

PRECURSOR STRUCTURE - FIBER PROPERTY RELATIONSHIPS
IN POLYACRYLONITRILE-BASED CARBON FIBERS

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FINAL TECHNICAL REPORT

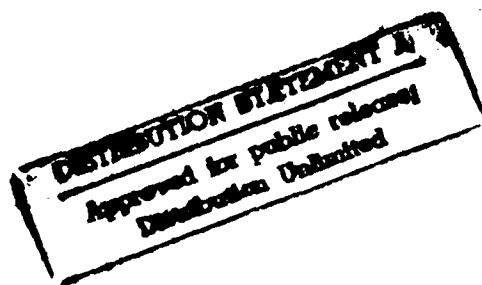


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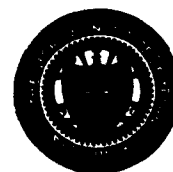
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I. INTRODUCTION

Carbon fibers occupy a premier position among high performance fiber structures, with a combination of physical and mechanical properties, in tension and in compression, that makes them uniquely suitable for application in many advanced fiber-reinforced composites. Fundamental investigations pertaining to precursor fibers and conversion processes in the last decade have paved the way for significant improvements in mechanical properties, especially in the tensile properties of polyacrylonitrile- (PAN) based fibers. Much of the empiricism which existed in the early phases of carbon fiber development has been replaced by fundamental knowledge of the evolution of structure and properties. Georgia Tech has been a significant contributor to this global effort, with important contributions and current research spanning the range from acrylic precursor fiber formation, through oxidative stabilization, to carbonization.

Previous research in our laboratories on fundamental aspects of the conversion of PAN-based precursors to carbon fibers [1-14] led to the following significant results and conclusions:

- (a) The two-phase fibrillar morphology, originally proposed by Warner, et al. [15], is the most appropriate model of the structure of oriented acrylic precursors for carbon fibers. Knowledge of the morphology is valuable in establishing process and material variants which govern the ultimate properties of carbon fibers.
- (b) The tendency in oriented acrylic fibers to undergo rapid morphological rearrangements at high temperatures ($>220^{\circ}\text{C}$) can be used in a deformation process to yield precursor fibers of significantly higher order. This deformation would lead to a significant reduction in morphological flaws of the carbon fibers which can arise in the form of misoriented crystals. Such a high temperature deformation, combined with minimizing extrinsic sources of flaws (impurities) have been largely responsible for the recent dramatic improvements in tensile properties of commercial carbon fibers.
- (c) A multi-zone stabilization process, with the computer-assisted control of the stress field in each zone, can be used to effect maximum transfer of order from the oriented precursor to the carbon fibers. It can also be used to combine desirable high temperature deformation with stabilization.
- (d) In spite of the enormous complexity of the numerous reactions and the transport of resulting species which occur in stabilization, a mathematical

model which judiciously groups similar reactions together has been developed. This model represents the first promising effort to examine theoretically the gradients which evolve within the filaments in a stabilization process.

- (e) Among the many criteria which have been proposed to identify the state of stabilization which is appropriate for carbonization, obtaining a precursor-dependent critical density has been shown to be the most consistent for this purpose.
- (f) Two mechanisms can produce a hollow core in carbonization, namely, (i) "burning off" of the core material when an incompletely stabilized fiber from a diffusion-controlled solid-state stabilization process is carbonized, and (ii) propagation of the consolidated carbonized structure inward from the skin when a well stabilized fiber is raised rapidly to carbonization temperatures. The latter mechanism might be used to produce well consolidated hollow carbon fibers.
- (g) In order to establish the optimum conditions for carbonization, of any precursor, it is necessary to establish the evolution of chemical structure and morphology *within* a carbonization process. Morphological evolution follows the chemical changes to the carbonized structure which occurs rapidly in this process. The key to obtaining the best combination of properties in tension *and* compression is likely to be in reaching the appropriate combination of lateral order (or disorder) and orientational order.
- (h) Plasticized melt spinning of precursor acrylic polymer yields a morphology which is entirely appropriate for high performance carbon fibers. This approach can offer a better solvent system for precursor fiber formation in the future.

Much progress has been made in establishing the fundamental material and process interactions in the formation of high performance carbon fibers as a result of research conducted at Georgia Tech and in other industrial and academic laboratories. A two-fold increase in modulus as well as tensile strength has been achieved primarily through the combination of increased morphological order and reduced levels of contaminants. Significant progress has also been made in reducing processing times, in fiber uniformity at each stage and in physical and analytical monitoring of the evolution of structure in the conversion processes. Such progress notwithstanding, several significant aspects of carbon fiber formation demand continued research. It is necessary to continue current comprehensive research efforts on the chemical and morphological aspects of the conversion of precursor polymers to carbon fibers in order to improve significantly our understanding of the evolution of structure, and thereby the properties, of these critical materials. The study reported here has focussed on aspects of improving the stabilization process on the one hand, and conducting a detailed analysis of the evolution of structure and properties during carbonization of well stabilized fibers on the other.

II. OBJECTIVES

The primary objectives of the research reported here have been to strengthen the fundamental knowledge base and to provide rational directions for advances in precursor fiber structures and process routes to generate new morphologies and superior mechanical properties in PAN-based carbon fibers. Significant progress in this direction has been made through a general emphasis on exploration of the fundamental aspects of the chemical and morphological evolution from PAN-based precursors to carbon fibers. "Material-Process-Morphology-Property" relations have been explored at each of the three major stages in the conversion of PAN-based polymers to carbon fibers [1-14]. The major emphasis in this most recent study has been on the following aspects.

(i) **Lower cost material-process options:** Large scale application of high performance carbon fibers is feasible only if its cost can be significantly reduced. One of the primary bottlenecks in the conversion process is the slow oxidative stabilization step. A process for rapid stabilization of acrylic precursors has been examined in this study.

(ii) **Evolution of structure and properties in continuous carbonization:** Although the carbonization process as a function of carbonization temperature has been extensively studied, little attention has been paid to the evolution of structure and properties during continuous carbonization. It is necessary to identify the morphological state *during* the evolution of carbonized structure that would yield the best combination of properties in tension *and* compression. It is also necessary to understand the organization of structural elements in carbon fibers so that rational processes can be designed to achieve a desired combination of properties.

III. EXPERIMENTAL PROCEDURES AND RESULTS

III.1. Materials

III.1.1 Precursors for Stabilization Studies

A major part of this study was conducted using a commercial acrylic fiber containing 2% methyl acrylate (MA) as comonomer. This was the base precursor in this study. Properties of this precursor, solution spun using DMAc as the solvent, are typical of commercial acrylic fibers. In addition, three other precursors (a homopolymer, a terpolymer with 6% methyl acrylate and 1% itaconic acid, and a copolymer containing 3% itaconic acid) were also investigated. Except for the copolymer with 3% itaconic acid, which was produced at Georgia Tech, all other materials were commercial precursors.

Table 1. Properties of Precursor Fiber Containing 2% MA Comonomer.

No. of Filaments	3000
dTex/Filament	1.14
Tenacity (cN/dTex)	3.7
Breaking Elongation (%)	8.4
Sonic Modulus (cN/dTex)	128
Intrinsic Viscosity (dL/g)	1.46

III.1.2 Preparation of Fiber Samples for Carbonization Studies

A broad range of samples have been sought for the proposed investigations regarding the evolution of compressive strength in the formation of carbon fibers. The motivation here has been to explore not only the evolutionary aspects in the conversion of current commercial precursors, but also the mechanisms by which different morphologies can be obtained in the carbon fibers. The following have been investigated in this regard.

(i) Role of Carbonization Temperature:

It is well known that the extent to which chemical and morphological transformations to a turbostratic graphite-like structure occurs (even with prolonged exposure) increases monotonically from the low end of carbonization temperatures (800°C) to the high graphitization temperatures (>2500°C). In order to explore these morphologies and the consequent mechanical properties, one set of experimental carbon fibers that had been processed at different temperatures have been obtained from an industrial laboratory. These fibers will be referred in this study as *terminal* fibers.

(ii) Evolution within a Continuous Carbonization Process

We have shown earlier that the chemical and morphological changes occur at different rates in a carbonization process, with the former having to necessarily precede the latter in forming the carbonized structure [11]. Thus a carbonization process with a set maximum temperature is fully characterized in this regard only when the role of time-stress-temperature interactions are established. Carbonization, being a relatively slow process, lends itself well to such studies, i.e., it allows the generation of samples with increasing extent of transformation. This has been accomplished in the present study by (i) initially allowing continuous carbonization to reach a steady state, (ii) cutting the fiber at the exit of the furnace, and (iii) withdrawing the fiber rapidly from the inlet end. This length of fiber is cut into sections and the fibers within each section are characterized for their morphological features, chemical composition and mechanical properties. In order to ensure that a high quality of processing, fibers processed in the above described manner were also

obtained from an industrial pilot research facility, with the fibers processed under conditions of a linearly increasing temperature profile (to the maximum temperature). Results from studies of these fibers are reported in section III.6.2.

III.2. Procedures for Stabilization of PAN-based Precursors

III.2.1. Batch Stabilization

Batch stabilization was carried out using a tubular oven mounted on rails. A 15 cm long fiber loop was held by Kevlar from both ends through a hook. The oven was preheated to the required temperature and moved into position such that the fiber loop was well within the constant temperature zone of the tubular furnace. For constant length stabilization studies, the Kevlar ends on both sides of the sample were tied and the sample was not allowed to shrink. For free length stabilization studies, Kevlar from one end of the sample was anchored to a stationary post, and the other end was passed over a smooth pulley and attached to a very small load, corresponding to .002 cN/dTex tension. The change in fiber length was measured by monitoring the movement of the weight at the free end. The changes in length taking place in the Kevlar leader at the temperatures of this study were negligible in comparison with the changes being monitored in the acrylic fibers. The fibers were heated for the required time, and the heater was then moved and the samples were collected for characterization.

The batch stabilization studies on the MA-containing precursor were conducted at different temperatures with N₂, air or air/ammonia environments, and temperatures of 250°C and higher were used. In the presence of ammonia, since the stabilization reactions occurred rapidly, lower temperatures (200, 220 and 240°C) were also used. Homopolymer precursor was stabilized at 250°C. The fibers containing itaconic acid comonomer were stabilized at 230°C, since the stabilization exotherm appeared in this case at lower temperatures compared to the fiber containing MA.

The effects of inert (nitrogen), oxidizing (air) and ammonia environments on stabilization were studied. For stabilization in N₂, the controlled gas flow rate (≈500 cc/min) created an inert environment in the heater. The nitrogen purge was started at least 15 minutes before insertion of the sample to ensure an inert environment. For air stabilization studies, either ambient air was pumped in or air from a cylinder was used and monitored by a flow meter.

To obtain ammonia containing air environment, air from a pressurized cylinder was passed through a beaker containing ammonium hydroxide solution and then into the heater. The dropper maintained a continuous supply of ammonium hydroxide into the beaker so that its concentration in the beaker was not diluted with time. In addition, two cylinders, one containing 5% ammonia in

nitrogen (referred to as N_2/NH_3) and another containing anhydrous ammonia (referred to as Ammonia) were employed. These gases were used directly from the respective cylinders, and also after mixing with air. A gas proportioner was used for mixing the gases in required proportions.

III.2.2. Continuous Stabilization

For continuous stabilization, a tubular heater was used. The heater consisted of a 1.5 meter long glass tube closely fitted inside a heated aluminum tube, heated by three heating tapes, each of which was controlled by a separate temperature controller, thus dividing the heater into three zones. The gas or gas mixture was pumped from both ends into the glass tube to obtain the required stabilization environment.

III.2.3. Continuous Carbonization

Carbonization of the stabilized fibers was conducted by passing them under constant tension through a Lindberg furnace at $1200^\circ C$. Two small heaters installed at the entry of the Lindberg furnace provided a 60 cm long precarbonization zone to avoid thermal shock and very high heating rates during carbonization. Nitrogen was passed from both ends to maintain an inert atmosphere inside the furnace. A line speed of 15 cm/minute was used for carbonization (residence time = 8min.).

III.3. Testing of Carbon Fiber Filaments

III.3.1. Recoil Test for Compressive Strength

Measurement of the compressive strength of single filaments of carbon fibers was performed using the recoil technique [16]. In order to facilitate routine and reliable testing of different carbon fiber samples, an experimental rig, shown schematically in Fig. 1, was fabricated.

A standard Instron 1125 instrument with a 500 g load cell was used. Since the fiber samples typically failed at forces less than 20 gf, the full scale range selected on the load cell amplifier was 20g. Apart from the usual electronic calibration, a crosscheck was also performed by hanging accurately known weights to the clamp.

The fiber specimen was glued onto a precut paper tab which allowed for a gauge length of 1 inch. In order to prevent blotting of the adhesive, a commercial non-drip, cyanoacrylate formulation was used. Any possible damage to the fiber from cutting the tab was reduced by cutting one side of the tab prior to sticking the fiber onto the tab.

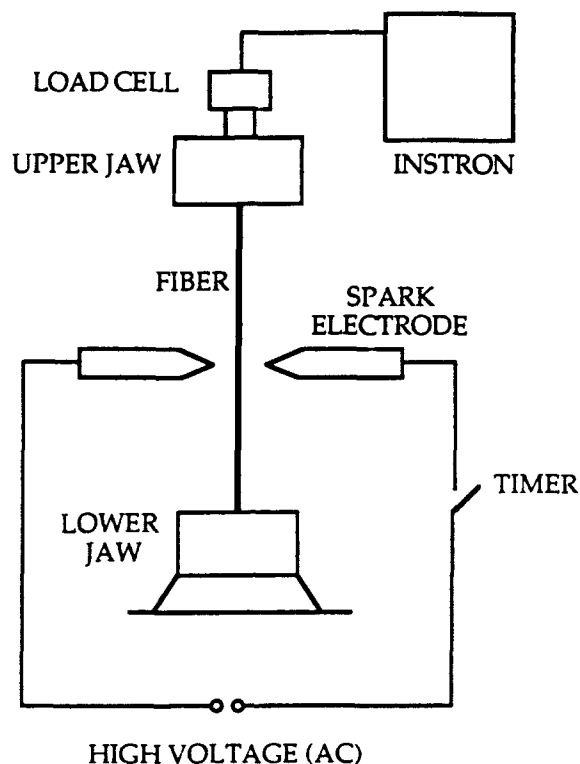


Fig. 1. Schematic of Recoil Test Apparatus.

A typical test for detection of a compressive failure involved the following procedure. The paper tab (with the specimen) was mounted carefully on the Instron tester. The top part was gripped using a spring loaded fiber clamp supplied by Instron. The tab was next gripped at the bottom using pneumatic clamps. Vertical mounting was checked visually. The tab was next separated by cutting the bridging paper segment using a pair of scissors. Any lack of care at this point would result in jarring which could break the mounted single filament sample. This proved to be the single most common cause of wastage of specimens. The fiber sample was next loaded to a predetermined tensile force using a digital multimeter to monitor the output of the stress transducer. A resolution of 0.01V yielded a corresponding force resolution of 0.01 gf. The crosshead speed utilized for this pretensing was initially 0.1 inch/min, with slower speeds of 0.02 and 0.005 inch/min used for fine control once a force level in the vicinity of the desired level was reached.

The cutting of the fiber in tension was performed using an electrical spark generated between two pointed metal electrodes. The spark was generated using a 10kV transformer powered from a 110V AC wall outlet. The spark gap was $\approx 5/8$ inch. In order to remove any uncertainty involved in the spark duration, a timer was introduced in the power line to facilitate a 'power-on' time of 0.1 sec. (Subsequent testing seemed to indicate that spark times of 0.1 s and 0.5 sec gave the same results.) Since aligning the electrodes around the specimen was both time-consuming and tedious, a small mechanical stage, mounted on linear bearings

that allowed smooth horizontal movement, was fabricated. By sliding the stage, the spark gap could be made to align around the fiber in tension. The registration obtained with this device was sufficiently precise for this test and helped cut down the test time significantly.

It should be noted that the method of cutting employed by Allen [16] was a sharp pair of scissors. This scheme was investigated prior to using an electric spark, which was used originally by Wang et al. [17]. As expected, a much larger variation in values was seen with manual cutting. The discrepancy between the compressive strength values obtained with manual vs. spark cutting was especially severe with higher modulus fibers. This could be due the significantly larger stresses developed in the high modulus material during the process of inadvertently deforming the fiber while cutting it manually.

The recoil method involves inspection of the fiber near the clamps after the cutting has been performed. With carbon fibers, a break is believed to occur when the stress built up during the recoil exceeds the compressive strength. Absence of the fiber segment between the tab and the cutting point therefore represents a failure in compression. The occurrence of a break in one tab and a no-break in the other tab was recorded as a break and a no-break. Once a value in the vicinity of the compressive strength of the sample was reached, a break implied lowering the next test's tensile load by 0.2 gf, while a no-break implied raising the next test's load by 0.2 gf. (This has also been referred to as the "up-down" or "staircase" method.) The range from the maximum force level at which the samples almost never failed to the minimum at which they almost always failed was typically about 1 gf, but larger ranges of 1.5 to 2.5 gf have also been observed.

Since the actual diameter of the fiber was not measured on each test specimen, the stress value corresponding to each failure was not known. The range of force values, combined with the average diameter of the fibers, were used to estimate the average, the minimum and maximum values of the failure stress.

The method of data collection and analysis described above does not provide much meaningful statistics regarding the nature of recoil strength distribution and its possible relationship to the true axial compressive strength of fibers. More extensive measurements and statistical analysis were, therefore, performed with PAN-based carbon fibers produced through carbonization at 1000°C. Twenty to forty specimens are tested at each force level, separated by 0.5 gf in the case of 1 inch and 3 inch gauge length samples, and by 1 gf in the case of 0.5 inch gauge length samples. The results from a refined statistical procedure for analysis of these recoil test data that lends itself easily to the estimation of physically meaningful characteristic material parameters such as "zero gauge length" (ZGL) compressive strength are presented by Jiang *et al.* [18] who have performed such an analysis on a 1000°C PAN-based CF, by testing 20-40 fiber specimens at various load levels. The distribution functions were modeled with both a Weibull and a Logistic model. It should be noted that accurate interpretations from such studies require testing a very large

number of samples. In order to obtain an accurate estimate of the cumulative function, a sample size that is very large (>100) has to be tested at several load levels.

While the rigorous method described above is useful in examining the actual distribution of recoil strengths, this entails testing a prohibitively large number of specimens, which is not practical for routine testing. The simplest alternative scheme is based on listing the applied stresses in increasing rank, and selecting the range of stresses over which a transition from survival of both fiber fragments to failure of both fiber fragments occurs [19, 20]. The average stress value of this transition range is defined as the recoil strength of the fiber sample. Allen [16] and Wang *et al.* [17] have defined the lowest stress level in the transition range as the fiber recoil strength.

The transition zone of stresses is distinct in most cases. In earlier investigations, instances where outliers produced a failure (or survival) in the low stress range (or the high stress range) have been handled subjectively. Crasto and Kumar [20] have disregarded such specimens; inclusion of these could result in an overly-wide transition range. Since low-value outliers would significantly depress recoil strengths when the criterion proposed by Allen [16] and Wang *et al.* [17] is used, it is preferable to define the average strength in the transition zone as the mean recoil strength of the fiber. It is to be noted that depending on the magnitude of the change in stress levels, it is possible to transit from survival of both fragments to failure of both fragments when stress levels are increased (and vice versa) by a single discrete increment. Smaller load increments/decrements near the transition zone reveal cases where only one of the fragment fails and the other survives.

In this study, a minimum of 15 fiber specimens were tested for each fiber sample. This resulted in 30 test cases. The loading schedule followed is called the 'staircase method' or the 'up-and-down method' [21]. Load levels were increased when both fragments failed, and were decreased when the fragments survived. In cases where only one fragment survived/failed the load level was alternately increased or decreased. The advantage of this scheme is that the testing loads are predominantly within the transition zone, with enough samples at the extremes to mark the transition zone. Load increments were usually 1 gf (smaller increments of 0.5 gf were used for fiber samples which had recoil strengths less than 2 gf). The average of the transition range is reported as the fiber recoil load. In order to determine the corresponding fiber recoil strength, the fiber recoil load was divided by the average fiber cross-sectional area.

III.3.2. Torsion Modulus

Shear moduli of fiber samples were estimated using a torsion pendulum in a vacuum chamber at a pressure of 5 inches of mercury. For ease of handling, fiber samples were glued on to the same cardboard tabs that were used for tensile and compressive testing. This was attached to an inertia-disc using adhesive tape of constant dimensions, and the webs of the tab were cut so as to have identical tab

pieces on the bottom end for each fiber specimen. This procedure ensured a constant moment of inertia of the rotating mass for all specimens. The pendulum was perturbed by quickly opening and closing the vent valve of the vacuum chamber, thereby introducing a small air current in the chamber. Care was taken to obtain a final constant vacuum level of 5 inches of mercury (~ 127 Torr) for all samples tested. Measurements were taken after one complete cycle in order to eliminate transient dynamics. It was possible to always measure time-periods and amplitudes for at least two full cycles prior to excess decay of amplitude. Corrections for viscous dissipation were made prior to calculation of the shear modulus. Details of the measurement techniques are given in reference 22.

III.3.3. Wide Angle X-ray Diffraction

These were performed in order to estimate - (1) orientation of graphitic domains and (2) size of graphitic domains in the fiber samples. All data were acquired on a Rigaku-Rotaflex diffractometer with a rotating copper anode, operated at 100 mA and 45 kV. A standard nickel filter was employed for attenuating the K_{β} component in the radiated beam. The nominal wavelength of the K_{α} radiation was 0.154 nm.

Graphite has a hexagonal lattice with the reflections due to the 002 and 100 planes (at diffraction angles of 26° and 44° , respectively) conveying information regarding the size and orientation of the crystallites. It is to be noted that for the turbostratic structures found in carbon fibers, two-dimensional periodicity results in an elongation of the $hk0$ -type reciprocal lattice points along c^* (reciprocal lattice vector). Thus the intensity diffracted by the 100 planes is a 'line of intensity' and is termed a reciprocal lattice rod. Fiber samples of the entire tow were carefully mounted on a sample-holder so as to maintain parallelism between the individual filaments. The holder had movable clamps on each end, which were slightly separated after mounting the fiber bundle in order to collimate the bundle into a parallel array of filaments. Transmission diffraction scans were collected on a $\theta/2\theta$ goniometer in the 10 - 60° range. Similar scans were conducted for each fiber sample at six different azimuthal inclinations of the fiber bundle (0° , 5° , 10° , 20° , 30° and 40°) with respect to the plane of the goniometer. The data acquired were corrected for contributions from air-scattering, sample absorption and Lorentz-polarization effects. Details of the measurement techniques are given in reference 22, including a discussion of the diffraction geometry and the physical meaning of the measured parameters. It should be noted that instead of using an azimuthal scan of the 002 reflection, which can produce erroneous estimates of the extent of preferred orientation of the graphitic domains in the fiber, integrated 002-peak intensities at fixed azimuthal inclinations of 0° , 5° , 10° , 20° and 30° were employed in this study

III.4. Ammonia Stabilization of PAN-based Precursors

III.4.1. Background

Manufacture of carbon fibers from polyacrylonitrile (PAN)-based precursor fibers consists of low-temperature oxidative stabilization in air followed by high-temperature carbonization in an inert atmosphere. During oxidative stabilization and subsequent carbonization, the linear alkyl structure of the precursor is transformed to a planar, aromatic structure. Rings are formed due to cyclization of the nitrile groups of PAN during stabilization, followed by ring aromatization and condensation during carbonization to give planar sections oriented along the fiber axis. The new structure is a consequence of chemical as well as morphological transformations.

In terms of commercial processing, oxidation is a crucial part of the conversion process. It should ensure maximum transfer of the appropriate elements of order from the precursor to the carbonized fibers. Since oxidation is also the rate-controlling step in carbon fiber manufacture, development of faster oxidation techniques is of interest. There are a variety of chemical and structural changes taking place during stabilization and these are affected by precursor composition and pretreatments, and by stabilizing conditions, such as temperature, time, environment, stress, etc. Thermal analysis of precursor fibers reveals a net exotherm from the different stabilization reactions. Among these reactions, the cyclization which occurs through the reaction of the nitrile groups is believed to be the primary contributor to this exotherm. Through a careful study of the effects of introducing into the stabilization environment, gases which evolve during stabilization, Peebles observed a pronounced accelerating effect of ammonia on the disappearance of this exotherm [23]. Ammonia being one of the by-products of the cyclization reactions, its introduction from an external source into the stabilization environment had not been thoroughly investigated. The usual approach to increase the reaction rate would be to shift the equilibrium favorably by removing the ammonia formed during the natural course of stabilization. However, initial thermal analysis studies of Peebles indicated that introducing ammonia in the stabilization environment might lead to considerable acceleration of the process.

A better understanding of the effects of time, temperature, stress and environment in the PAN stabilization process should enable one to reduce the stabilization time and/or to improve the properties of carbon fibers. The research reported here was aimed at achieving these goals. In addition to oxygen-containing (air) and inert (nitrogen) environments, the prospects for using ammonia as an accelerator for the stabilization process were investigated. Acrylic fibers were stabilized in oxidizing, inert, ammonia and mixed environments. Fibers stabilized for different times in these environments were characterized using several techniques to determine the extent of reactions as well as the change in morphology during the process.

The changes in morphology and the chemical structure of different acrylic precursor fibers which occur with the progress of stabilization were followed in the present research. The influence of lateral order, or crystallinity, on the stabilization process were elucidated. Possible mechanisms for the accelerating effect of ammonia, leading to the stabilized state in shorter times, were also developed.

III.4.2. Results from Stabilization in Ammonia

Ammonia was shown to accelerate stabilization of certain non-acidic acrylic precursors in the production of carbon fibers. This can be shown by, for example, the increase in density on stabilization (Fig. 2). Density is a good indicator of the extent of stabilization. During stabilization, density of the fibers increases from ~1.17 to 1.50 g/cc. Studies with a broad range of PAN-based precursors have shown that densities in the range of 1.33 to 1.40 g/cc have to be achieved in stabilization before the fibers can be cohesively carbonized. Other techniques that follow the extent of stabilization also show similar trends, for example, residual DSC exotherm, thermogravimetric analysis, color change, burning potential, oxygen content and sonic modulus [35]. About five per cent by volume of ammonia in air led to maximum acceleration of the stabilization process (Fig. 3).

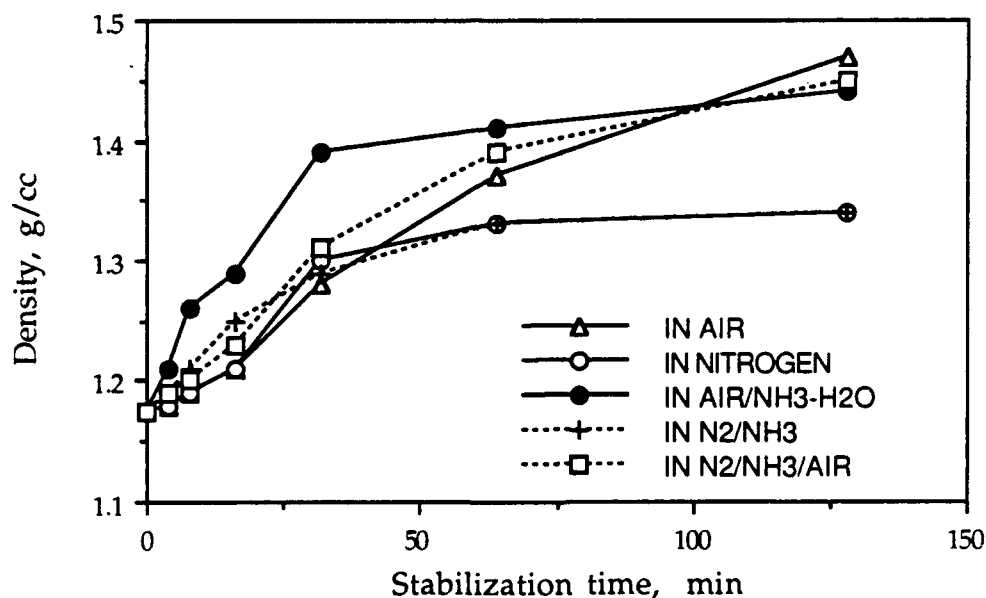


Fig. 2. Increase in density during stabilization at 260°C.

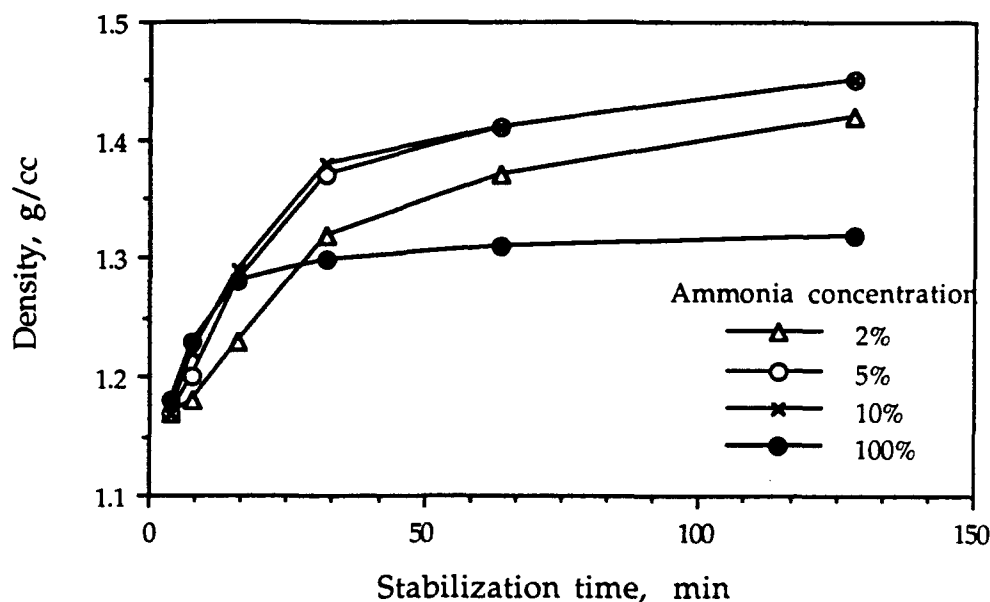
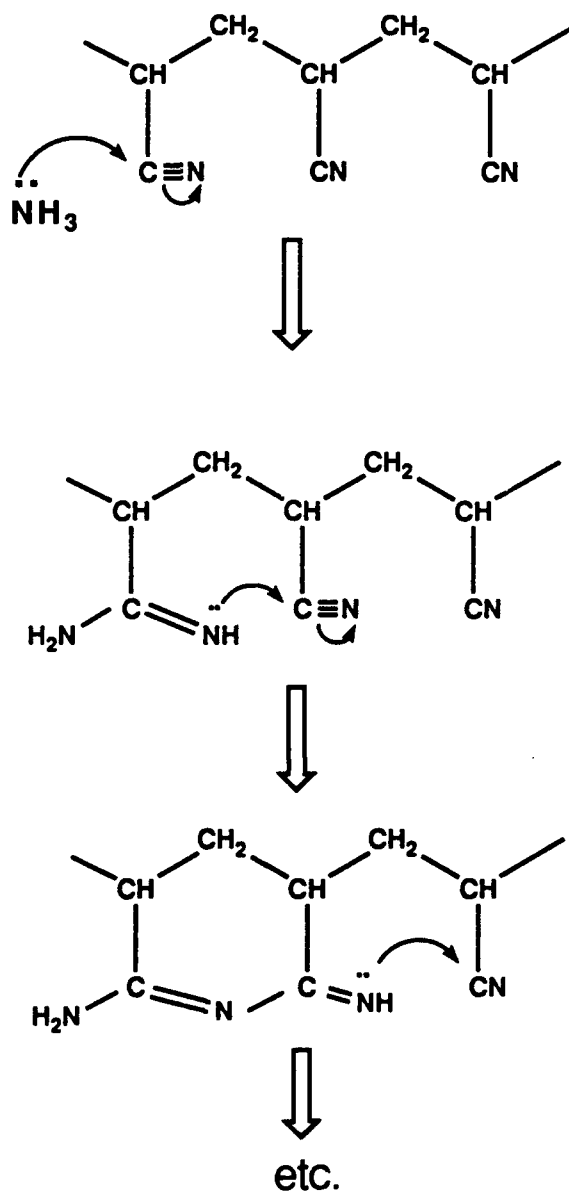


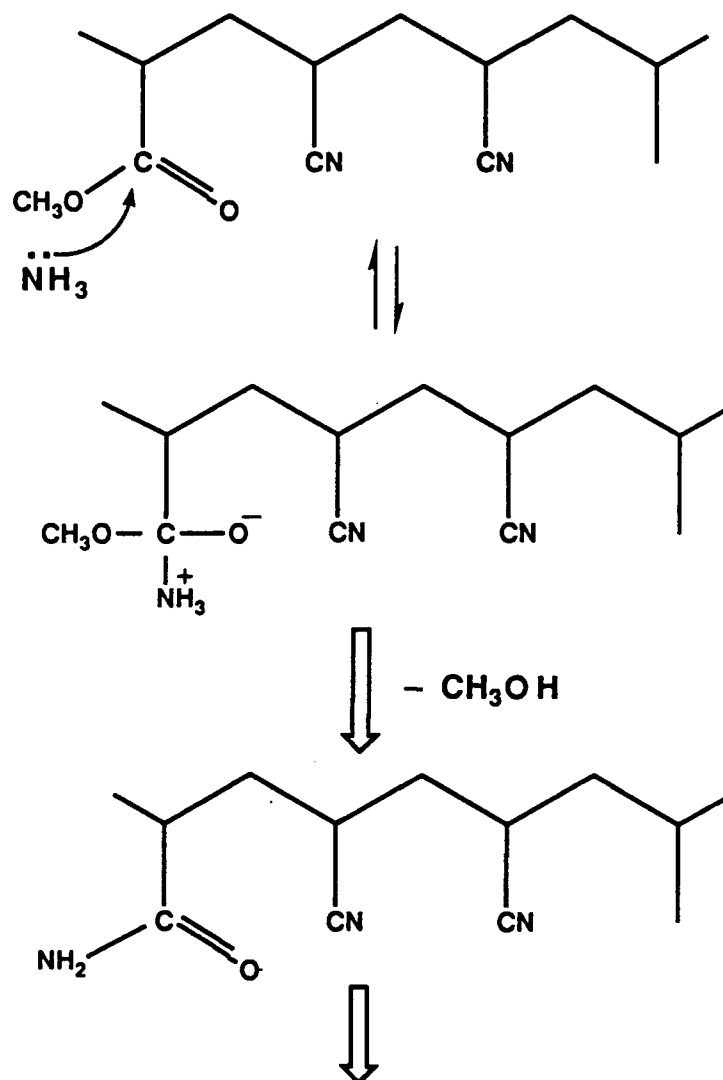
Fig. 3. Change in density during stabilization in different concentrations of ammonia at 260°C.

The presence of oxygen is essential for achieving complete stabilization, even with ammonia present in the atmosphere. In nitrogen or anhydrous ammonia, stabilization did not go to completion, with treated fibers not turning black and burning when exposed to flame. Correspondingly, fibers heated in the absence of oxygen did not carbonize cohesively. The role of oxygen lies in increasing the aromaticity of the developing stabilized fiber via hydrogen stripping reactions [24]. The increased concentration of conjugated sequences leads to deepening of color, eventually turning the samples black. NH_3 alone cannot substitute in this chemical role. In the presence of NH_3 and absence of oxygen, while nitrile cyclization and a decrease in the population of nitrile groups were proven by FTIR studies, the samples did not turn black even after prolonged heating.

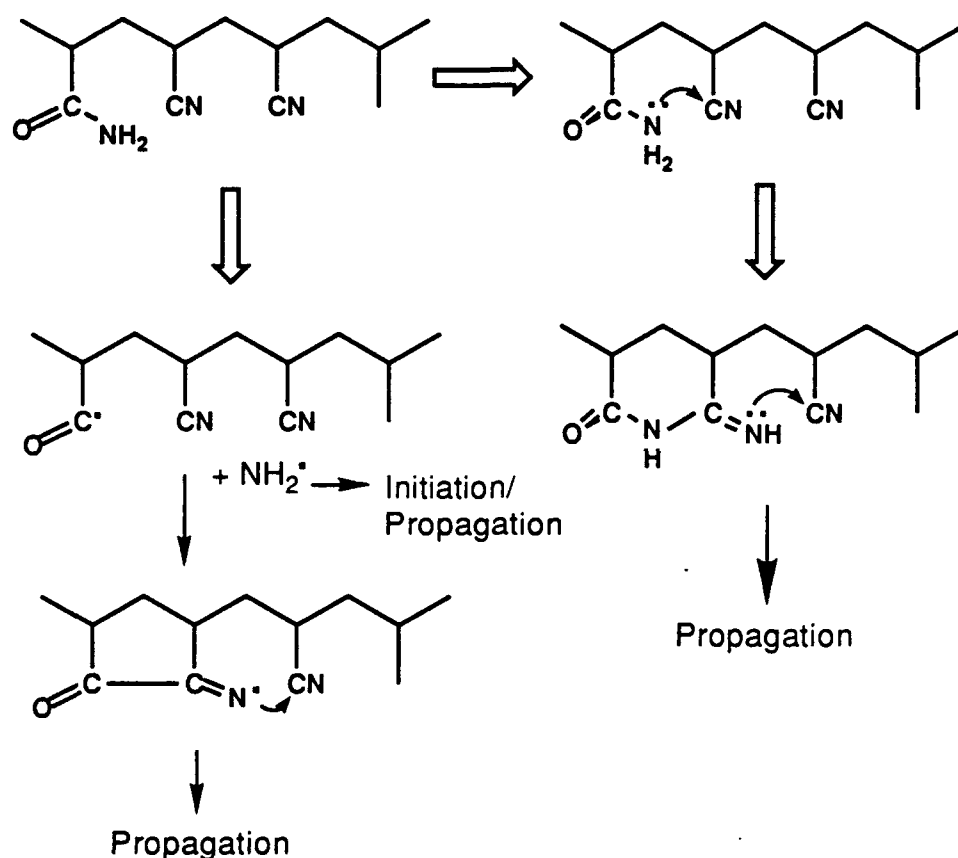
Ammonia, acting as a nucleophile under stabilization conditions, initiates cyclization at nitrile sites (Scheme 1). As the initiation is faster and can occur at multiple sites, stabilization reaction sequences proceed much faster, intra- as well as inter-molecularly. In the case of fibers containing methyl acrylate and no acidic comonomer, cyclization can also be initiated by secondary functional groups produced by reaction of ammonia at comonomer sites, leading to further acceleration. Faster disappearance of $\text{C}=\text{O}$ groups (from methyl acrylate comonomer) was observed by FTIR spectroscopy with ammonia present in the stabilization environment. Incorporation of nitrogen from ammonia into the stabilized fiber structure was also confirmed by a preliminary ^{15}N -NMR study.



Scheme 1. Proposed initiation of cyclization by ammonia.



Scheme 2. Proposed action of ammonia on methyl acrylate and initiation of cyclization.



Scheme 3. Possible paths of initiation of cyclization by an acrylamide comonomer.

For the 2% MA precursor, air/ammonia-stabilized samples approached limiting oxygen content and limiting density values lower than fibers stabilized in air alone. The reaction of ammonia with this acrylic copolymer to initiate cyclization and produce new functional groups left amine-imine and amide type structures at the reaction sites. The presence of such species in the structure led to increased nitrogen content, and thus reduced the weight per cent of oxygen. Density increase, which accompanies the incorporation of oxygen during stabilization, also reached a limiting value.

Lateral order disappeared much faster during stabilization in the presence of ammonia. The rapid decrease occurred both in the presence and absence of oxygen. Crystals disappeared in less than 16 minutes of stabilization in the presence of ammonia (both with and without air), as evidenced from both WAXD and plasticized melting studies. Up to one hour was required to reach this stage in the absence of ammonia. For example, plasticized thermal analysis is a useful technique for obtaining relative estimates of crystallinity in the acrylic fibers. Plasticized melting and recrystallization experiments show the characteristic enthalpic changes associated with first order transitions. The heat of melting (ΔH_m) reflects the

amount of crystals or ordered regions present in the fibers while the heat of crystallization (ΔH_c) represents the potential for crystallization of the polymer melt in an unoriented state under quiescent conditions. The exotherm associated with plasticized recrystallization can be correlated with the extent of reactions that have taken place in the system. As the sample gets stabilized, its potential to recrystallize decreases, approaching a stage when no recrystallization occurs. Results from plasticized DSC which show that the ordered regions are absent in samples stabilized in Air/ NH_3 - H_2O for 16 minutes or more (Table 2), are consistent with the observations from WAXD. During stabilization in air or nitrogen, ordered regions that can be detected by plasticized melting disappear only after 30 minutes.

Table 2. Change in Enthalpy During Plasticized DSC of 2% MA Precursor Stabilized in Different Environments at 260°C (cal/g)

Stabilization time	Stabilization Environment					
	N_2		Air		Air/ NH_3 - H_2O	
	ΔH_m	ΔH_c	ΔH_m	ΔH_c	ΔH_m	ΔH_c
4min	18.5	9.6	18.6	9.7	11.2	5.3
8min	16.2	8.4	17.2	8.9	11.6	4.9
16min	12.6	6.2	14.2	6.2	n.d.	n.d.
32min	3.6	2.1	9.9	2.9	n.d.	n.d.
64min	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

ΔH_m - Heat of Melting; ΔH_c - Heat of Crystallization; n. d. - Not Detected

The ammonia also had a plasticizing effect on the 2% MA precursor, and faster stabilization was probably due to the synergistic effects of plasticization (leading to enhanced gas transport in and out of the fiber) and overall chemical kinetic acceleration resulting from NH_3 attack. Ammonia, because of its affinity for the highly-polar nitrile groups, can form a complex with the latter, thus reducing the strong intermolecular attraction between the PAN chains. Plasticization by ammonia improves diffusion of gases in and out of the fiber structure, further aiding the stabilization process.

Stabilization of the 2% MA precursor was conducted at lower temperatures in the presence of ammonia (Fig. 4). If the residence time allowed for stabilization was the same as in air alone and the fiber linear density were invariant, the maximum temperature could be reduced by about 40°C, with the same level of stabilization

achieved. A possible consequence of lowering stabilization temperature is reduced orientational relaxation, and thus retention of higher order in the stabilized fiber.

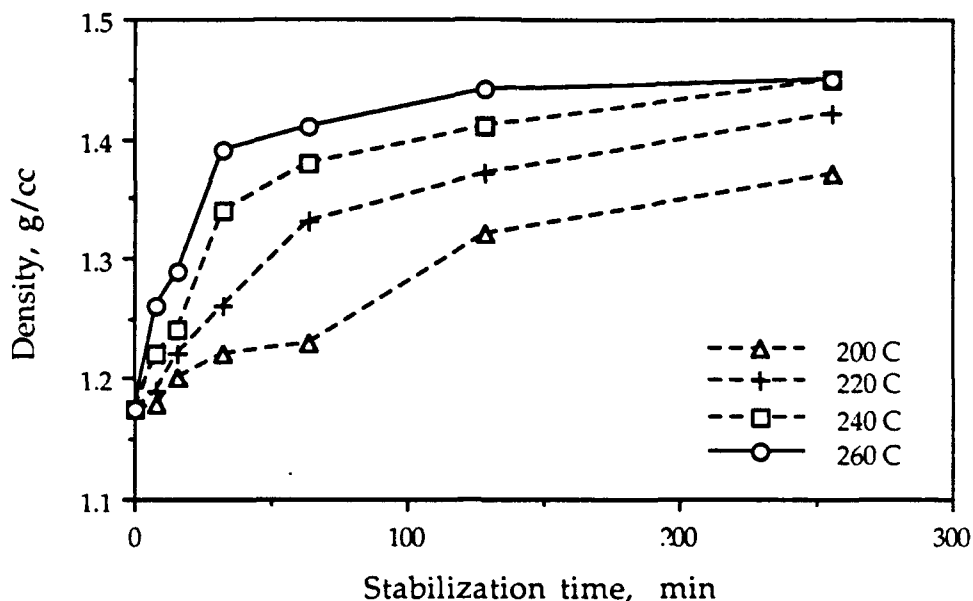


Fig. 4. Change in density during stabilization in Air/ $\text{NH}_3\text{-H}_2\text{O}$ at different temperatures.

The accelerating effect of ammonia was seen throughout the studies on the stabilization of 2% MA precursor. During sequential stabilization studies, the accelerating effect of ammonia was apparent even when introduced after the samples were first heat-treated in air or air/ammonia environments for four to eight minutes. Although the fibers treated in air/ammonia for four minutes showed significant reaction (for example, disappearance of all the carbonyl groups), further stabilization in air was not rapid. The introduction of ammonia led to a significant accelerating effect in these sequential stabilization studies.

For precursors containing acid comonomers, the accelerating effect of ammonia was not observed. Although, calorimetric observations showed some minor effect, the rates at which color and density changed were not significantly higher (Fig. 5). Rapid initiation of stabilization by the nucleophilic acid groups appeared to be more than sufficient to overwhelm any influence of ammonia in these precursors. However, plasticized DSC and X-ray diffraction studies showed that crystals in the acid-containing fibers disappeared much faster in the presence of ammonia, as seen earlier with the 2% MA precursor. Stabilization can thus not be accelerated by only making crystals more accessible to a reactive gaseous species, at least for acid-containing precursors with their built-in, "hot" initiation chemistry.

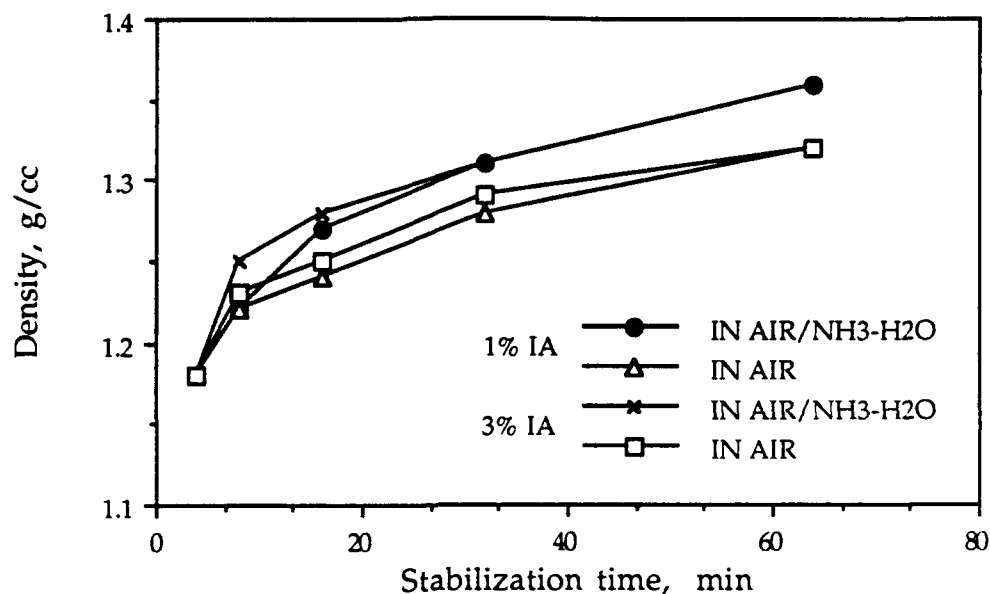


Fig. 5. Change in density during stabilization at 230°C for fibers containing itaconic acid comonomer.

Air/ammonia stabilization led to hole formation in the stabilized fiber and subsequently in the carbon fibers produced from them. Rapid stabilization in the presence of ammonia resulted in a rigid, impermeable skin, and as the stabilization wave progressed inward, a hole formed in the center, with material in the center moving towards the initially-stabilized skin. Morphology along the radius of the air/ammonia-stabilized fiber was nonuniform.

Ammonia, a byproduct of the stabilization reactions, has an accelerating effect on the stabilization kinetics of non-acidic precursors when intentionally introduced into the stabilization environment. The combined result of the two effects are evident: the nucleophilic action of ammonia's unshared pair of electrons in initiating the intra- and inter-cyclization of nitrile groups and in conversion of the poor-initiating acrylate functionality into the fast-initiating acrylamide functionality; and the plasticizing effect of ammonia allowing cyclization reactions to propagate much faster in the laterally ordered regions due to facilitated gas transport in and out of the fiber. The main advantage of using ammonia in the stabilization environment, as opposed to incorporating suitable additives into the fiber, is that the gas will not have any effect on fiber processing (and thus morphological development) prior to the stabilization process.

Rapid stabilization of acrylic fibers in the presence of ammonia also has commercial implications in reducing the cost of carbon fiber production. In addition, ammonia also allows reduction of the stabilization temperature which in turn may reduce the orientational relaxation at this stage. A complementary study

to identify an optimum combination of stabilization and carbonization conditions is necessary before commercial relevance of the process is realized.

III.5. Structural Evolution in Carbonization

III.5.1. Results from Wide-Angle X-ray Diffraction Studies

The stack height (L_c) of graphitic domains and dimensions of basal-planes ($L_{a||}$ and $L_{a\perp}$) of the 'terminal' samples are shown in fig. 6. Since the 270°C fiber had an intense peak at $17^\circ 2\theta$, the crystal lattice is essentially a vestige of the precursor PAN (the 100 peak for PAN is centered at $2\theta \sim 17^\circ$). Analysis for crystallite size was therefore not performed for the 270°C fiber. This peak disappears in the 400°C fiber and is replaced by a peak at $\sim 26^\circ (2\theta)$, which is indicative of lateral periodicity between sheets of aromatic planes. Large increases in stack-height (L_c) are clearly seen at temperatures above 1700°C. Further, L_c is dependent on the orientation of the crystallite, and this dependency is emphasized at higher carbonization temperatures. Larger crystallite dimensions of the more-aligned domains have been reported earlier [25], and has been attributed to the smaller thickness of misaligned graphitic planes that interlink the more-aligned domains in the ribbon model. It is also possible that enhanced crystallite growth of the aligned domains, caused by the existing preferential orientation of molecules in the stabilized fiber, results in orientation-dependent crystallite size.

A rapid increase in $L_{a||}$ occurs only at high temperatures and appears to correlate with a similar increase in L_c . In-plane dimensions of the crystallites (L_a) are larger than the stack-height (L_c), and basal-plane dimensions are observed to be larger along the direction of the fiber axis than in the perpendicular direction. It is to be emphasized that, since dimensions obtained from x-ray experiments are indicative only of the planar sections of the diffracting domains, 'wrinkled' or curved basal-planes may have larger dimensions than determined using the above method. Further, peak broadening may be caused by crystallite size, by inhomogeneous strain in the lattice, or by instrumental effects. Thus, the estimated dimension, based on peak-widths, is only a lower-bound for the true dimension. The reported data can, therefore, only serve as a rough estimate of the actual dimensions of the domains. However, information regarding the magnitude, and rate of change of dimensions with respect to temperature can be reliably estimated through such measurements.

Crystallite dimensions for the 'on-line' samples are shown in fig. 7. Since the maximum carbonization temperature was 1400°C, crystallite dimensions are small in all the fiber samples, and roughly correspond to those observed in the low-temperature 'terminal' samples. L_c remains approximately constant in the 1-1.5 nm range over the entire range of furnace temperatures. Since the inter-planar separation is about 0.35 nm for turbostratic graphite, these dimensions indicate associations of 3 or 4 basal planes. This corroborates transmission electron

microscope studies by Guigon *et al.* [26], who have reported evidence of the formation of such domains at low temperatures. Owing to the low 100-peak intensities, in-plane dimensions were determined reliably only for the 90°-azimuth case ($L_{a||}$).

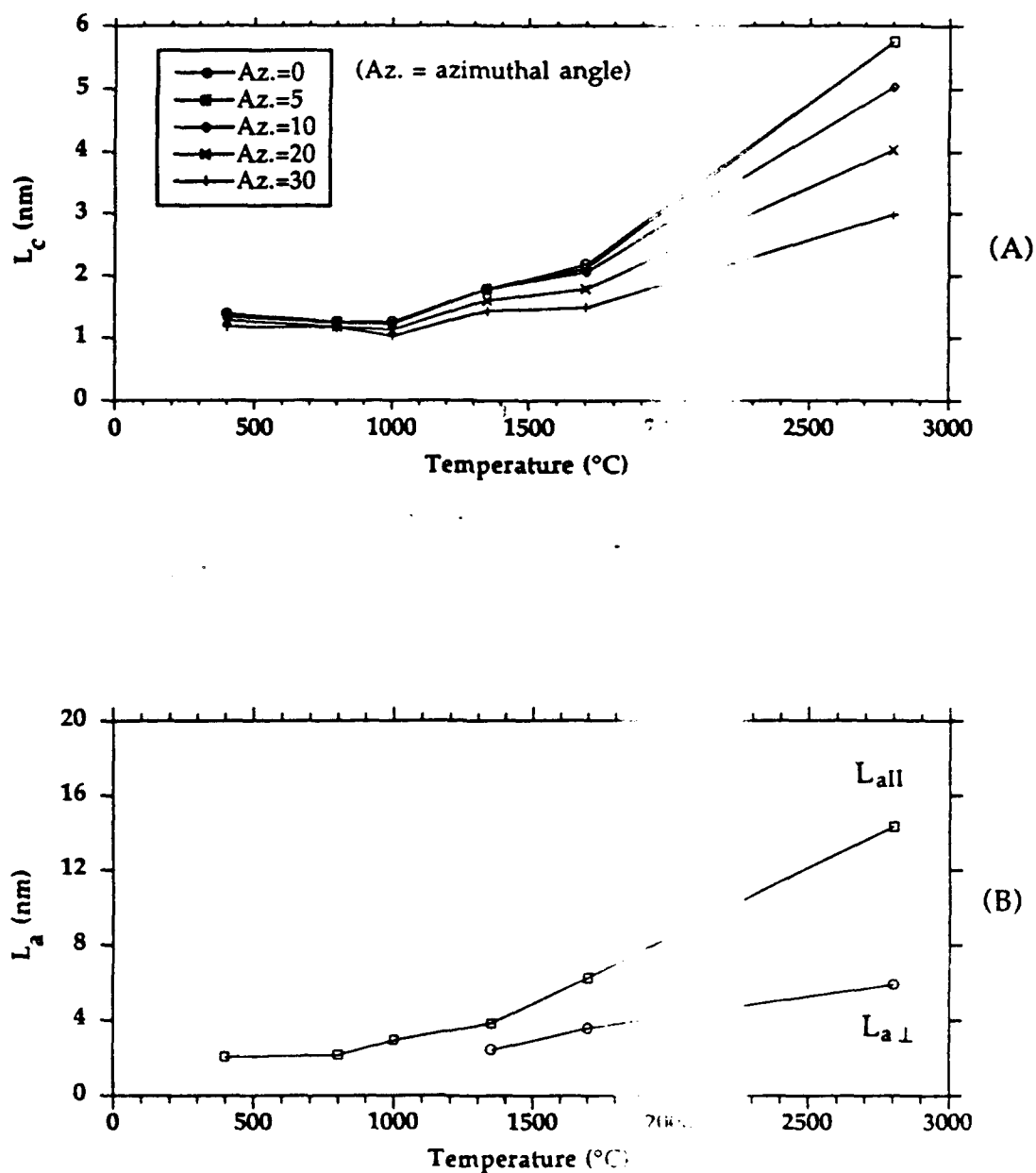


Fig. 6. (A) Stack Height (L_c) vs. Temperature for terminal samples. (B) Basal Dimensions ($L_{a||}$ and $L_{a\perp}$) vs. Temperature for terminal samples.

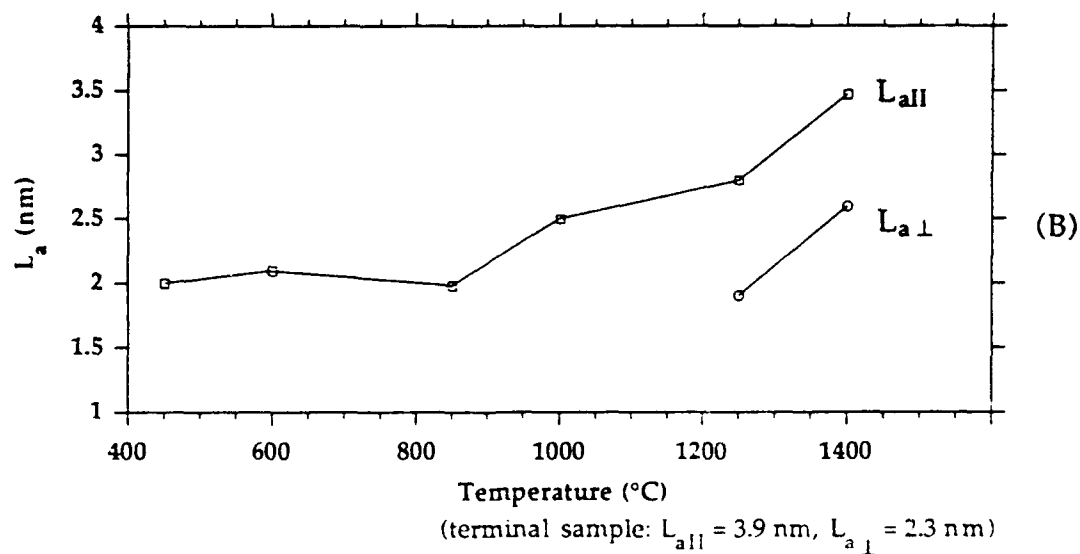
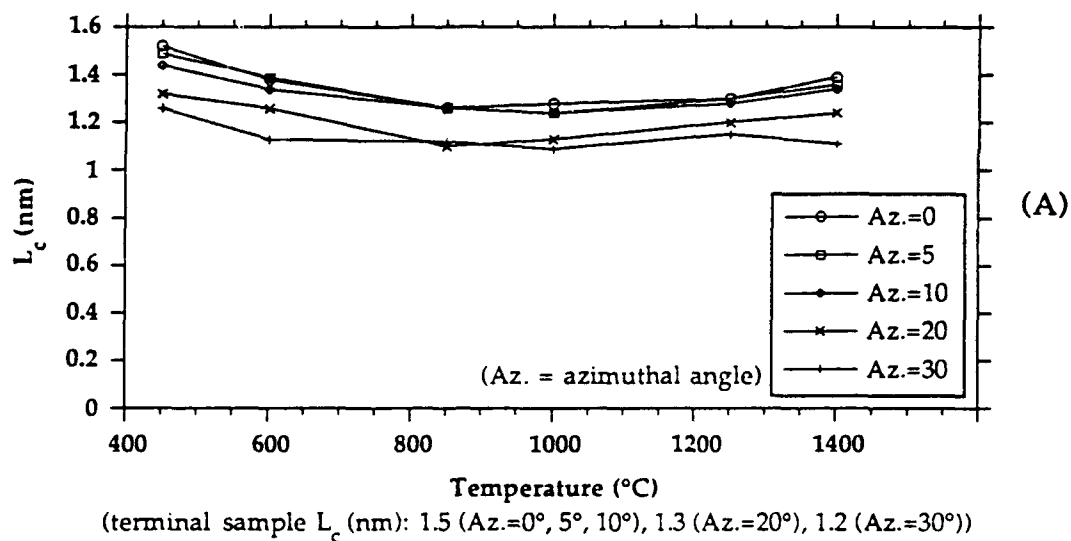


Fig. 7. (A.) Evolution of Stack Height (L_c) During Continuous Carbonization of 1400 $^{\circ}\text{C}$ 'on-line' sample. (B.) Evolution of Basal Dimensions ($L_{a||}$ and $L_{a\perp}$) During Continuous Carbonization of 1400 $^{\circ}\text{C}$ 'on-line' sample.

The advantage of using integrated 002 peak-intensities for determining the crystallite orientation function has been discussed earlier (section III.3.3). Graphs of the probability functions representing the orientation distributions are shown in figs. 8 and 9. The continuous lines represent the best-fit curves, while the individual points represent the observed relative x-ray peak-intensities. A significant evolution of orientation occurs at high temperatures as is illustrated by the 2800°C fiber (fig. 8). All fibers in the 800-1700°C range show only small differences in their crystallite orientation, while the orientation in the 400°C fiber is markedly less. The on-line samples (fig. 9) have about the same orientation over the entire range of furnace temperatures. It can, therefore, be inferred that orientation enhancement in the fiber carbonized to intermediate-temperatures (1200-1400°C range), over that in low-temperature carbonization (~500°C) is not large.

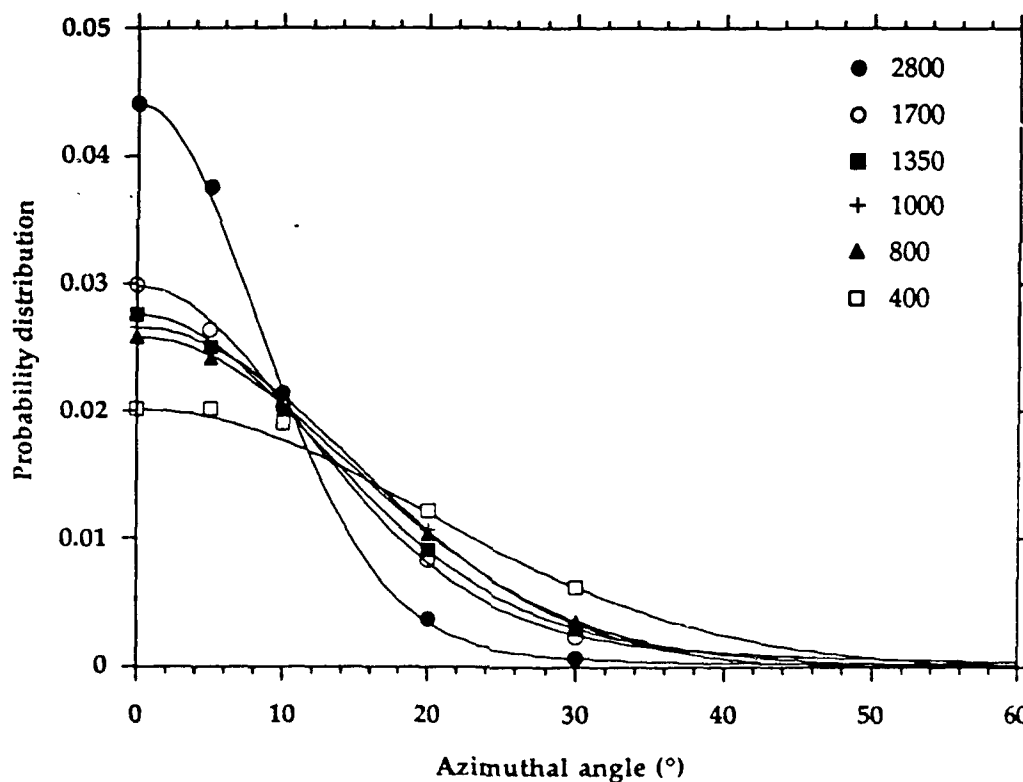


Fig. 8. Orientation Distribution Functions of 'Terminal' Samples.

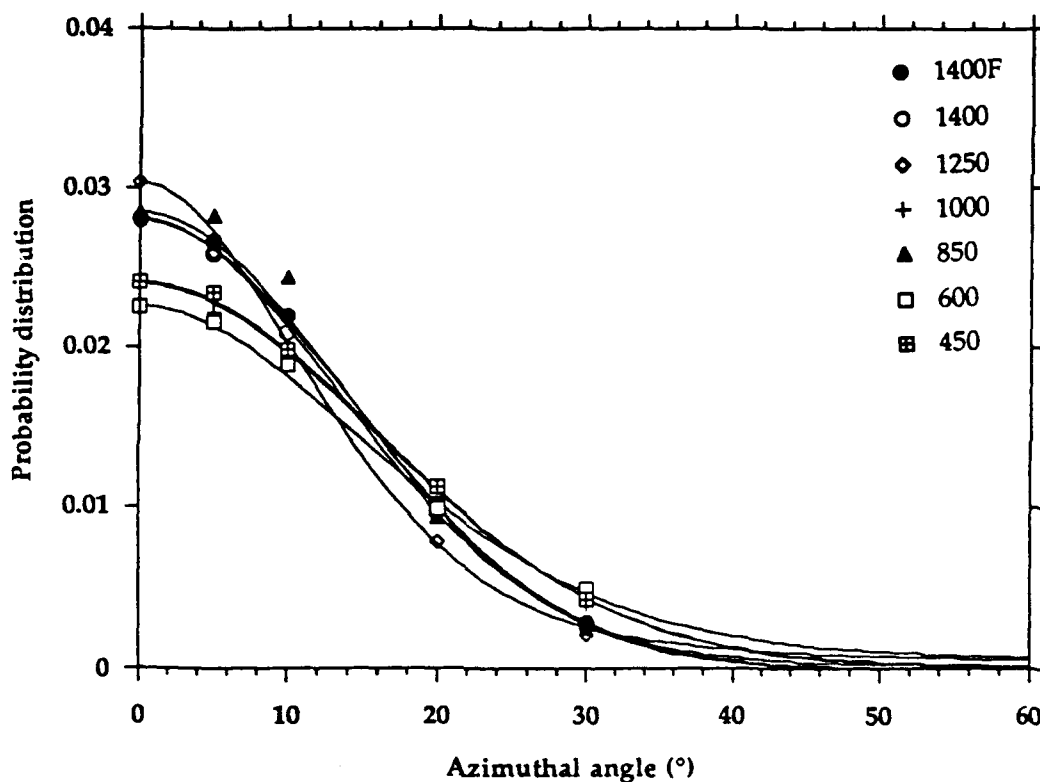


Fig. 9. Orientation Distribution Functions of 1400°C 'on-line' Samples.

III.5.2. Elemental Composition

The mass fractions of carbon, nitrogen and hydrogen were determined from fiber samples submitted to a commercial laboratory and are shown in figs. 10 and 11. Oxygen was assumed to be the only other element present and was computed by difference. The expected trend of increasing carbon content, with simultaneous reductions of other atoms is observed in all the fiber samples. Oxygen and hydrogen are lost at lower temperatures than nitrogen, and corroborates the chemical scheme proposed by Watt, where water is lost at low temperatures. Significant amounts of nitrogen remain even after carbonization at 1350°C, as is seen in fig. 10. It has been reported that up to 7% nitrogen could remain in fibers carbonized to intermediate temperatures. The nitrogen contents of fibers examined in this study were also in this range, and could exist as a substitutional element in the lattice as proposed by Watt [27]. Additional loss of nitrogen occurs by processing at higher temperatures, but levels off, as indicated by the approximately constant elemental compositions of

the 1700°C fiber and 2800°C fiber. The 2800°C sample was found to contain 2.2% residual nitrogen.

In each of the on-line fibers, the loss of nitrogen and oxygen is accelerated after the furnace temperature exceeds 1000°C. It is to be noted that the elimination of heteroatoms (N, O and H) is accompanied by only marginal changes in crystallite dimension in all the on-line samples. The situation is similar for terminal samples processed to temperatures below 1350°C. However, very large increases in crystallite dimensions occur between 1700°C and 2800°C, when the fiber is predominantly comprised of only carbon. It is possible that high temperatures (>2500°C) and high carbon contents (>98%) are necessary requirements for the formation of large graphitic domains.

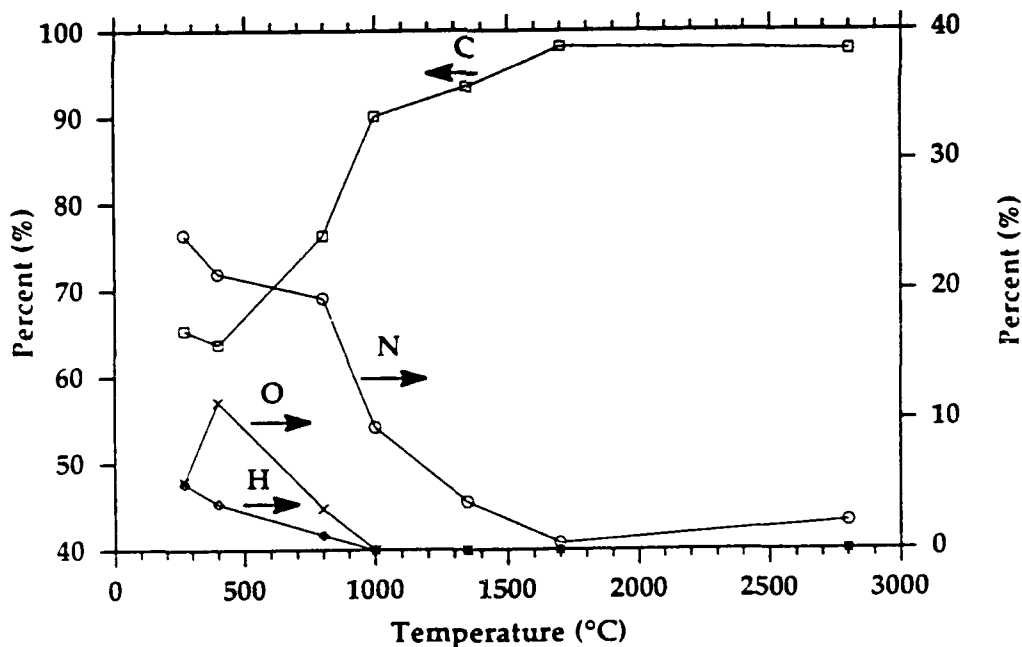
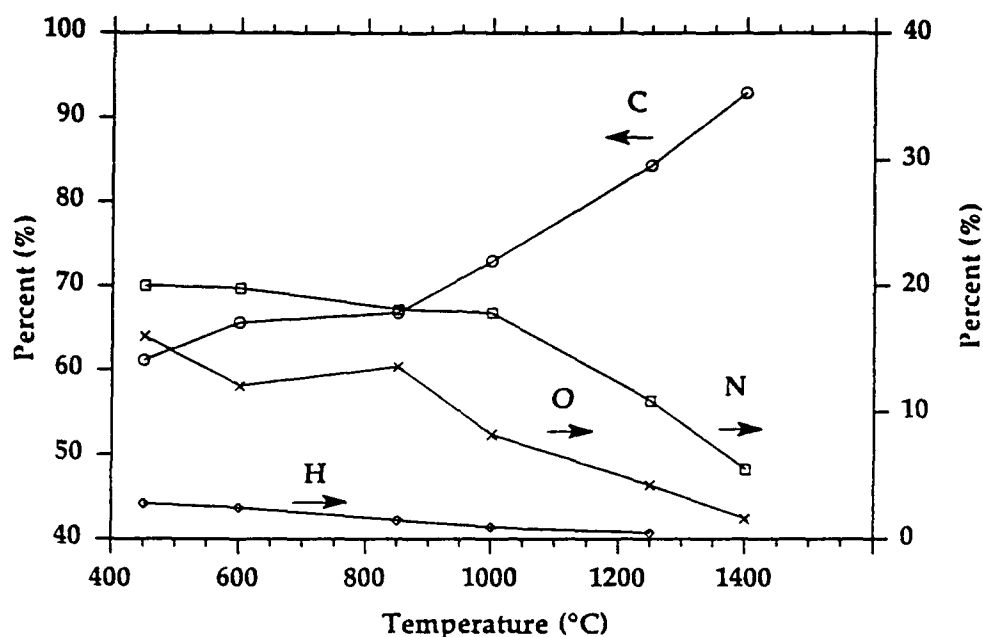


Fig. 10. Elemental Compositions of 'Terminal' Samples.



(terminal sample: C=94.9%, N=4.8%, O<0.5%, H<0.5%)

Fig. 11. Elemental Compositions of 1400°C 'on-line' Samples.

III.5.3. Fiber Density, Diameter and Electron Microscopy

Fiber density increased from 1.34 g/cc for the 270°C fiber, to a relatively high value of 1.83 g/cc for the 800°C fiber in the terminal samples. Similar increases in densities were observed in the on-line fiber samples starting in the 800-1000°C range. The maximum densities of the on-line samples was ~1.8 g/cc and is consistent with the densities of terminal samples of comparable carbonization temperatures.

The average fiber diameters were measured by scanning electron microscopy. Due to loss of mass and an increase in density, diameters of fiber decrease monotonically with increasing carbonization temperature.

Fracture surfaces of all high-temperature fibers (>600°C), and most low-temperature fibers (<600°C) that were broken in tension revealed a radiating pattern indicative of the direction of crack propagation. Fractures originated predominantly from the surface of the fiber and could be attributed to the presence of surface-flaws in the fiber. Alternatively, large, misoriented crystallites in the region near the surface of the fiber could rupture as per the mechanism proposed by Reynolds and Sharp [28], and result in surface-initiated tensile failure of the fiber.

A few samples of the low-temperature fibers from each series revealed fracture surfaces different to those mentioned above. These fibers do not appear to have fractured starting from the surface. Such instances comprised roughly 25% of the low-temperature samples that were examined, and could be attributed to the weak, stabilized structure still present in the low-temperature fibers. However, on reaching carbonization temperatures higher than 600°C in the case of the on-line samples, or 800°C in the case of terminal samples, the fracture surfaces were uniformly suggestive of surface-originated fracture.

A two-zone fracture surface was predominantly observed in all the fibers that failed during recoil. Such surfaces have been observed by others and are a result of flexural failure. The section under tensile stressing usually revealed a radiating pattern, while the compressive section was characterized by sharp vertical corrugations. Evidence of more drastic compressive damage was sometimes observed, as revealed by deep vertical cleavages. There was no discernable difference in the fracture surfaces of fibers that broke during recoil testing and those that broke subsequent to a tensile break. It therefore appears that in spite of the essentially uniaxial deformation that exists during tensile deformation, the subsequent recoil process still leads to flexural strains. It is possible that the tensile fracture process, due to its asymmetric surface origination, contributes to bending strains during recoil, subsequent to tensile fracture.

Details of the evolution of density, diameter, and electron microscopy can be found in reference 22. Jiang et al. have also conducted extensive studies of the nature of the recoil process [18], and have extensively catalogued the recoil fracture surfaces.

III.6. Mechanical Properties of Carbonized Fibers

III.6.1. Fibers Processed at Different Temperatures

The results from fibers which had been processed in an industrial laboratory are summarized in Table 3 and Fig. 12. It appears that the evolution of mechanical properties in tension and in compression do not occur proportionately at different temperatures of carbonization. It also appears that compressive strength goes through a maximum at a lower temperature of carbonization than tensile strength.

The only aspect that appears to be significant here is that the evolution in compressive strength occurs in the temperature range corresponding to the formation of basal planes in the structure. It should be noted here that extensive crosslinking and aromatization of the structure would have preceded the formation of basal planes. Both tensile and compressive strengths diminish significantly in the low processing temperature range, up to 400°C, in which extensive ladder polymerization and crosslinking occur in the structure. The inference that might be drawn here with regard to high tensile performance organic fibers is that any hope

for achieving a high compressive strength in them would rest on producing a more *laterally extensive primary* structure. Introducing a crosslinked network in a linear polymer, however dense, does not appear to be an appropriate path to achieving high compressive strength. If the evidence from the evolutionary path in the formation of PAN-based carbon fibers can be generalized, the inference would have to be that crosslinking might be detrimental to both tensile and compressive strength.

III.6.2. Evolution within Continuous Carbonization

The conversion to carbonized structure and the evolution of fiber properties in continuous carbonization with the maximum furnace temperature of 1400°C are shown in Figs. 13–17. These “on-line” fibers were obtained in the manner described earlier in section III.1.2. The results obtained from these experiments are similar to those with fibers obtained at the end of carbonization at different temperatures. Evolution in both tensile and compressive strengths require the development of the carbonized fiber morphology. The monotonic increase in the failure forces (Fig. 12) shows that a true increase in the load bearing capacity¹ occurs with the conversion of the crosslinked “stabilized” structure to the carbon fiber structure with its characteristic basal planes.

Strong positive correlations between torsional modulus and fiber compressive strength have been reported in the literature for a wide class of materials [20, 29, 30]. It should be noted here that while much of the gain in torsional modulus occurs in the 800°C to 1000°C range (possibly caused by lateral couplings in the structure), there is a significant enhancement of recoil strength well beyond this range. It appears that enhancement in torsional stiffness is not the sole mechanism governing the evolution of recoil, or compressive, strength.

¹Enhancement in failure stresses would be greater due to loss of material as well as densification of the structure.

Table 3. Mechanical Properties of PAN-Based Carbon Fibers*

Processing Temperature (°C)	Tensile Strength (GPa)	Tensile Modulus (GPa)	Recoil Compressive Strength (GPa)	C/T ratio	Elongation %
270	0.33	1.9	C.S. $\approx$ T.S.	–	17.4
400	0.14	0.7	0.1	0.9	20
600	0.79	25	0.6	0.7	3.1
800	1.6	69	0.9	0.6	2.3
1000	2.6	143	1.9	0.7	1.8
1350	4.1	243	2.0	0.5	1.7
1700	4.4	310	1.8	0.4	1.4
2800	3.4	412	1.0	0.3	0.8

* Experimental fibers obtained from Courtaulds, U.K.

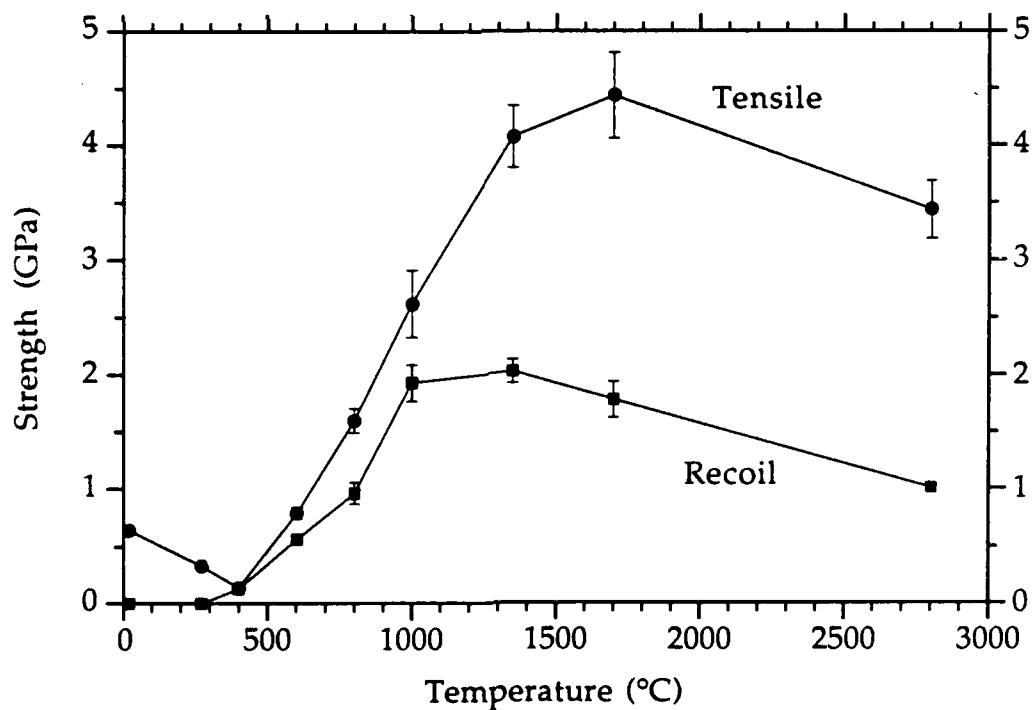


Fig. 12. Evolution of tensile and recoil compressive strengths of PAN-based carbon fibers as a function of carbonization temperature.

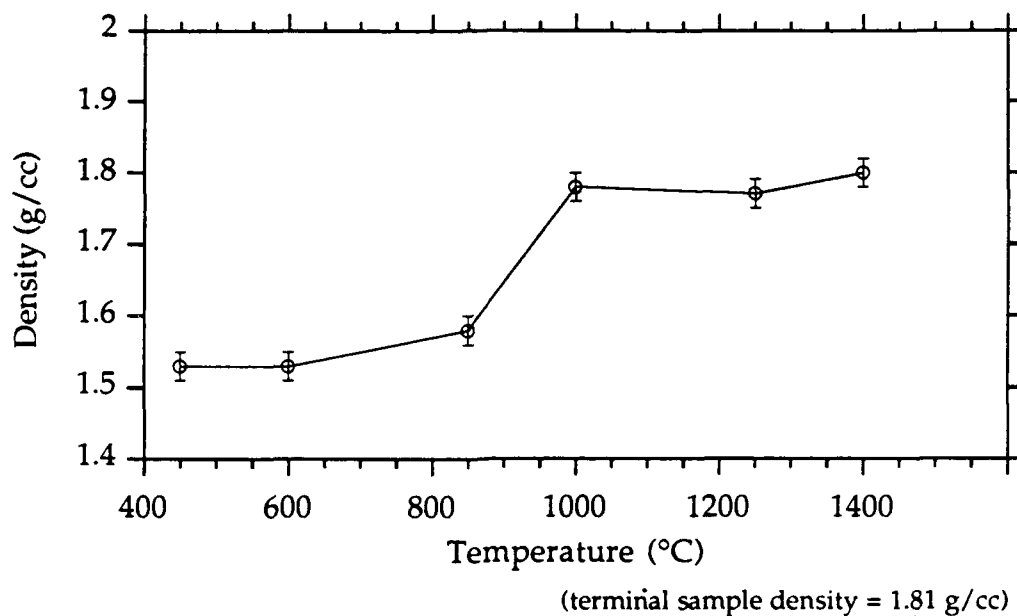


Fig. 13. Evolution of density in samples produced by continuous carbonization of a PAN-based carbon fiber at 1400°C.

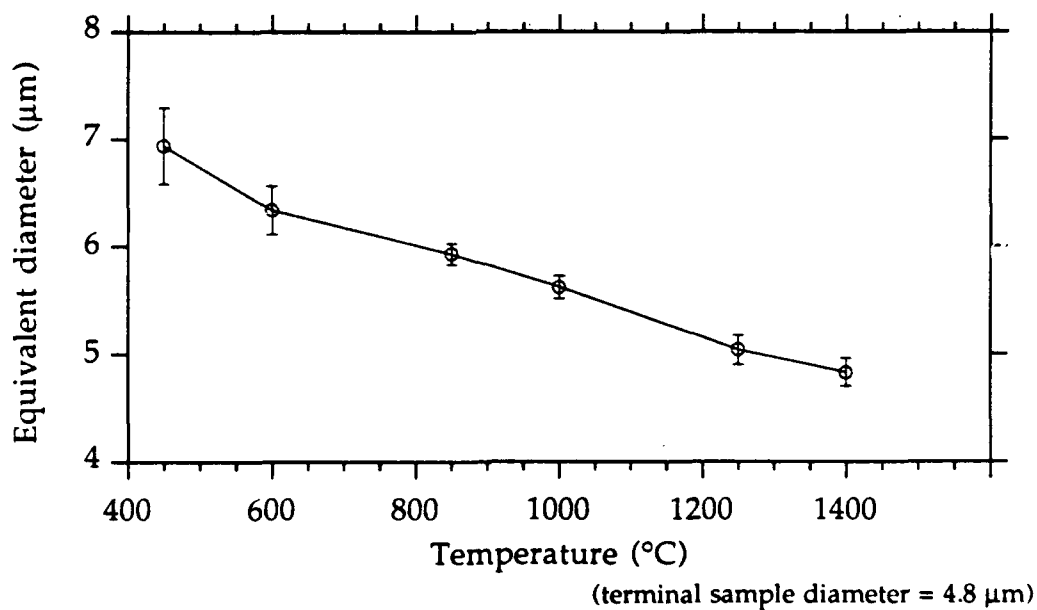
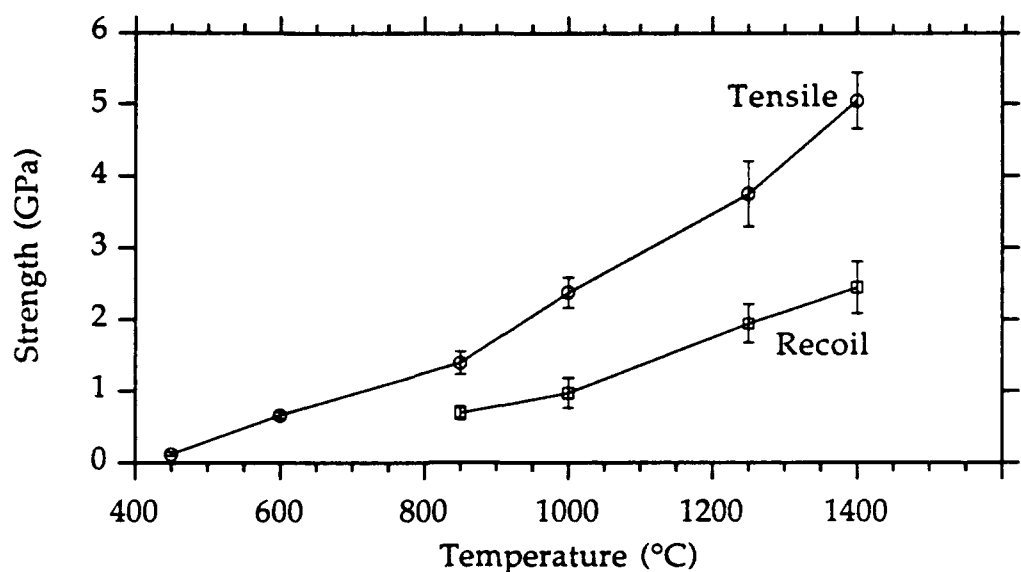
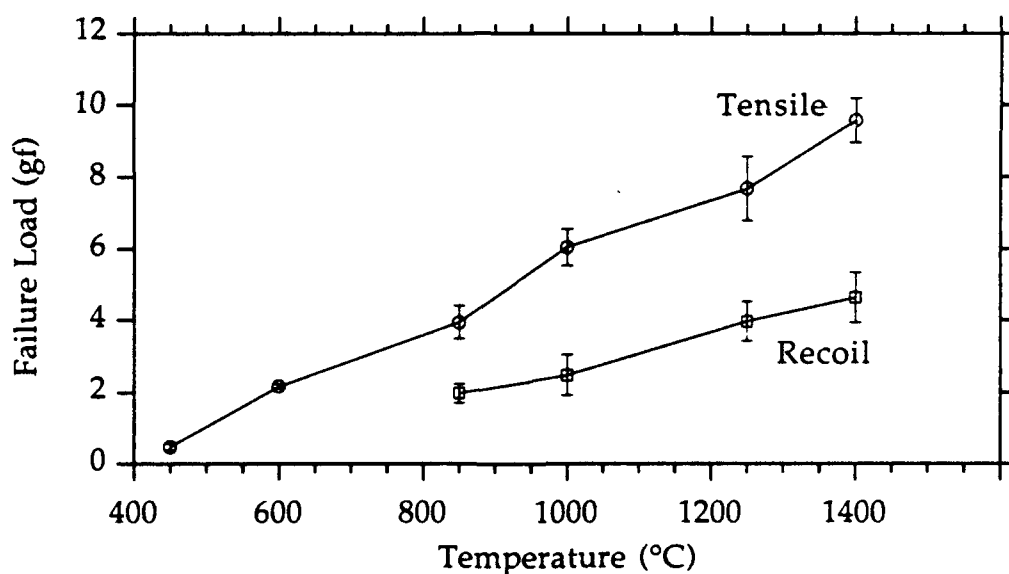


Fig. 14. Equivalent fiber diameters of carbon fibers carbonized at 1400°C.



A

(terminal sample: tensile strength = 4.7 GPa
recoil strength = 2.5 GPa)



B

(terminal sample: tensile load = 8.6 gf
recoil load = 4.5 gf)

Fig. 15. Evolution of mechanical properties in samples produced by continuous carbonization of a PAN-based carbon fiber at 1400°C. (A) Tensile and Recoil strengths; (B) Failure loads. Gauge length = 1.0 inch.

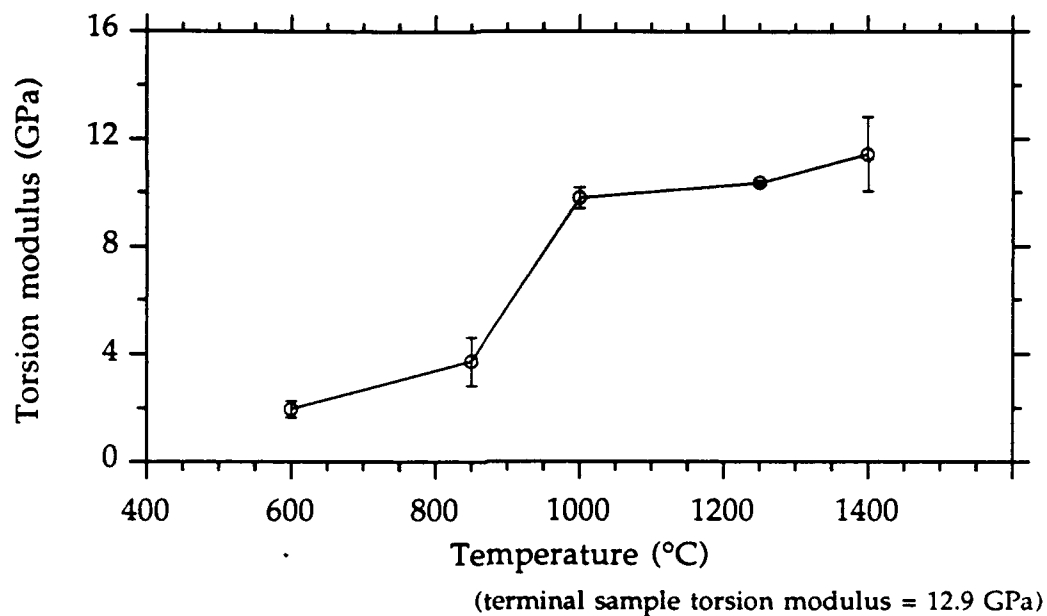


Fig. 16. Evolution of torsion modulus in samples produced by continuous carbonization of a PAN-based carbon fiber at 1400°C.

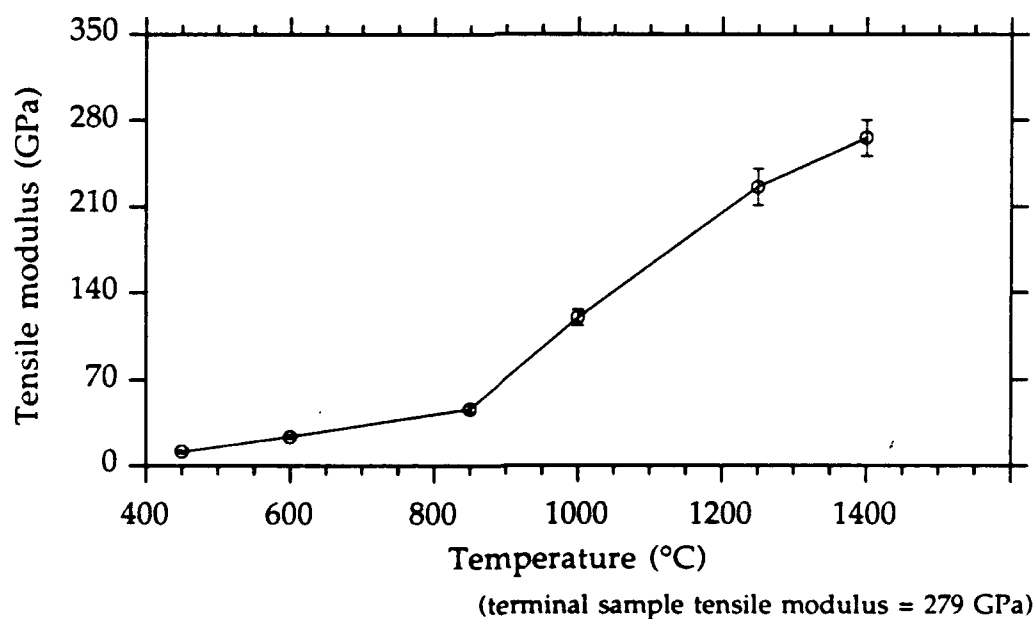


Fig. 17. Evolution of tensile modulus in samples produced by continuous carbonization of a PAN-based carbon fiber at 1400°C.

III.7. Models for Fiber Structural Organization

Since tensile modulus is a strong function of the orientation of the graphitic domains, a significant improvement in modulus occurs by carbonizing at high temperatures. In contrast to tensile strength, the increase of modulus with temperature is monotonic (Table 3), and for this reason commercial high-modulus fibers tend to have relatively low strengths.

In the case of the on-line fiber samples, moduli values of ~280 GPa are attained for the 1400°C fiber series (fig. 17). These are in agreement with those observed for the terminal fiber samples that were carbonized at these temperature ranges. As mentioned earlier, the orientation distribution of fibers within each of the fiber series ('terminal' and on-line) show only marginal differences within a temperature range of approximately 800-1700°C. However, the changes in the tensile moduli in this range are significant. It was therefore deemed appropriate to examine various models for predicting the observed tensile moduli, in order to explain this increase in tensile moduli for approximately constant orientation distributions.

The constant-stress model, the constant-strain model, and Ruland's 'modified' constant-strain model are three possible schemes that have been employed in earlier investigations of models for structural organization of carbon fibers. Usually the fibers examined were fully carbonized/graphitized fibers. Due to the processing temperatures involved, which resulted in low concentrations of non-carbon atoms, the form of carbon in these fibers was assumed to be essentially graphitic, with a large defect population. Literature values of the elastic constants for graphite are therefore valid estimates of the elastic properties of the structural domains, with appropriate adjustments to s_{44} .

The constant-stress model and the modified constant-strain model are capable of yielding reasonable estimates of the fiber axial tensile modulus. Additional assumptions of low shear compliances due to inter-linked planes in the former model, and of large shear compliances due to imperfections in the graphitic structure in the latter model are necessary in order to obtain accurate predictions of the fiber moduli. While large shear compliances of graphitic structures have been measured in pyrolytic graphite, the assumption of low shear compliances resulting from inter-linked planes is based on intuitive reasoning. There is no physical basis to ascribe greater validity to either one of the above approaches. Therefore, both models were examined in this study in order to evaluate their applicability in describing the structure of the fiber samples.

Assuming graphite-like structures, with a range of shear compliances in the 0.25-5.0 GPa⁻¹ range, tensile moduli were computed using the constant-stress, and the 'modified' constant-strain models. The predicted tensile moduli from each model, and the experimentally observed moduli are juxtaposed in figs. 18 and 19. The experimental value is represented by a solid circle for each sample. Even with the

value of shear compliance of perfect graphite (0.25 GPa^{-1}), the moduli of only a few of the low-temperature fibers can be estimated to a reasonable degree, with the constant-stress model. An assumption of an alternate scheme of linkages between the structural domains is necessary in order to make reasonable predictions. The modified constant-strain model performs adequately in this regard. Physically, the transition between these models could correspond to the formation of lateral cross-links between the structural domains, thereby imparting a more parallel character to the coupling of structural units.

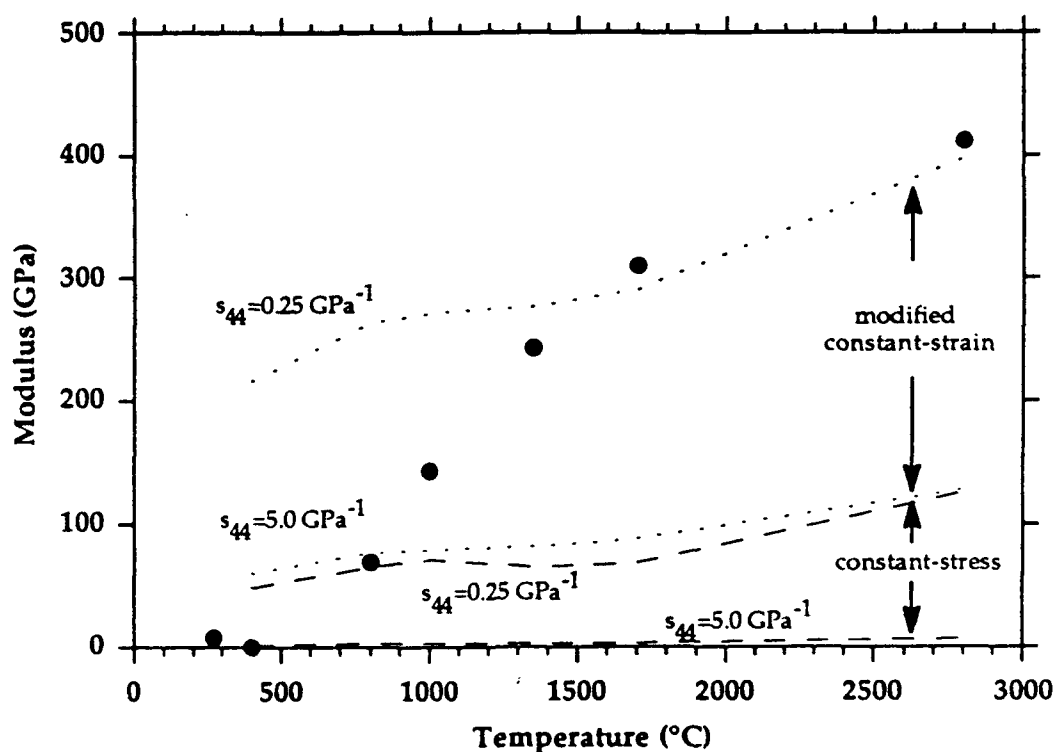


Fig. 18. Model Comparisons for Terminal Samples.

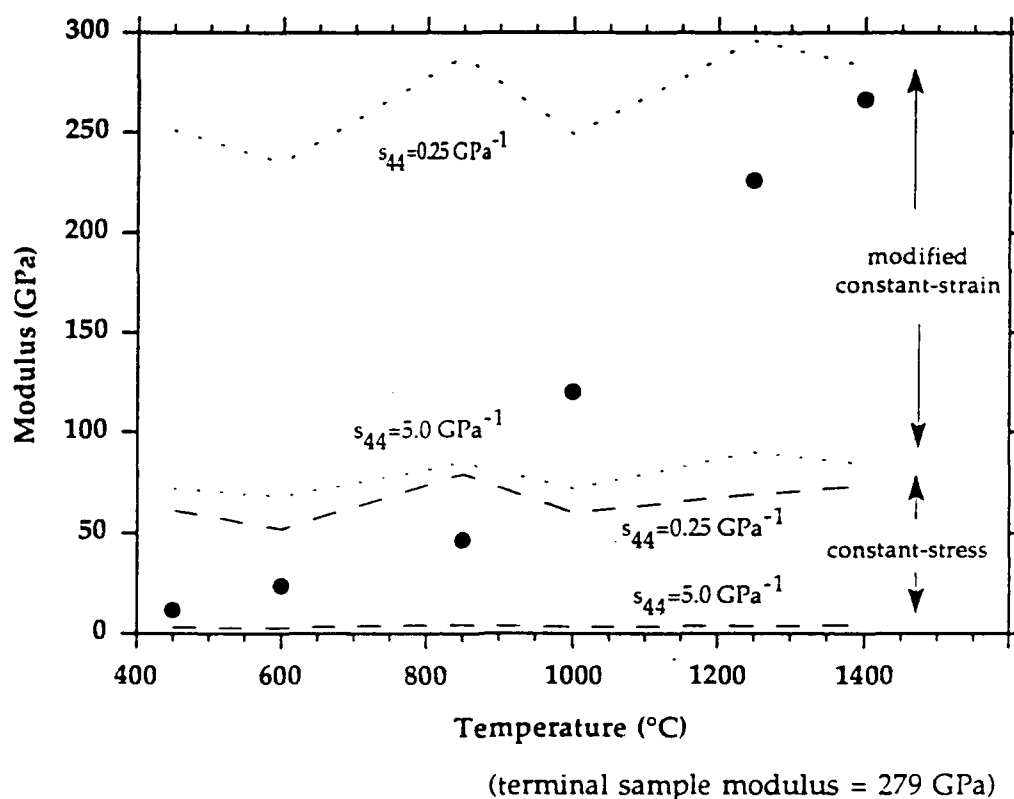


Fig. 19. Model Comparisons for 1400°C 'on-line' Samples.

An alternate approach consists of allowing values of shear compliance, s_{44} , that are less than those of perfect graphite. Kennedy *et al.* [31] have attributed this to inter-ribbon coupling. Values for s_{44} were computed based on the constant-stress model, and the modified constant-strain model in order to accurately predict the observed tensile modulus of each of the fiber samples. Results of this analysis are shown in figs. 20 and 21. Moduli of low-temperature samples (<800°C) are predicted with reasonable accuracy using s_{44} values which are characteristic of graphitic structures. By assuming shear compliances less than 0.25 GPa^{-1} , it is possible to obtain reasonable predictions using the constant-stress model. The smallest value of s_{44} necessary to accomplish this was 0.027 GPa^{-1} , which is in the range computed by Ruland [32]. It is to be emphasized that enhanced inter-linking between structural domains above ~800°C is indicated by this model.

In either of the two models examined above, there is an implication of lateral-coupling above $\sim 800^\circ\text{C}$. In one case it was that of transition from a series-type organization to one with more parallel character, while in the other it was due to the requirement of enhanced shear stiffness in the structure. Further, a large increase in torsional stiffness occurs between 800 and 1000°C . Due to the similar temperature ranges for both the above effects, there is a strong likelihood that a common mechanism of enhanced lateral cross-linking governs both processes.

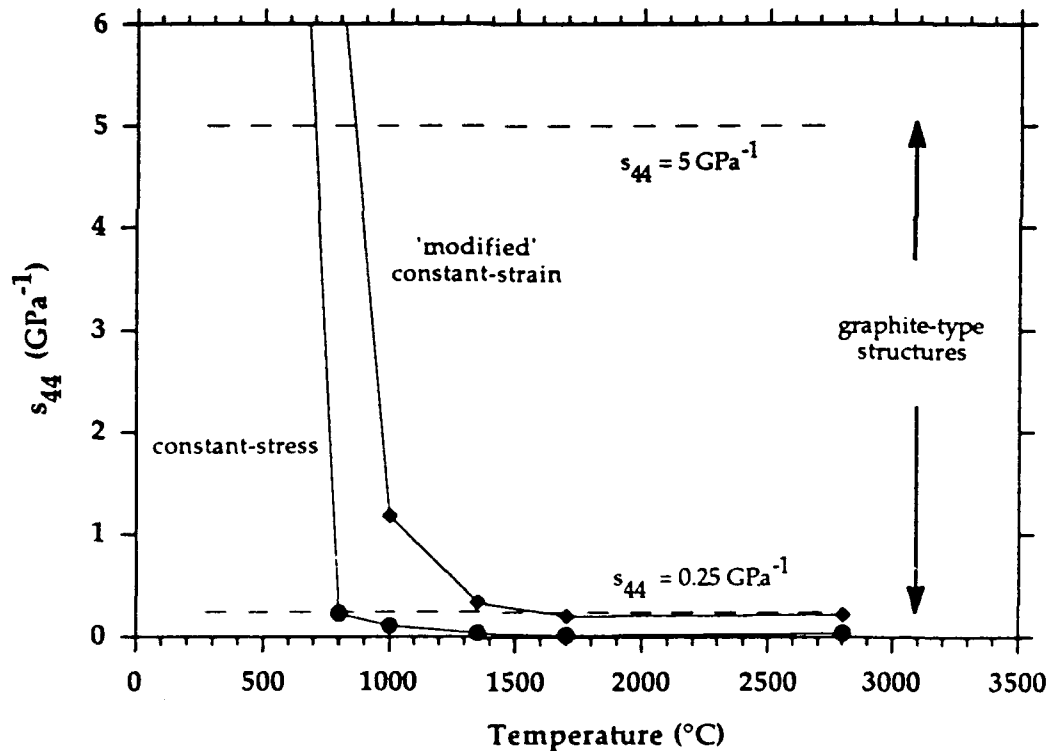


Fig. 20. Computations of Shear Compliances for Terminal Samples.

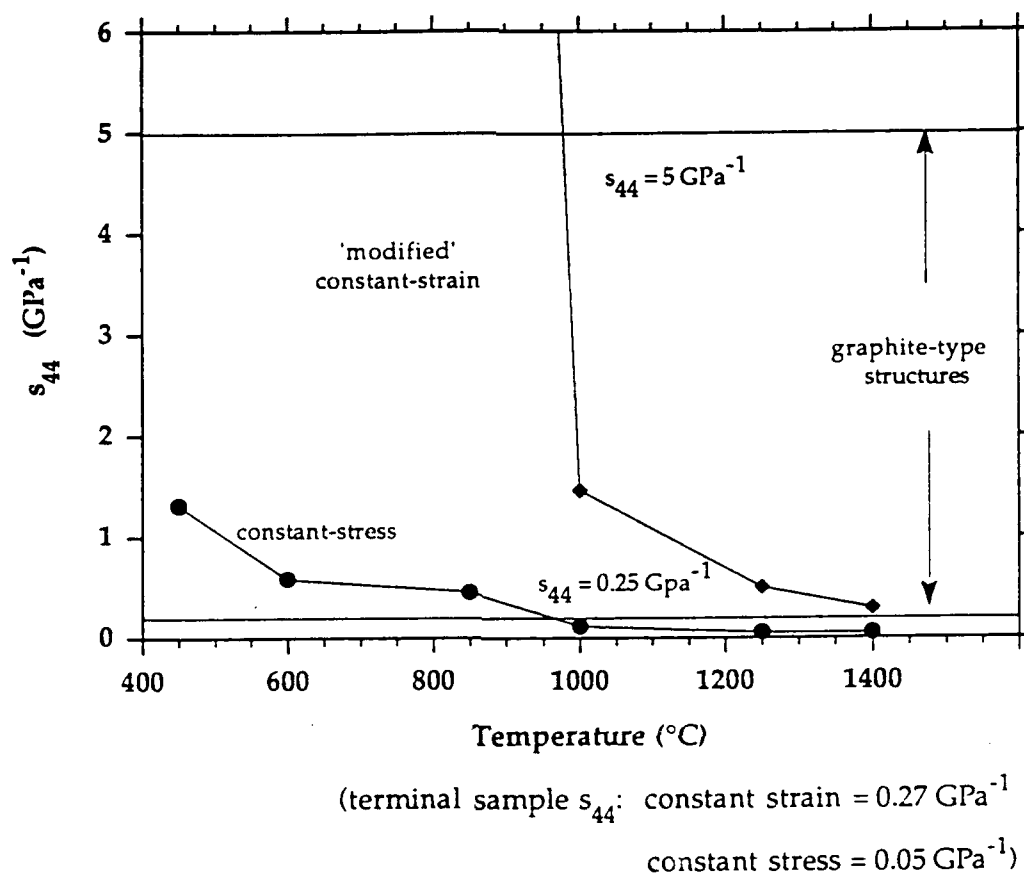


Fig. 21. Computations of Shear Compliances for 1400°C 'on-line' Samples.

IV. CONCLUSIONS

A better understanding of the effects of time, temperature, stress and environment in the acrylic fiber stabilization process may enable one to reduce the stabilization time and/or to improve the mechanical properties of carbon fibers. The research reported here was aimed, in part, at achieving these goals. In addition to oxygen-containing (air) and inert (nitrogen) environments, the prospects for using ammonia as an accelerator for the stabilization process were investigated. Acrylic fibers were stabilized in oxidizing, air, ammonia and mixed environments. Fibers stabilized for different times in these environments were characterized using

several techniques to determine the extent of reactions as well as the change in morphology during the process.

Ammonia was shown to accelerate stabilization of certain acrylic precursors in the production of carbon fibers. About five per cent by volume of ammonia in air led to maximum acceleration of the stabilization process.

Presence of oxygen is essential for achieving complete stabilization, even in the presence of ammonia. In pure nitrogen or anhydrous ammonia atmosphere, stabilization did not go to completion. Correspondingly, fibers heated in the absence of oxygen did not carbonize cohesively. Also, in the absence of oxygen, while nitrile cyclization and a decrease in the population of nitrile groups were shown to occur by FTIR studies, the samples did not turn black even after prolonged heating.

Ammonia, acting as a nucleophile, initiates cyclization at nitrile sites under stabilization conditions. As the initiation is faster and can occur at multiple sites, some stabilization reaction sequences proceed much faster. In the case of fibers containing methyl acrylate and no acidic comonomer, cyclization can also be initiated by ammonia at comonomer sites, leading to further acceleration. Incorporation of nitrogen from ammonia into the stabilized fiber structure was confirmed by a preliminary ^{15}N -NMR study.

For the 2% MA precursor, air/ammonia-stabilized samples approached limiting oxygen content and limiting density faster when compared to fibers stabilized in air alone. The reaction of ammonia with this acrylic copolymer to initiate cyclization produced amine-imine and amide type structures at those sites. The presence of such species in the structure led to increased nitrogen content in the stabilized fiber, and reduced the oxygen weight per cent. Density increase, which accompanies the incorporation of oxygen during stabilization, also reached a limiting value.

Lateral order disappeared much faster during stabilization in the presence of ammonia. The rapid decrease occurred both in the presence and absence of oxygen. Crystals disappeared in less than 16 minutes of stabilization in the presence of ammonia (both with and without air), as evidenced from both WAXD and plasticized melting studies. Up to one hour was required to reach this stage in the absence of ammonia. Ammonia also had a plasticizing effect on the acrylic precursor, and the faster stabilization was probably due to the combined, synergistic effects of plasticization (leading to enhanced gas transport in and out of the fiber) and overall chemical kinetic acceleration resulting from NH_3 attack.

For precursors containing itaconic acid comonomers, the accelerating effect of ammonia on stabilization was not observed. Although calorimetric observations showed some minor effect, the rate at which color and density changed were not significantly higher. Rapid initiation of stabilization by the nucleophilic acidic groups was more than sufficient to overwhelm any influence of ammonia in these precursors. However, plasticized DSC and X-ray diffraction studies showed that

crystals in the acid-containing fibers disappeared much faster in the presence of ammonia, as seen with the 2% MA precursor.

Ammonia, a byproduct of the stabilization reactions, had an accelerating effect on the kinetics when introduced into the stabilization environment. The combined result of two effects were dominant: the nucleophilic attack of the unshared pair of electrons of ammonia in initiating the cyclization of nitrile groups; and the plasticizing effect of ammonia enhancing its ability to propagate cyclization reactions much faster in the laterally ordered regions. Rapid stabilization of acrylic fibers in the presence of ammonia also has commercial implications as it may reduce the cost of carbon fiber production. In addition, ammonia allows reduction of the stabilization temperature, reducing the orientational relaxation that might occur at this stage.

The research reported here has also produced important results pertaining to the measurement of axial compressive strength of high performance fibers and to the evolution of properties in carbon fibers. The most important of these may be summarized in the following:

Evolution of structure and properties during carbonization of PAN-based precursor fibers was studied in order to obtain direct correlations between the structure and resulting properties of the fiber. As indicated by x-ray experiments, very little growth in the size of graphitic domains occur during intermediate-temperature carbonization (1200-1500°C). Evidence of such domains was observable at relatively low temperatures (>400°C), and consisted of lateral associations of approximately 4 basal-planes, with in-plane dimensions of roughly 2 nm X 1 nm (the larger size corresponded to the direction of the fiber axis). Using transmission electron microscopy, Guigon *et al.* [26] have reported evidence of similar entities in fibers carbonized in these temperature ranges. Considerable increase in crystallite size occurs by graphitizing the fiber (>2500°C), and is accompanied by a high extent of orientation with respect to the fiber axis.

Tensile and recoil strengths evolved monotonically with temperature for intermediate-temperature carbonization (<1500°C). In the on-line fiber samples, a considerable increase in tensile and compressive strengths occurs above 1000°C, which correlates, to some extent, with the elimination of nitrogen and oxygen. It is not clear if the higher carbon content, resulting in a more graphitic form, or subtle alterations in morphology (such as the formation of lateral linkages) with little overall change in size and orientation is responsible for the evolution of strengths during intermediate-temperature carbonization. Reduction of fiber tensile strength by graphitization at high temperatures was observed in the case of the 2800°C fiber, and is consistent with observation of earlier investigations [33, 34].

Tensile modulus monotonically increased with temperature. While increases over the 400-1400°C occurred with negligible enhancements of the orientation of the graphitic domains, evolution in the higher-temperature ranges was accompanied by

significant orientation enhancements. Of the three models available in literature for predicting tensile moduli, reasonably accurate estimates are possible with the constant-stress model and the 'modified' constant strain model. In either case, an assumption of enhanced lateral connectivity is required in order to explain the increasing moduli for approximately constant orientation distributions of the crystallites. The 800-1000°C temperature range marked this transition to enhanced lateral connectivity. Torsional stiffness of the same fibers increased significantly in the same temperature range, and supports the concept of increasing lateral connectivity.

Mechanical properties of fibers at different extents of progression toward the graphite fiber structure reveal that the evolutions of tensile and compressive properties are not synchronized. The results suggest that the degree of lateral correlation in the carbon fiber structure at which tensile strength reaches the maximum may be higher than that for maximum compressive strength. However, the differences in the observed patterns of evolution in tensile and axial compressive strengths are not large enough to warrant extensive further studies.

Substantial enhancements in both tensile and compressive strengths of carbon fibers occur only with the development of the carbonized morphology with its characteristic basal planes as the fundamental structural units. While there is also a monotonic increase in torsional modulus in this region, the compressive strength (as measured by the recoil method) and the torsional modulus are not as strongly correlated as implied in previous literature [20, 29, 30]. It is noteworthy that the temperature range of maximum gain in torsion modulus (800-1000°C) was accompanied by negligible gains in recoil strength. It appears that the enhancement in torsional stiffness (possibly caused by lateral coupling) is not the mechanism that governs evolution of recoil strength during *intermediate-temperature carbonization of PAN-based carbon fibers*.

The implication from the carbon fiber studies for axial compressive strengths of high tensile performance organic fibers is that significant enhancement in this regard is not likely to result from merely crosslinking an oriented linear polymeric fiber. It does point, however, to the need for exploring possible "ordered crosslinking" of the structure, i.e., introducing regular crosslinks that enhance, or at least retain, the lateral order in these fibers.

The recoil test method, originally proposed by Allen [16], has been refined to reduce measurement-induced variations. Fracture surfaces of specimens from this experiment do not necessarily reveal failure in a simple compression mode and especially includes bending. A comprehensive atlas of fracture morphologies created during the recoil process has been compiled that show details of fracture initiation. It is be noted that all fiber samples, which had negligible yielding tendencies, *always* failed in recoil subsequent to a tensile failure. While this is suggestive of lower compressive strengths than tensile strengths, the flexural-mode of failure in recoil results in non-uniaxial strains, and precludes a definitive conclusion.

V. SUGGESTIONS AND RECOMMENDATIONS

The research on the evolution of carbon fiber structure from PAN-based precursors at Georgia Tech² and in other laboratories has contributed significantly to the two-fold increase in both modulus and strength that has been achieved in the last decade. Significant further advances are, however, necessary before one can realize the full potential of these fibers in terms of their mechanical properties and also make them economically attractive for utilization in large volume composites. The major current limitations pertain to their relatively low axial compressive strength and their high cost.

1. New Routes for Precursor Fiber Formation:

It is clear that extrusion of fibers from plasticized melts of PAN-based polymers produces a morphology that is similar to those of current carbon fiber precursors [14]. Significant problems remain, however, in relation to stability of mass transfer in fiber extrusion, primarily due to crystallization above the normal boiling point of water. Current research in our laboratories with ternary solutions of polymer, water and cosolvent shows much promise in achieving lower temperature crystallization and also in generating a broad range of controlled morphologies. It is necessary to explore these new routes which can offer a combination of technical and economic advantages.

2. High Compressive Strength Morphologies:

The recent advances in achieving superior tensile performance have, unfortunately, not been accompanied by any progress vis-a-vis behavior in compression. Many critical structural applications have been limited by the fact that the compressive strength is only a fraction of the tensile strength of carbon fibers. Among the approaches one might follow here are synthesis of new precursors to form dense carbon network which would still be oriented, and use of precursor polymer alloys to create a higher level of lateral disorder. It is possible to copolymerize AN with other monomers containing pendant groups that can lead to altered lateral -C-C- bonding sequences in the resulting carbon fibers. The aim here should be to increase lateral disorder while maintaining orientation of the carbon fibers. It is also necessary to identify the morphological state during the evolution of carbonized structure which would yield the best combination of properties in tension and compression.

3. Highly ordered precursors:

The next generation of high performance PAN-based carbon fibers is likely to be obtained from highly ordered precursor fibers. Ultrahigh molecular weight

²Summarized in this report and in report N00014-85-K-0636

precursors that can be ordered through "gel spinning → drawing" to a higher extent than any of the current precursors offer a promising path in this regard. High temperature deformation of acrylic precursors leads to improved performance properties in carbon fibers. Ammonia has a definite plasticizing effect on acrylic precursors at high temperatures. The plasticizing effect of ammonia can be utilized to draw these precursors at high temperatures, especially during early stages of stabilization, to increase the orientational order and reduce the fiber diameter, the latter facilitating in/out gas transport.

4. Lower cost material – process options:

Large scale application of high performance carbon fibers is feasible only if its cost can be significantly reduced. New, lower cost precursor materials (eg., lignin, chitin) and simplified, rapid conversion to carbon fibers should be explored for this purpose.

Much of the improvement in the tensile properties of PAN based carbon fibers that has been made in the last decade can be traced directly to inferences from rational studies of their evolution from the precursor polymer to the carbon fiber. It is necessary to continue this approach in order to eliminate the last two barriers in broadening their applications, namely, relatively low compressive properties and high cost.

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APPENDIX I.

PAPERS AND PRESENTATIONS RESULTING FROM RESEARCH WITH FULL/PARTIAL SUPPORT FROM Contract Number N00014-89-J-1855

- (i) "New Aspects in the Conversion of Acrylic Precursors to High Performance Carbon Fibers," G. Bhat, S. Damodaran, P. Desai, L. H. Peebles, Jr., A. S. Abhiraman, AIChE Annual Meeting, San Francisco, CA, Nov. 6-9, 1989.
- (ii) "New Aspects in the Stabilization of PAN-based Precursors for Carbon Fibers," G. S. Bhat, F. L. Cook, L. H. Peebles Jr., and A. S. Abhiraman, *Proc. 19th Biennial Conf. on Carbon*, University Park, PA, 252 (1989).
- (iii) "New Aspects in the Stabilization of Acrylic Fibers for Carbon Fibers," G. S. Bhat, F. L. Cook, A. S. Abhiraman, and L. H. Peebles, Jr., *Carbon*, **28**(2-3), 377 (1990).
- (iv) "Evolution of Compressive Strength during Carbonization of PAN-Based Fibers," S. Damodaran, Fall Technical Meeting of The Fiber Society, Nov. 1-3, 1989, Raleigh, NC.
- (v) "Evolution of Compressive Strength in PAN-Based Carbon Fibers," S. Damodaran, Southeastern Graduate Polymer Conference, Knoxville, TN, March 19-20, 1990.
- (vi) "New Aspects in the Formation and Properties of PAN-based Carbon Fibers," G. Bhat, S. Damodaran, P. Desai, L. H. Peebles, Jr., A. S. Abhiraman, Symposium of Polymer Processing Society, Nice, France, April, 1990.
- (vii) "Carbon Fibers from Poly(p-Phenylene Benzobisthiazole) (PBZT) Fibers: Conversion and Morphological Aspects", H. Jiang, P. Desai, S. Kumar and A. S. Abhiraman, *Carbon*, **29**, 635 (1991).
- (viii) "Analysis of Tensile Recoil Method for the Compressive Strength Measurement of PAN-based Carbon Fibers", H. Jiang, S. Damodaran, P. Desai, S. Kumar, A. S. Abhiraman and K. Tsui, PMSE Proceedings, vol. 64, pp. 383-384, ACS Spring Meeting, Atlanta, GA, April 14-19, 1991.
- (ix) "Analysis of Failure in Recoil from Tension of PAN-based Carbon Fibers", H. Jiang, A. S. Abhiraman and K. Tsui, manuscript submitted to *Carbon*.

At least three (3) additional refereed publications are anticipated from the completed research work.