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Professor D. R. Uhlmann
Massachusetts Institute of Technology

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The present investigation of the stabilization of acrylic fibers and the development of structure in fabricating carbon-carbon composites has directed attention to the structural features of the materials, their variation with processing and their implications for the properties of the final materials. The work on the stabilization of acrylic fibers has demonstrated that various mantle-core structures are observed at intermediate stages of stabilization, that the dark mantles seen in optical thin sections can be related to the etched mantles seen on exposure to solvents for PAN, that the mantles seen on fractured fiber ends reflect the underlying structure of the partly-stabilized fibers, that the development of these various mantles with time depends on the nature of the precursor fibers and the processing conditions, that liquid droplets can be produced during fracture of fibers during stabilization, and that the fracture of even a small number of fibers can produce effective cementation of a yarn during processing. The study of the interaction between mesophase material and carbon fibers has directed attention to the precipitation, growth and coalescence of mesophase material, which processes require ordering of small molecules in a viscous medium. On this basis, dynamic motion in the fluid rather than the presence of nucleating substrates is suggested to be the controlling factor in the structural development. Where dynamic motion is restricted, as in the interstices of a yarn, mesophase formation and growth are also restricted. Alignment of mesophase material with a substrate is primarily controlled through motion of the mesophase droplets in flow, which generally do not wet the substrate. Certain well-ordered surfaces are wetted by the mesophase material, but the effect is primarily noted on surfaces of comparable size to the droplets.

I. INTRODUCTION

This report summarizes the work carried out under AFOSR-[redacted] 77-3466 during the period September, 1977 to September, 1980. The research dealt both with the stabilization of acrylic fibers and with microstructural development in carbon-carbon composites. A number of papers based on this work are presently being prepared for publication, and will be submitted to AFOSR upon their completion.

The work was carried out under the technical supervision of Professor D. R. Uhlmann, with considerable technical input from Dr. L. H. Peebles, Jr. The experimental phases of the investigation were carried out by Dr. I. G. Plotzker (now at the Experimental Station of du Pont), as well as by Mrs. J. H. Cranmer and Mr. C. B. Brogna. Mrs. Cranmer has recently submitted her M.S. thesis at MIT: and Mr. Brogna will shortly be submitting his Sc.D. thesis based on work carried out under the grant.

The team of investigators found the investigation to be most stimulating. It uncovered a number of highly interesting phenomena in both areas of study. It is believed that these phenomena have significant implications for the processing of carbon fibers and carbon-carbon composites. The investigators wish again to express their appreciation to AFOSR for the support of this work.

II. STABILIZATION OF ACRYLIC FIBERS

The investigation of the stabilization of acrylic fibers was concerned broadly with the changes of chemistry and structure which take place during stabilization, and with the implications of these changes for the structure and properties of the resulting carbon fibers. The work directed attention to a number of areas, including: (1) the mechanical properties of the fibers at elevated temperatures as a function of temperature, precursor fiber and degree of stabilization; (2) the cementation of fibers and yarns resulting from fracture of partially stabilized acrylic fibers at elevated temperatures; (3) the development of various mantles during the stabilization of acrylic fibers, including fracture mantles, optical mantles, etched mantles and polished mantles; and (4) the development of models which take into account the differences in Poisson's ratio and other mechanical properties between stabilized and unstabilized material as well as the stability of cylindrical structures, and are used to explain the phenomena observed during stabilization of acrylic fibers.

The results obtained on the high temperature mechanical properties of acrylic fibers, as well as on the various mantles observed during stabilization and their dependence on fiber type and conditions of stabilization, and the models developed to explain these phenomena, are presently being finalized in the draft of Mr. Brogna's Sc.D. thesis. Rather than attempt a brief and provisional presentation of the results in these areas, it seems decidedly preferable simply to submit a copy of Mr. Brogna's thesis as an appendix to the present report when it becomes available (within a few months). In the present section, therefore, we shall discuss only the results obtained on fiber cementation.

When yarns of acrylic fibers are stabilized under high strain, high temperature conditions in an oxidizing atmosphere, the yarns emerging from the reaction zone can be stiff and boardlike. Although individual fibers are clearly discernible, the yarn bundle is fused or cemented together. If only a small amount of fusion/cementation has occurred, the individual fibers can be separated one from another by passing the yarn over a series of guides to flex the fibers and thereby break the inter-fiber bonding. The presence of cemented fibers within a yarn leads to a degradation in properties of the carbon fibers and composites made therefrom. The cause of the cementation process was not understood because the surface texture of the cemented fibers is essentially unchanged from that of the non-cemented fibers. One speculation was that the exterior of the fiber is a solid while the interior is a molten liquid which can leak through the exterior shell.

The present work involved a study of a number of acrylic fibers, both homopolymers and copolymers, which were partially stabilized for various times in air at 225 C and subsequently tested at the same temperature using an Insrron testing machine provided with an environmental chamber.

After preliminary heat treatment in air for 0, 61 and 133 minutes, droplets were observed for both Orlon and Acrylan type fibers taken to fracture. No evidence for the formation of droplets was found after these fibers were processed for 210 minutes (also at 225 C). Courtelle fibers, which are compositionally similar to Orlon fibers but contain

1% itaconic acid in addition, were observed to fracture with the formation of droplets after 61 minutes of stabilization, but not after 133 minutes. Previous work has indicated that the rate of stabilization of Courtelle type fibers is faster than that of the Acrylan and Orlon type fibers because of the presence of the itaconic acid in the Courtelle.

The droplets were only observed near the fractured ends of the fibers. They were not observed on fibers or yarns which were loaded to stresses near, but somewhat less than, the fracture stress at elevated temperature; and such yarns did not show any evidence of cementation. The droplets were only observed on fibers which contained comonomers; no droplets were seen on fibers prepared from homopolymer PAN by either dry spinning or wet spinning techniques. Residual solvent and/or moisture do not appear to play a significant role in the formation of droplets, as droplets were observed on samples that had been extracted with acetone or had undergone extensive vacuum drying prior to high temperature fracture.

It is unlikely that the fibers as a whole were molten before fracture because of the fine textural details observed on the fiber surfaces (which are closely similar to those observed on fibers which were not taken to fracture). It is unlikely that even the central regions of fibers were really molten prior to fracture, because of the detail noted within the regions of fracture. In some cases, textured interiors surmounted by drop-like structure at the tips of the fiber ends were observed. The progression from a textured structure to a resolidified structure as the fiber end is approached suggests that a liquid phase is formed during the fracture process. If this is indeed the case, then the droplets observed on the fibers are a result of material being sprayed out of the fiber ends at the moment of fracture. The droplets may well be composed of relatively low molecular weight acrylic polymer; but the total amount of material in the droplets was too small to be recovered from the fibers and characterized.

It is suggested that the formation of droplets is a result of localized heating due to fracture. Upon fracture of the fibers, this localized heating and melting result in a spraying out of liquid droplets from the immediate region of the fracture. The sprayed out liquid droplets resolidify along the fibers and in the inter-filament spaces, producing a cementation of the fibers. On this basis, particular care must be exercised to avoid fracture of even a few fibers during processing if this form of cementation is to be avoided.

III. DEVELOPMENT OF MICROSTRUCTURE IN CARBON-CARBON COMPOSITES

The investigations of the development of microstructure in carbon-carbon composites were concerned with: (1) the interactions between the carbon fibers and mesophase material and (2) with the coalescence of mesophase material. The work on the interaction between carbon fibers and mesophase material made extensive use of the classic work of Brooks and Taylor (1, 2) on the characteristics of mesophase spherules formed in the 400-500°C range from a graphitizable pitch. Of particular concern here were questions such as the influences of solid additives on the nucleation and growth of the spherules, and whether such additives can be used to alter the properties of the resulting pyrolyzed material.

Brooks and Taylor found a marked association between the quinoline insoluble particles which exist in certain pitches and the mesophase spheres. They observed that in the early stages of mesophase formation no spheres were formed except in regions adjacent to the insoluble material; but these particles did not become incorporated into the spheres (the particles were never observed within the ordered regions). Magnesium oxide acts similarly to the quinoline insolubles. In contrast, finely divided nuclear graphite showed a marked association for the mesophase material, with accompanying alignment of the mesophase on the graphite surface. The same effect was observed with mica flakes, but the alignment was somewhat less perfect. Furthermore, the mesophase droplets had large contact angles with the mica. Aluminum oxide and carbon blacks showed no obvious effects. Any solid surface such as the glass container walls appeared to be preferred sites for mesophase growth. The nucleating effect seemed to increase with the available surface area; yet the authors also state that the presence of solid particles may impede the transformation of pitch to mesophase.

Dubois et al. (3) separated the soluble material from the quinoline insolubles and examined the formation of mesophase in the presence and absence of natural graphite flakes and of calcined needle coke. No enhanced nucleation was observed in the presence of the substrates. Marsh et al. (4) examined the effect of spheron 6 (a carbon black) and graphon (a graphite made therefrom) on the formation and growth of the botryoidal non-coalesced spheres from anthracene under high pressure (130 MPa). The average size and the uniform growth of the spherules were reduced in the presence of additives. Sterling FT (a carbon black) acted similarly but with less effect on spherule formation. These authors also found that SP1 Fines (graphite flakes) and quartz powder prevented the development of the non-coalesced botryoidal spheres (nominally observed on pyrolysis of anthracene under their pyrolysis conditions), but these pigments did allow wetting and alignment to form a coalesced mesophase.

Marsh and Walker (5) suggest that the predominant mechanism of spherule formation is through homonucleation, that addition of carbon black does not seed the growth of mesophase in the traditional sense of nucleating agents. The additives interfere with the growth and coalescence of mesophase and can result in production of isotropic bulk properties. Marsh et al. (6) state that heterogeneous nucleation is not required for initiation of mesophase growth and that the quinoline insolubles impede coalescence. In view of the preceeding, White (7) feels that speculation on the mechanism of mesophase nucleation should be deferred pending more definitive experiments.

In the fabrication of carbon-carbon composites, a three-dimensional structure of carbon fiber yarns--the yarns generally conforming to orthogonal axes--is impregnated with pitch and then heat treated to form a graphitic matrix. Because of the loss of volatiles on the conversion of pitch to graphite, the impregnation-heat treatment process must be repeated several times to attain bulk densities in the range of 1.9 g ml^{-1}. When impregnation, carbonization, and graphitization are carried out at low pressures, the mesophase lamellae tend to align parallel to the fiber surfaces, producing a sheath around each filament (8-10). At atmospheric pressure, the parallel alignment was observed regardless of fiber molecules, fiber precursor (pitch, PAN, or rayon),,morphology (round or crenulated) or in the presence or absence of a chemical vapor deposited (CVD) coating. These observations lead Evangelides (10) to conclude that the alignment was determined by the presence of the surface rather than by the characteristics of the surface.

In contrast, Jortner (11) observed graphite platelets oriented perpendicular to the fiber axis when the impregnation-graphitization cycles were carried out at high pressure (103 MPa) on a rayon-based carbon fiber perform that had been rigidized by CVD treatment prior to the first impregnation cycle. Evangelides suggested that pressure was the causitive factor of matrix orientation relative to the fibers. At low pressure (less than 6.7 MPa), the matrix is essentially oriented parallel to the fiber axis--except at large distances from the fiber where more random orientations exist. Under high pressure processing conditions (103 MPa), however, the pitch microstructure was significantly different. A sheath of parallel orientation formed about the fibers; then the orientation abruptly changed to a transverse orientation. A CVD coating was found to increase the amount of transverse orientation.

The effect of pressure was attributed to an inhibition of spherulite coalescence away from the fiber. Because the spherules are formed independent of one another, the orientation within each spherule is not correlated with the orientation of adjacent spherules. The orientation on a microscale results in a general random orientation on a macroscale after transformation is complete. These conclusions are consistent with those of Huttinger and Rosenblatt (12) who found that increased pressure in bulk samples decreased the extent of orientation.

Gebhardt (13) has further investigated the phenomenon in carbon-carbon composites. He found that the perpendicular orientation is primarily peculiar to the rayon-based fiber coated with an isotropic CVD layer, and to pultruded pitch fiber-epoxy matrix rods which have undergone pyrolysis to remove the bulk of the epoxy material and leave an isotropic char. Heat treated isotropic coatings, on the other hand, produced either random or parallel orientation of the graphite layers. The CVD coating could be varied from isotropic to anisotropic and crystalline depending on the processing conditions. The transverse structures could also form somewhat on acrylic-based and on pitch-based fibers; but the necessary processing conditions required to obtain parallel, random or perpendicular orientations are not so clear cut.

To gain more information on the process of mesophase formation and coalescence, a two-pronged investigation was undertaken using carbon fibers, other fibers, and carbon materials as substrates. Some of the substrates were given various treatments to alter the surface structure. One investigation involved following the formation of mesophase with an optical microscope and determining how the mesophase domains interacted with the substrates. A second investigation involved partial formation of mesophase in the presence or absence of the substrates, cooling the mixture to room temperature, and examining the resultant structures. A great many combinations of mesophase forming materials, substrates, and processing conditions at atmospheric pressure were examined during this work. We present here an overall view of the phenomenological patterns that resulted.

A petroleum pitch (Ashland A240) and two coal tar pitches (Koppers and Allied Chemical 15V) were examined along with acenaphthalene. The last is a pure chemical compound which produces a graphitizable carbon and whose pyrolysis has been extensively studied (14). Typical properties of the pitches are given in Table I.

Properties of the as-received fibers are listed in Table II. The carbon fibers were chosen to cover a wide range of modulus, precursor type and morphology. The T-300 and the VYB fibers had received only a low temperature heat treatment, 1400°C, whereas the others had received heat treatments in the range of 2800°C. The T-300 and VYB fibers were considerably less ordered than the others. The carbon fibers were used either as received or after scouring with neat hydrofluoric acid to remove any manufacturer-applied finish (15). The fibers were also oxidized with hot aqueous nitric acid to alter their surface properties. Two additional fibers were examined: E-glass and Kevlar 29. These last fibers provided quite different surfaces from those of the carbon fibers while retaining the same geometry and dimensions.

In addition to the Pyrex and Vycor containers used to hold samples during pyrolysis, several other carbon substrates were examined to ascertain the effect of surface order. The most anisotropic surface was highly oriented pyrolytic graphite (HOPG) and the most isotropic was vitreous carbon. Intermediate surfaces were provided by Graphnol, AGOT (a high purity nuclear graphite) and AGKSP grade polycrystalline graphite (a rotating disk electrode).

Dynamic observations of the mesophase-substrate interaction were made by hot stage microscopy with the aid of a Reichert optical microscope equipped with polarizing filters and a Sorenson XLS1 xenon light source. A small, well insulated furnace was constructed for use on the microscope stage. The furnace was fitted with a quartz window and ports for a thermocouple, gas inlet and exhaust, and power leads. All openings were sealed with silicone rubber. A cover slip attached to a wire leading out through the lid seal was positioned to collect any condensation prior to observations, at which time the slip was pulled aside.

For each run, approximately 0.1 g of pitch or acenaphthalene was placed on a 2.5 cm x 7.5 cm microscope slide with a 0.8 mm central well. The substrate under investigation was added after the pitch had melted. The quartz window with its cover slip was then clamped into position. After a two minute nitrogen purge, the furnace was heated to 420°C at 20°C min^{-1}, the cover slip pulled aside, and observations begun. The pitch-substrate mixture was heated to 450 C, then held at this temperature. After mesophase spherules had formed, the rate of flow of mesophase past the substrate could be controlled by varying the heat input and hence the rate of convection.

A second, static type of procedure was also employed. In this case, Pyrex or Vycor tubes containing several grams of pitch or acenaphthalene, either alone or with one or two yarns of fiber or a piece of non-fiber substrate, were heated in an Inconel resistance furnace in flowing nitrogen at atmospheric pressure. Usually three or four dozen samples were treated simultaneously to ensure equivalent processing conditions. The samples were heated to the desired temperature at about 10 C per hour, held for a selected soak time, then cooled slowly to room temperature while maintaining the nitrogen atmosphere.

Specimens were prepared for optical microscopy using standard metallographic techniques. Each sample was cut, mounted in resin, ground with three grades of silicon carbide paper, followed by polishing with two grades of alumina. If necessary, a final polish was applied by hand on Corfam impregnated with Syton. Specimens were examined by polarized reflected light on a Vickers research optical microscope with a Polaroid camera attachment.

The Ashland A240 pitch was used for all the dynamic studies. The substrates included E-glass fibers, Kevlar 29, T-50, VYB, vitreous carbon, AGOT, graphnol, and HOPG. Mesophase domains appeared to form only in the bulk isotropic pitch, and not at the substrate interfaces. The growth of a birefringent area adjacent to the substrates appeared to form only through contact with mesophase spherules. This area had an uneven, "lumpy" character as if the coalesced drops did not flow quickly into a smooth interface. All of the substrates were wetted by the pitch; but only the Kevlar 29 appeared to be wetted by the mesophase material. Otherwise, the nature of the substrate and its surface treatment had little or no influence on the formation or coalescence of the mesophase. Rather, the rate of formation and of coalescence seemed to depend on the rate of flow of molten material. In this regard, it should be recalled that the rate of flow was generated by a temperature gradient, which also should influence the rates of polymerization, nucleation and coalescence.

If the rate of flow was slow, spherules formed in the bulk were carried with the flow until they came in contact with something moving at a slower rate. These items could be the substrate, the walls of the container, a region of slower flow, or a stagnent region. The quantity of coalesced material attached to the substrate decreased as the substrate became oriented with the direction of flow. The greatest quantity of coalesced material existed on the upstream side of the substrate.

At a more rapid rate of flow and with a short fiber segments, the streamline split around the fiber and formed eddies at one or both ends, depending on the orientation of the fiber relative to the flow. The spherules tended to coalesce within the eddies and spread out along the downstream side of the fiber.

At very fast flow rates, the substrates tended to orient with the flow. If the substrate remained at an angle to the flow, spherules were observed to flow directly over or under the substrate. Some of these spherules stuck and coalesced on the downstream side, but bits of coalesced material were also pulled away from the substrate. If the substrate moved along with the flow, little or no mesophase adhered to the surface. Thus the position of accumulation and the rate of accumulation of coalesced material depended strongly on the fluid dynamics of the system, and not on the surface characteristics of the substrates.

In the static studies, the isotropic pitch readily wet the fibers and considerable wicking was observed--more than 5 cm on carbon fiber yarns that extended out of the pitch melt-pool. In general, the mesophase spherules in contact with the fibers did not wet them. Neither fiber modulus, nor degree of graphitic order nor fiber morphology (with an exception to be noted), appeared to influence the interaction between fibers and mesophase spherules. The only surface treatment that produced an observable effect was extensive oxidation of low modulus fibers. Those portions of the spherules in contact with the fibers showed alignment with the fibers.

The 4104B pitch fiber was peculiar in that the polished ends are highly birefringent, the fiber texture is radially aligned, and a wedge-shaped crack is observed, perhaps caused by circumferential shrinkage of the fiber during processing. When such fibers came in contact with mesophase domains, the outside of the fiber is oriented towards the untransformed pitch, whereas the wedge is in contact with and wetted by the mesophase. Mesophase spherules contacting the radially cracked areas do show small contact angles where the remaining surface is not wetted.

When a sufficient amount of mesophase has formed between two adjacent fibers, the coalesced material is aligned along the surface of both fibers, but growth appears to take place by growth of the attached spheres followed by coalescence as the spheres meet.

The fibers in general do not act as nucleating sites for mesophase formation. Cross sections of yarns embedded in partially transformed pitch typically showed a fiber bundle surrounded by a band of coalesced material; but within the yarn and farther away from the yarn, transformation had progressed to a markedly less extent. On occasion, large mesophase spherules were observed attached to portions of the yarn embedded in isotropic material, with smaller spheres clustered near the larger spherules away from the yarn rather than adjacent to the yarn.

The quinoline insoluble particles in coal tar pitches are not incorporated within the spherules but rather collect at the surfaces of the spheres. Whether the insolubles are actually adsorbed onto the surfaces of the spherules or result only from a "sweeping action" is currently not known. Clear agglomerations with the insolubles associated with mesophase leaving clear untransformed areas, as shown by Brooks and Taylor (1) were not observed. Similarly, individual filaments were in contact with the spherules rather than contained within the spherules. The exception again is the 4104B pitch fibers where individual filaments were included within coalesced regions. Most of the filaments were in transformed regions rather than in the isotropic phase. Despite the difference in wettability between the surface and wedge portions of fibers, the exinction bands in the transformed matrix are continuous with those within the fibers. Extinction bands in the matrix also originate from the intersection of the wedge surface and the outside surface of the filaments, suggesting that the radial orientation of the wedge is propagated into the bulk mesophase--sometimes over several fiber diameters.

The pattern of extinction lines in the matrix intersecting the fiber perimeter at a near normal angle was also observed in the T-50 and T-300 fibers, which are, respectively, rayon and PAN based fibers. Similar observations have been made by Rubin et al. (16). With these fibers, the mesophase is aligned parallel to the fiber exterior. The mesophase is also aligned parallel to the fiber wall with the 4104B fibers, where the extinction bands based from the fiber interior through the wall into the transformed phase. A shift in orientation occurs, however, on passing through the wall.

Chemical oxidation of the more highly graphitic fibers GY70 and T50 for up to 96 hours with nitric acid resulted in no obvious change in the fiber-mesophase interaction or alignment within the mesophase. An effect was observed with T300 and VYB fibers oxidized for 3.5 hrs., particularly with the latter. Small quantities of mesophase are observed within the yarn bundle, but the extent of transformation appears to be far less than in the surrounding region. The diameter of the T300 and VYB fibers had been significantly reduced by the oxidation treatment (18 and 37%, respectively). Fibers oxidized for shorter times did not exhibit any altered changes in interaction with mesophase.

With solid (not fiber) carbon substrates, coalesced mesophase was observed coating the carbon substrates and aligned with the surface. Untransformed material existed at short distances away from the sheath-like coalesced layer. Although mesophase alignment was observed, this does not mean that a coherent bond forms with the substrate. Indeed, the vitreous carbon rod fell out of the aligned matrix when the sample was inverted. The microstructure of the rod was unaltered by the heat treatment. The highly oriented pyrolitic graphite specimen showed more mesophase coalescence near the substrate surface than did the other carbon materials. Scanning electron microscope examination of these specimens showed no structural discontinuities in the pitch near the graphite interface. The E-glass fibers also did not enhance mesophase formation as individual filaments were observed in both phases. In contrast, the Kevlar fibers were always completely encapsulated by the transformed pitch.

In discussing these results, it should first be noted that the process of the nucleation, growth, and coalescence of mesophase material is complex and infolves polymerization of the isotropic material, phase separation into droplets, growth-of droplets, coalescence of droplets, and wetting of surrounding substrates. Marsh and Walker (5) pointed out that the role of polymerization can materially affect the resultant texture: too rapid polymerization leads to hardening before alignment can occur. The extensive studies on the use of additives to control nucleation apparently have not considered that phase separation can only occur after polymerization has progressed sufficiently to form the larger molecular species. It is possible that some additions can delay the polymerization reactions, but studies aimed at controlling polymerization with additives such as aluminum chloride (17) or free radials (18) have not been very successful.

Pressure can have two effects which act in opposition: at intermediate pressures, the high boiling volatiles are retained in solution to increase the fluidity and enhance alignment (19); while at high pressures motion is restricted, coalescence does not occur, and botryoidal spheres result (20). The presence of colloidal material retards or inhibits coalescence, whereas impingement of mobile spherules onto larger particles or surfaces causes alignment of the spherules with the substrate surface. The aligned material may actually be separated from the substrate surface by a thin layer of isotropic material. Note that all of the substrates were readily wetted by molten pitch, whereas only a very few were wetted by the mesophase spherule. The presence of an interphase region of isotropic pitch seems reasonable because: (a) the mesophase is incompatible with the isotropic phase; and (b) to wet a surface, the mesophase must either displace or incorporate the intervening isotropic layer.

Phase separation of mesophase from isotropic pitch is itself a complicated process, much like the fractionation of a polymer: a distribution of molecular weights should exist in both phases, but there is a significant difference in the average molecular weight of each phase. Such differences have been demonstrated by comparing the molecular weight of the isotropic pitch with that of the mesophase after hydrogenation to effect solubilization (21). The mesophase spherules contain isotropic material which is undergoing polymerization. The spherules can grow by adsorbing isotropic material much like a polystyrene bead absorbs monomer during emulsion polymerization. The precise details of the locus of polymerization--whether interior to or at the spherule surface or both--must await further studies.

The processes of polymerization, phase separation, growth, and coalescence involve orientation of the smaller molecules to form sheet-like molecules, and orientation of the sheet-like molecules into ordered regions. To facilitate these orientations, there must be dynamic motion within the fluid. Indeed Rester and Rowe (22) show that the quantity of transformed material is greater near bubble walls, and that bubble tracks contain larger-sized spherules. In areas where flow was restricted in the present study, as in the interior of yarns and between yarn bundles, less mesophase formation is observed. The coalescence of mesophase onto yarn bundles occurs by impingement of the mobile spherules with the substrate. The less fluid, non-wetting mesophase cannot easily penetrate into the yarn bundles. The mesophase is therefore formed inside the yarns at a slower rate owing to the diminished amount of dynamic flow.

There must be a critical surface area for "ordinary materials" to initiate mesophase alignment. If the particle is too small, alignment is impeded and the particle may just be attached to the spherule surface without actually being wetted by the spherule. For a larger surface or container walls, the surfaces have sufficient area to allow alignment. The term "ordinary materials" is used because the critical surface area must also depend in part on the surface characteristics of the substrate: the wedge portion of 4104B fiber, Kevlar fiber, and pieces of HOPG are readily wetted by mesophase; but the other substrates are not. The various surface characteristics involved in mesophase/substrate interactions could be due to differences in the surface energy of the substrate, the polar component of the surface energy, the particular chemical functionalities present on the surface and/or the degree of structural order at the surface. The polar and dispersion force components of the surface tension for some carbon fibers and carbon substrates are collected in Table III. It is quite difficult to obtain precise surface tensions of carbon fibers because of the small (<10 μm) filament diameters. From the data presented in Table III, it appears that the manufacturer- applied surface coating or surface treatment greatly increases the polarity of the fiber. There is also a high dispersive component as well. The results of Donnet et al. (26) indicate that the dispersive component of the surface energies of the fibers is larger than that of HOPG or vitreous carbon. One might have expected the fibers to have an intermediate value because of the intermediate degree of surface order. The situation is further confused because Hawthorne and Teghtsoonian (27) found that the contact angle and wettability data of pitch-based fibers are independent of fiber modulus. Unfortunately, the surface energy characteristics of Kevlar fibers, which are wetted by mesophase, are not yet available. For these reasons, it is not yet possible to correlate the surface energy characteristics of the substrates with wettability by mesophase spherules.

The oxidation of carbon fibers by nitric acid tends to produce a higher proportion of carboxyl groups at the surface compared with oxidation by gaseous oxygen or air (28). It is also reported that the ability of carbon fibers to be oxidized increases with decreasing fiber modulus (29), and that the rate of nitric acid attack is higher for the less ordered fibers (30, 31) and for the less organized zones within a fiber (32). These observations are consistent with the present observations on the effect of nitric acid on T-50, GY-70, VYB-103.2 and T-300 fibers. A number of structures suggest that a skin of 30-30x10^3 nm in thickness exists on carbon fibers prepared from pitch or PAN precursors. The skin is more highly organized relative to the interior (33, 34); but since the observed thickness of the skin varies with the method of observation, the precise character of the surface layer remains a subject of debate (35-39).

The oxidation of the well ordered carbon fibers by nitric acid for 96 hours had little effect on fiber diameter or on the coalescence onto the fibers. On the other hand, oxidation of the less well ordered fibers, particularly VYB, showed significant reduction in fiber diameter. The lack of coalescence of mesophase in regions adjacent to the highly disorganized etched fibers provides additional evidence on the influence of surface structure. It seems, however, that alignment of mesophase with a given surface is primarily controlled by the initial contact with flow across a surface of sufficient size to allow flow within the mesophase. Surface order is a secondary effect that is most readily observed when comparing surfaces in a macroscale.

The study of the coalescence of mesophase droplets in a transforming pitch has been studied experimentally using cinematography of the surface of the pitch. To provide an experimental geometry for which the results could be analyzed in detail, the thickness of the sample was made small so that the mesophase material could be analyzed as cylinders rather than spheres. This specification of the geometry made possible a detailed description of the process.

In analyzing the coalescence of mesophase cylinders, a modification of the analysis of Frenkel was carried out. This modification follows the approach of Frenkel, but considers the geometry of cylinders rather than spheres. The flow field assumed in this analysis is a simplified one; but the results have been found in many studies of a variety of materials to predict the correct dependence of the observed sintering rate on material characteristics such as size and viscosity. The present results indicate that the radius of the neck between cylindrical mesophase domains should increase as the cube root of time and as $(\text{radius})^{2/3}$ and inversely as $(\text{viscosity})^{1/3}$. For comparison, the radius of the neck between spherical particles is predicted to increase as the square root of time, and as the square root of the radius and inversely as the square root of viscosity.

It should be emphasized that this analysis is carried out for the interpretation of experimental results in the laboratory. Once the appropriate kinetic parameters are obtained for the coalescence of cylindrical mesophase domains under experimental conditions, extrapolation to the case of spherical domains in bulk samples is straightforward, and can be carried out using the kinetic parameters determined in the laboratory studies.

IV. CONCLUSIONS

The present investigation of the stabilization of acrylic fibers and the development of structure in fabricating carbon-carbon composites has directed attention to the structural features of the materials, their variation with processing and their implications for the properties of the final materials. The work on the stabilization of acrylic fibers has demonstrated that various mantle-core structures are observed at intermediate stages of stabilization, that the dark mantles seen in optical thin sections can be related to the etched mantles seen on exposure to solvents for PAN, that the mantles seen on fractured fiber ends reflect the underlying structure of the partly-stabilized fibers, that the development of these various mantles with time depends on the nature of the precursor fibers and the processing conditions, that liquid droplets can be produced during fracture of fibers during stabilization, and that the fracture of even a small number of fibers can produce effective cementation of a yarn during processing.

The study of the interaction between mesophase material and carbon fibers has directed attention to the precipitation, growth and coalescence of mesophase material, which processes require ordering of small molecules in a viscous medium. On this basis, dynamic motion in the fluid rather than the presence of nucleating substrates is suggested to be the controlling factor in the structural development. Where dynamic motion is restricted, as in the interstices of a yarn, mesophase formation and growth are also restricted. Alignment of mesophase material with a substrate is primarily controlled through motion of the mesophase droplets in flow, which generally do not wet the substrate. Certain well-ordered surfaces are wetted by the mesophase material, but the effect is primarily noted on surfaces of comparable size to the droplets.

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TABLE I

TYPICAL PITCH PROPERTIES

	Coal Tar Pitches		Petroleum Pitch
	15V	Koppers	A240
Softening Point, °C	90-95	103-197	115
Benzene Insolubles, %	18-29	28	5
Quinoline Insolubles, %	5-10	3-7	0.5
Cooking Value, %	35 min.	60	47
Ash, %	0.25 max.	0.05	0.7
Specific Gravity, g cm^{-3}	1.26-1.32	1.31	1.25
Sulphur, %	0.75 max.	0.1	4.5

TABLE II

CARBON FIBER DATA

Fiber	Density (g cm^{-3})	Modulus (10^6 psi)	Precursor
T50	1.67	57	RAYON
VYB105.2	1.53	6	PAN
GY70	1.993	80.3	PAN
T300	1.76	33.4	PAN
4104B	Na	75-100	PITCH
VS0022	1.99	50	PITCH

Manufacturers: For GY70, Celanese. For all others, Union Carbide.

TABLE III

Surface Tension Components of Various Substrates

	γ^p_{sv}	γ^d_{sv}	Ref.
Diamond polished prosthesis carbon	2.4	53.3	17
Diamond polished vapor deposited carbon	3.2	34.5	23
2-Disotropic CVD carbon	3.6	33.0	23
Hercules HM untreated, heat cleaned	7.4	32.0	24
Hercules HM untreated not heat cleaved	8.1	33.0	24
Gulf vapor deposited carbon	11.3	32.2	23
Hercules HMS surface-treated, heat cleaned	12.8	30.2	24
Hercules HMS surface-treated, not heat cleaned	20.7	28.2	24
Hercules HMS surface treated, as received	26.8	26.1	25
Carbide Thornet 400 as received	23.4	25.5	23
Hercules HT-S	25.7	25.9	25
Morganite II	27.3	27.4	25
Modmor II	29.4	28.3	25

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