig. 5. Density

increases very rapidly during the 700 to 1200°C heating, suggesting significant rearrangements leading to consolidation of structure in the fibres, but it is followed by a sharp drop before levelling off upon continued heating at 1200°C. This decrease in the measured density of the carbonized fibres is quite significant and is observed in all fibres. A plot of densities of three samples from carbonization, using II-0.7-5 fibres stabilized at 250–275–300°C, shows that the trend is very reproducible (Fig. 5d). The reason for this drop in apparent density is not very clear at this point and is being explored further. A reason for this drop in apparent density could be the conversion of open pores to closed pores, i.e. some of the pores which are initially accessible to the solvents employed for the density measurement become inaccessible, resulting in a decrease in the measured density. This suggests that consolidation of the structure occurs around the pores during the high temperature

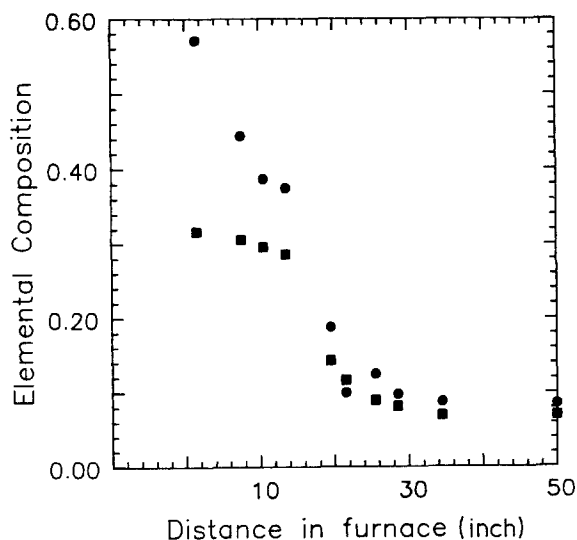


Figure 3 Change in elemental composition during carbonization of II-0.7-2.5-G-190-2.7 fibre (●) [H]/[C] ratio, (■) [N]/[C] ratio.

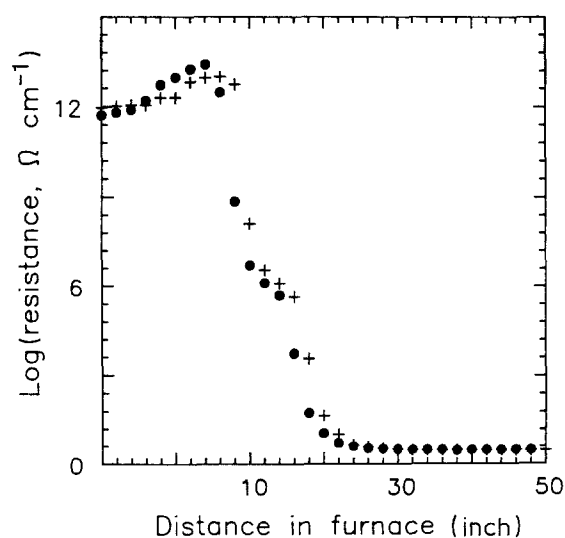


Figure 4 Change in electrical resistance during carbonization of precursor II. (+) II-0.7-5. (●) II-0.7-2.5-G-190-2.7.

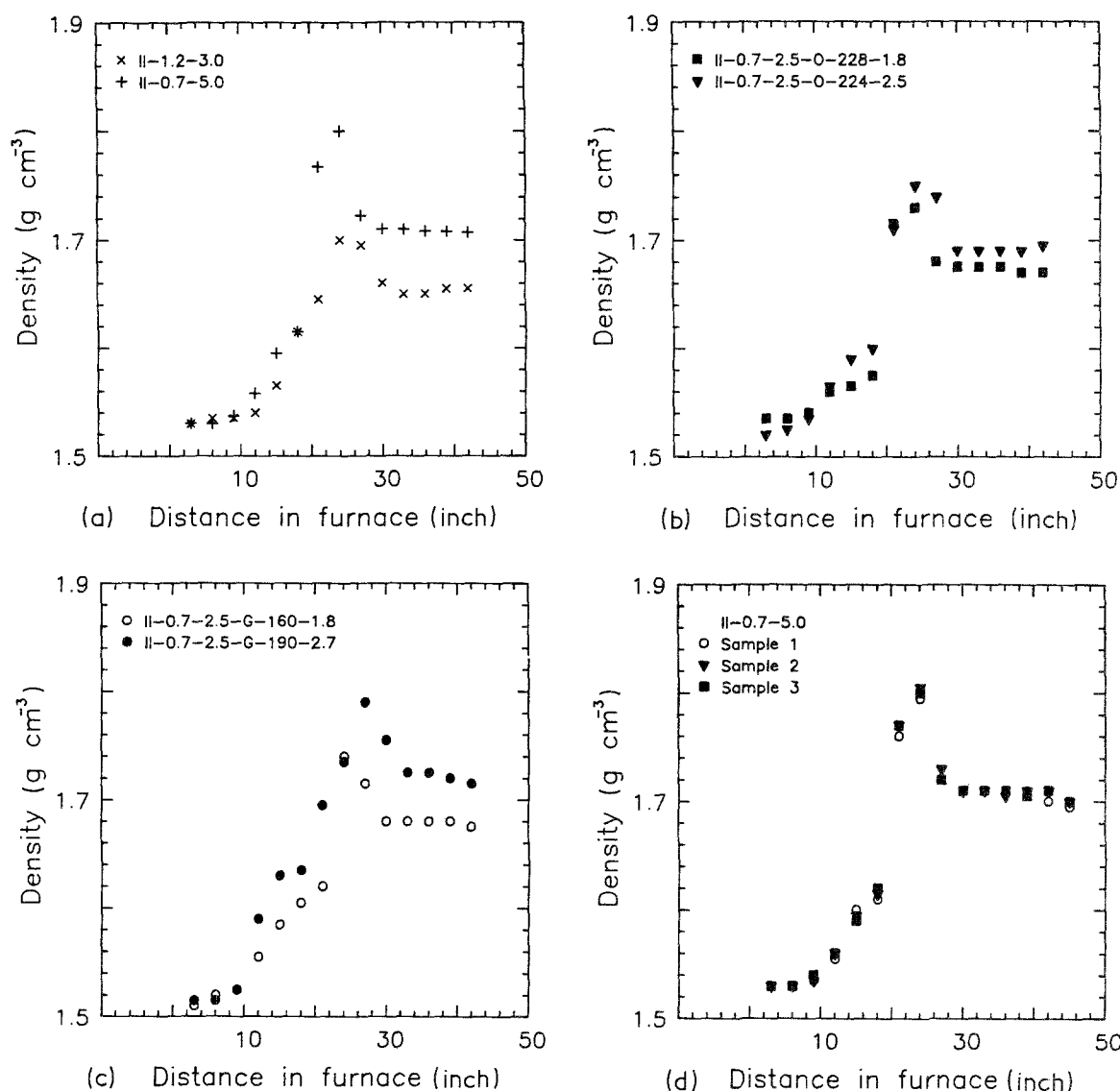


Figure 5 Change in density during carbonization of precursor II. (a) and (d) drawn in hot water; (b) drawn in hot water and hot oven; (c) drawn in hot water and hot godet. (The conditions of formation of the precursor fibres are given in the sample designations, d)

annealing in the latter stages. A similar explanation has been offered earlier by Gibson [6] for the decrease in density observed for carbon fibres produced at increasing temperatures in the range of 1000 to 2000°C.

The effect of continuous carbonization at different speeds was also explored with precursor II fibres. Sample II-0.7-5 was employed for this study and carbonization was carried out at speeds ranging from 0.5 to 3.9 ft min⁻¹, giving a residence time range of 1 to 8 min in the furnace (0.25 to 2 min in the 1200°C

zone). At speeds greater than 2 ft min⁻¹ very fuzzy bundles with many broken filaments were obtained. Electron microscopic examination of the cross-sections of the carbonized fibres showed holes in the centre of fibres processed at speeds of 2 ft min⁻¹ and higher (Table V). From the progression of changes in carbonization discussed earlier, it is apparent that the highest temperature which the fibre experiences during carbonization is important since limits on fibre properties are dictated by this temperature. In the

TABLE V Carbonization at different speeds

Take-up speed (ft min ⁻¹)	Residence time at 1200°C (min)	Carbon fibres from precursor II			Carbon fibres from precursor III			Denier
		Hollow core	Density (g cm ⁻³)	Sonic modulus (g denier ⁻¹)	Hollow core	Density (g cm ⁻³)	Sonic modulus (g denier ⁻¹)	
0.5	2.00	No	1.715	1061	-	-	-	-
1.0	1.00	No	1.705	1049	No	1.740	1210	1650
2.0	0.50	Yes	1.665	964	Yes	1.715	1195	1761
3.0	0.33	Yes	1.660	918	Yes	1.710	1066	1818
3.9*	0.26	Yes	1.650	908	Yes	1.710	1035	1805

*Maximum speed of the take-up unit.

Temperature profile in stabilization: Precursor II-0.7-5 250-275-300°C.

Precursor III 250-275-275°C.

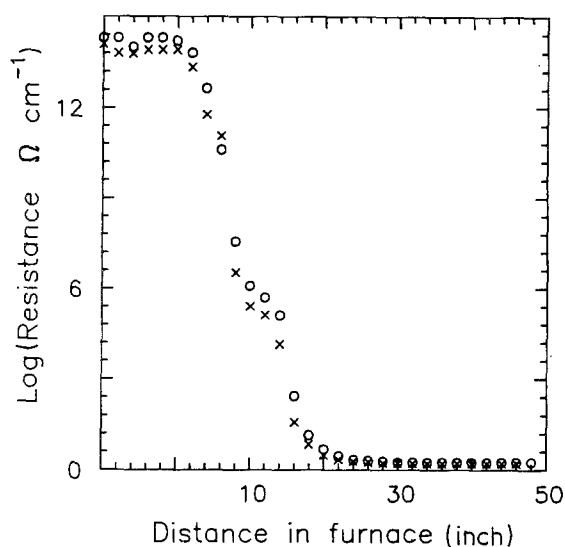


Figure 6 Change in electrical resistance during carbonization of precursor III. (O) 1 ft min⁻¹, (x) 6 inch min⁻¹.

experiments on carbonization at different speeds, the fibre was always exposed to the maximum temperature of 1200°C, but this temperature was reached at higher rates at the higher processing speeds. The formation of a hollow core when these apparently well stabilized fibres are carbonized at higher rates of heating suggests that more than a single mechanism exists for hole formation in the core. At the higher heating rates, an outer layer of the fibre may be carbonized rapidly, with subsequent consolidation of the structure from the sheath inwards, resulting in a hollow core at the end of the process. The decrease in sonic modulus and in the apparent density of carbon fibres (Table V) produced at higher carbonization speeds reflects also poor consolidation of structure under these conditions.

The progression of changes during continuous carbonization of precursor III fibres show the same features as seen with precursor II fibres (for example, Figs 6, 7). Linear densities were also measured on these samples. These measurements reveal once again (Fig. 8) simultaneous rapid loss of material and consolidation of the solid state structure in the initial zone where the temperature is raised to the maximum temperature, with little change beyond this point. When carbonization is carried out at different speeds, the development of a hollow core as well as evidence for incomplete consolidation (Table V) are seen again at processing speeds of 2 ft min⁻¹ and higher.

In order to establish the validity of the two different mechanisms that have been proposed to operate under different conditions of formation of a hollow core in carbon fibres, namely,

- i. "burning off" of the core material when an incompletely stabilized fibre from a diffusion controlled solid-state stabilization process is carbonized, and,
- ii. propagation of the consolidated carbonized structure inwards from the skin when a well stabilized fibre is carbonized rapidly,

additional measurements were carried out in a series of carbonization experiments with incompletely and sufficiently stabilized precursor III fibres. In

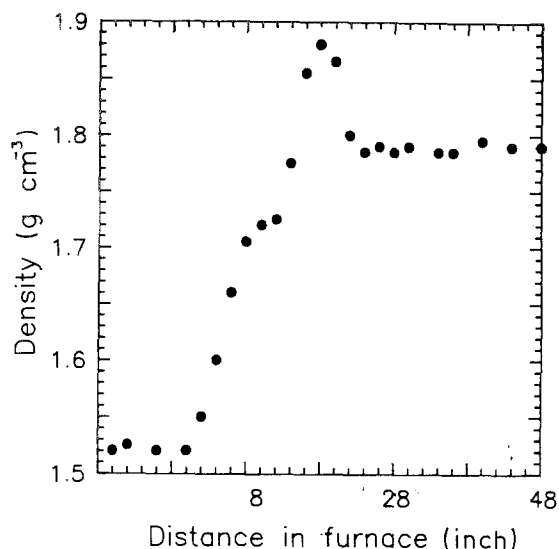


Figure 7 Change in density during carbonization of precursor III.

these experiments, the results of which are reported in Table VI, the linear densities and diameters of these fibres are compared. When the fibres are carbonized at low speeds (0.5 ft min⁻¹), the linear density of the carbon fibres from sufficiently stabilized precursor is significantly higher than that from the incompletely stabilized precursor indicating the expected loss of material in the latter through "burn off". Every filament in the latter bundle also exhibited a hollow core. When these two precursor fibres were carbonized at a higher speed (3.5 ft min⁻¹), a hollow core developed in both cases, but the linear density *and* the diameter of the sufficiently stabilized precursor were higher, consistent with the consolidation mechanism at the higher rates of carbonization proposed here. Comparison of the carbon fibres produced at different speeds from apparently well stabilized fibres shows little difference in linear densities, lending further support to the mechanism of consolidation inwards from the skin. Also, when the sufficiently stabilized precursor is carbonized repeatedly at 1.5 ft min⁻¹, a condition which yields a hollow core in about 60% of the filaments, little change in diameter is observed with

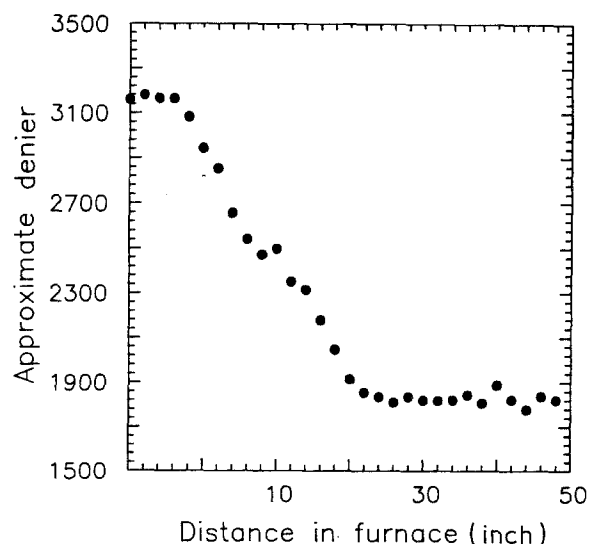


Figure 8 Change in linear density during carbonization of precursor III.

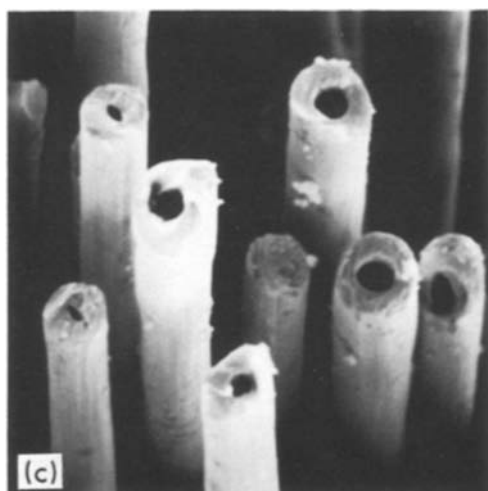
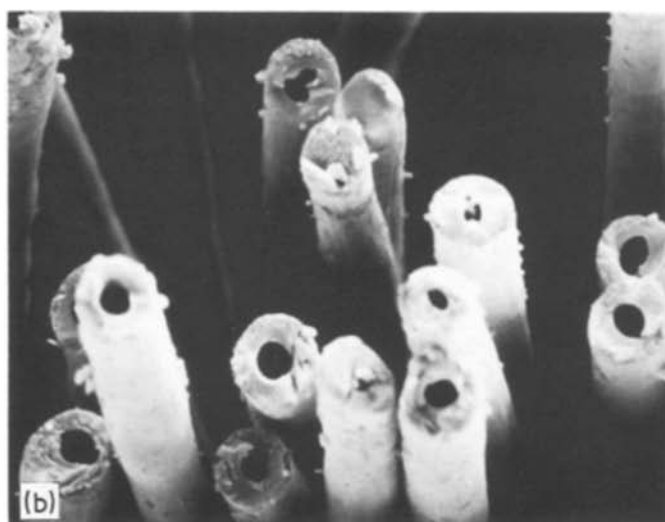
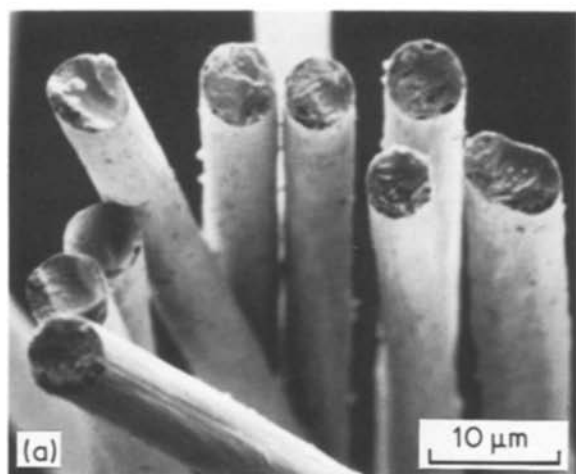


Figure 9 Typical cross-sections of carbonized fibres from precursor III. (a) Stabilized at 250–275–275, carbonized at 0.5 ft min^{-1} . (b) Stabilized at 250–275–275, carbonized at 3.5 ft min^{-1} . (c) Stabilized at 250–265–265, carbonized at 3.5 ft min^{-1} .

reconsolidation. Typical cross-sections from these experiments are shown in Fig. 9.

We see that the qualitative features of the progression of changes during the carbonization are not changed with composition (comonomer with AN) or the extent of orientational and lateral order generated in the formation of precursor fibres. Fundamental aspects of the evolution of properties revealed through the measurements in this study are thus believed to be the general characteristics of the formation of carbon fibres from acrylonitrile-based precursor fibres.

4. Conclusions

A number of significant results have been obtained through the research on continuous low temperature

carbonization reported here. These findings and the inferences from them regarding needed additional research are summarized in the following.

i. It is necessary to carry out the stabilization treatment until a critical density is reached in order to avoid the formation of a hollow core in carbon fibres processed under reasonably rapid carbonization conditions. This aspect has been known in commercial practice. The dependence of this critical density on composition remains to be explored.

ii. A hollow core is also formed when apparently well stabilized fibres are carbonized at rates higher than a critical rate. This suggests that more than a single mechanism exists for hole formation in the core and that structural/chemical changes are temperature/time dependent. The influence of low stabilization and slow carbonization against high stabilization and fast carbonization on ultimate properties was not determined. It is possible that, at the higher rates of the carbonization process, an outer layer of the fibre is carbonized rapidly and that subsequent consolidation occurs from the skin inwards, resulting in a hollow core at the end of the process.

iii. Properties such as electrical conductance and sonic modulus, which depend on the extent of formation of ordered basal planes, develop rapidly initially

TABLE VI Carbonization with sufficiently (A) and incompletely (B) stabilized precursor III fibres. Stabilization temperature sequence: A (250-275-275) and B (250-265-265) in °C.

Sample	Carbonization speed (ft min^{-1})	Density (gm cm^{-3})	Denier/filament	Diameter (μm)
A-1	0.5	1.73	0.60	5.6
A-2	3.5	1.71	0.59	6.5
A-3	1.5	1.73	0.60	6.6
A-3-1*	1.5	1.73	0.58	6.5
A-3-2†	1.5	1.76	0.58	6.6
B-1	0.5	1.71	0.54	5.3
B-2	3.5	1.71	0.53	5.5

* Re-carbonization of A-3.

† Re-carbonization of A-3-1.

in the carbonization process, with a slower asymptotic increase with continued heating at the highest temperature. Both the rate and the extent of increase in sonic modulus during carbonization increase with the extent of lateral and orientational order present in the precursor fibres which should promote the ordering process during carbonization. These trends are also reflected in [H]/[C] and [N]/[C] ratios which indicate the degree of aromatization and basal plane formation.

iv. The density of fibres rises in the initial stages of carbonization but reaches a relative maximum beyond which it decreases rapidly to a lower steady value. This apparent decrease is believed to be the result of consolidation of ordered domains around some of the micropores, converting them from "open" pores to "closed" pores, inaccessible to the measuring liquid. This hypothesis needs to be confirmed with a combination of SAXS and measurements based on volume filling of accessible pores and adsorption on accessible surfaces. The combination of density and accessible surface area measurements has been used by Kipling *et al.* [7] to infer open and closed pore structures in graphitizing and non-graphitizing carbons. Additional evidence can also be obtained by combining linear density with measurements of filament diameter along the carbonization line.

v. Procedures developed in this study for monitoring the evolution of carbon fibres in a continuous process can be valuable in optimizing the carbonization set-up. It is necessary to have the provision to alter the temperature profile in carbonization so that measurements of the evolution of properties during the process can be used to advantage in tailoring the appropriate time-temperature profile.

Note

Preliminary results from current research in our lab-

oratories indicate that while the levels of modulus that can be reached in carbonization may be dictated by the orientational order in the precursor fibres, the strength that can be obtained may be affected by both orientational and lateral crystalline order in the precursor fibres. A very high degree of crystalline order in the precursor fibres would diminish the orientational relaxation that can occur during stabilization, especially in the early stages, and thus reduce the concentration of the strength limiting misoriented crystallites in the carbon fibres produced from them. These aspects will be discussed later in this sequence.

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