

Microstructural Studies of In-Situ Mesophase Transformation in the Fabrication of Carbon-Carbon Composites

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1. Introduction

Injection of a low viscosity, fully transformed mesophase pitch into a fiber preform can be an effective approach to fabrication of advanced, high-performance carbon-carbon (C/C) composites [1]. Here, flow-induced microstructures can be stabilized by oxidation such that upon carbonization, the fibrous carbon needles running through the flow channels are retained. Using the injection and stabilization process, one can raise the density of C/C composites to reasonably high levels in a couple of cycles.

While the injection method is effective in making highly densified materials with controlled microstructure, it is not without constraints. This method is best applied to uniform geometries such as aircraft brakes, and the use of rigidized preforms is required to resist compaction under injection pressure. Severe injection conditions with diminishing return in density gain could be encountered if the process has to be carried beyond two to three cycles.

For non-uniform geometries such as nozzle cones that are not amendable to injection or a vacuum process, an efficient and low-cost impregnation process is needed to densify a C/C composite in multiple cycles. The selection of a matrix precursor having the ideal properties of low viscosity, good wettability, and high carbon yield is essential for efficient densification [2, 3]. In practice, however, one generally needs to seek a compromise to reach a final composite density. A low viscosity precursor with the ability to wet carbon fibers can result in uniform density and effectively fill fine pores and cracks in subsequent impregnation cycles, but such a precursor tends to have lower carbon yield. The carbon yield can be improved by applying high-pressure pyrolysis and carbonization with high cost equipment. Alternatively, a precursor with high carbon yield, such as partially or fully transformed carbonaceous mesophase, will reduce the number of impregnation cycles, but in this case, the viscosity of the precursor may not be sufficiently low.

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14. ABSTRACT Injection of a low viscosity, fully transformed mesophase pitch into a fiber preform can be an effective approach to fabrication of advanced, high-performance carbon-carbon (C/C) composites [1]. Here, flow-induced microstructures can be stabilized by oxidation such that upon carbonization, the fibrous carbon needles running through the flow channels are retained. Using the injection and stabilization process, one can raise the density of C/C composites to reasonably high levels in a couple of cycles. While the injection method is effective in making highly densified materials with controlled microstructure, it is not without constraints. This method is best applied to uniform geometries such as aircraft brakes, and the use of rigidized preforms is required to resist compaction under injection pressure. Severe injection conditions with diminishing return in density gain could be encountered if the process has to be carried beyond two to three cycles.					
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Based on the in-situ mesophase transformation of a very low viscosity precursor, the Air Force Research Laboratory has developed a rapid, low cost impregnation process that can be applied at ambient pressure for densification of C/C composites [4]. The Air Force method is based on the mesophase pitch synthesis process advanced by Mochida and co-workers [5, 6, 7]. They used controlled catalytic polymerization of pure aromatic hydrocarbons such as naphthalene to produce a low-viscosity liquid phase that is further transformed into mesophase with good control of the softening point. Their work is also the basis of the commercially available AR mesophase pitches that have been utilized for spinning filaments, injection of brake preforms, and in fabrication of anode materials for lithium ion batteries.

The principle behind the impregnation with in-situ transformation process is that a wetting molten monomer mixed with a catalyst can easily penetrate a fiber bundle or a void space in a preform by capillary forces. Once the preform is completely filled, in-situ polymerization of the monomer leads to formation of mesophase. Pyrolysis gases within the large void space tend to blow bubbles and exude carbon matrix from the larger voids. However, the mesophase formed within the fiber bundles and small pores are, to the most part, retained after pyrolysis. Even so, this impregnation and in-situ transformation approach will require more processing cycles than injection processes. On the other hand, this is an acceptable trade-off when one considers the relative ease and quickness of impregnation cycles.

In this work, we explored the evolution of microstructures at various stages during mesophase formation to better understand the transformation and impregnation with a wetting monomer and catalyst mixture. Naphthalene was the precursor monomer, and aluminum chloride was chosen as the catalyst. Even though AlCl_3 was retained in the final composite product, we consider its use as a much more environmentally benign alternative to using HF/BF_3 , with minimal impact on the final composite functionality. The microstructures of mesophase formation in bulk and within preforms were examined at various stages in temperature ranges critical to mesophase formation and hardening. Results of multiple cycle in-situ transformation were also compared with impregnation using fully transformed AR mesophase pitch under similar conditions.

2. Experimental Methods

To study the microstructures formed during mesophase transformation, the bulk phase pyrolysis experiments followed the approach described by White *et al.* [8, 9]. All transformation and impregnation runs were carried out in a pyrolysis chamber consisting of a cylindrical aluminum block with four slots machined precisely for tight fitting of aluminum test tubes (19 mm x 102 mm). The aluminum tubes were enclosed within the chamber with narrow gas ports to provide a continuous purge stream of nitrogen and to limit the return of volatilized material during pyrolysis. The entire chamber was wrapped in a clamp-shell heater and insulating material, but in a design that facilitated expedient intermittent sample removal.

In each run, 4 to 6 g of naphthalene (Aldrich Chemicals, 99% purity, Cat. No. 147141) was mixed thoroughly with 5 wt% AlCl_3 (Aldrich Chemicals, 99% purity, Cat. No. 237051) in a mortar before being placed in the aluminum tubes. For studies of the early

stages of in-situ mesophase transformation within a preform, a small rectangular piece of CVI-rigidized preform made of PAN fibers (about 7.5 mm × 7.5 mm × 15 mm or 18 mm × 18 mm × 15 mm) excised with a diamond cutter was also placed in the tube such that it was submerged once the naphthalene had melted. In subsequent multi-cycle densification studies, a soft preform with fiber volume fraction of 26% was used initially.

The temperature of the chamber was raised rapidly from room temperature to 100 °C at a rate of about 230 °C/h. From here, the temperature was raised with a constant ramp varying between 30 °C/h to 80 °C/h to the desired set point, which ranged from 300 °C to 480 °C, at which point the temperature was held constant for various periods up to 3 h. In experiments using preforms, the temperature was also kept constant for 0.5 h at 100 °C before starting the temperature ramp in order to allow in-depth penetration of naphthalene. The temperature ramping profile was implemented with a control program written in LabView. The temperature of the system was monitored by a K-type thermocouple embedded within the aluminum block and interfaced with the computer using an InstruNet (GW Instruments).

Samples were removed at various time intervals and quenched at room temperature. Each entire aluminum tube with its contents was mounted and sectioned to provide a full vertical profile for subsequent polishing. The microstructures of polished sections were examined by polarized-light microscopy.

Impregnation experiments were also performed using the AR mesophase pitch. This mesophase pitch has a softening point of 297 °C and a density of 1.3 g/cm³ [7]. About 9 g of AR mesophase pitch was placed in a sample tube together with a piece of preform. The temperature was raised from room temperature at a heating rate of 110 °C/h to a set point of 350 °C, where it was held constant for about 2.5 h. The quenched samples were oxidized and carbonized.

Oxidative stabilization was performed at 170 °C and ambient pressure for 25 h in a tube furnace purged with a gentle flow of oxygen [10]. Carbonization was also carried out in a tube furnace, but under a purging stream of nitrogen. Samples were carbonized at a rate of 60 °C/h starting from 100 to 600 °C and at a rate of 180 °C/h from 600 to 1150 °C. After carbonization, specimens were cut to expose the innermost section and embedded in epoxy before a series of polishing for microscopic analysis.

3. Results and Discussion

There is no unique processing procedure leading to the formation of carbonaceous mesophase. Therefore, the following micrographs illustrating the progressive morphological stages are only representative of several selected sets of plausible operating procedures based on previous studies [8, 9].

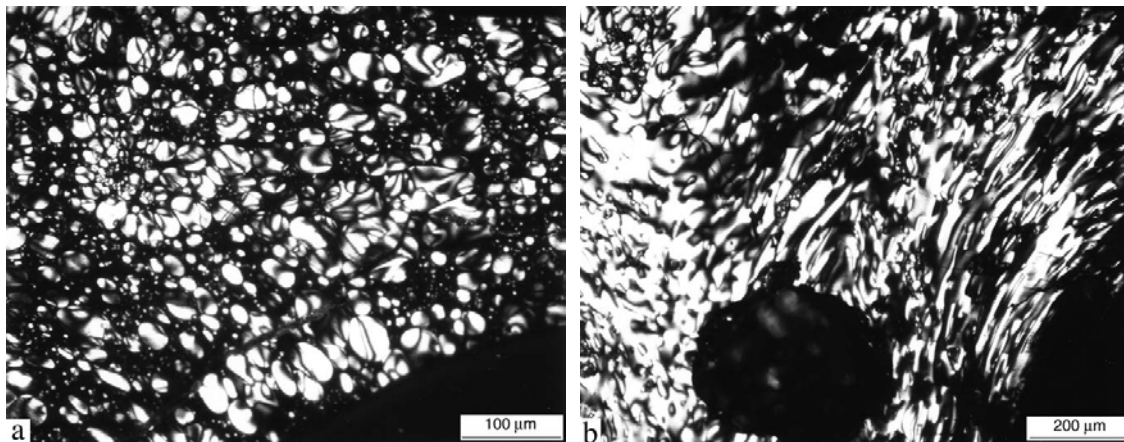
The gradual in-situ mesophase transformation during the earlier stages was examined under various heating profiles in CVI-rigidized preforms. In this step, we chose to use rigidized preforms in order to minimize damage to the as-impregnated fragile fiber bundles in the polishing process. The fiber lay-up consists of mat plies that are laid up in a regular rotational pattern from ply to ply. The preform architecture is governed

collectively by the organization of fiber bundles, the inter-fiber bundle regions, and the principal flow channels among the bundles.

The mesophase transformation in the bulk phase is presented first. The evolution of microstructures during transformation within a rigidized preform follows. The results of soft perform densification in multiple cycles will be addressed last.

3.1. Mesophase Transformation in the Bulk Phase

Overall, the formation of mesophase microstructures starting with naphthalene and AlCl_3 catalyst follows the common pattern of transformation from an isotropic phase to nucleation of Brooks-and-Taylor (B-T) spherules, and subsequent coalescence to form bulk mesophase. Formation and precipitation of anisotropic mesophase spherules was observed for the sample with a heating rate of $80\text{ }^\circ\text{C/h}$ that was removed and quenched at $350\text{ }^\circ\text{C}$ (Fig. 1a). The mesophase layers are aligned perpendicular to the polar diameter but curved to meet the interface with the isotropic phase at high angle. The spherules had a large size distribution, ranging from a few microns to approximately $50\text{ }\mu\text{m}$. As the pyrolysis proceeded to higher temperatures, the larger spherules were collected at the bottom of the tube and began coalescing to form bulk mesophase. Extensive mesophase deformation caused by bubble percolation was observed with increasing temperature and hold time. At this stage, the viscosity of the transforming fluid was sufficiently low to permit flow and structural rearrangement of the coalescing mesophase. The bubbles, mainly methane and hydrogen, were produced by pyrolysis via dealkylation and dehydrogenation reactions [5, 6, 11, 12].



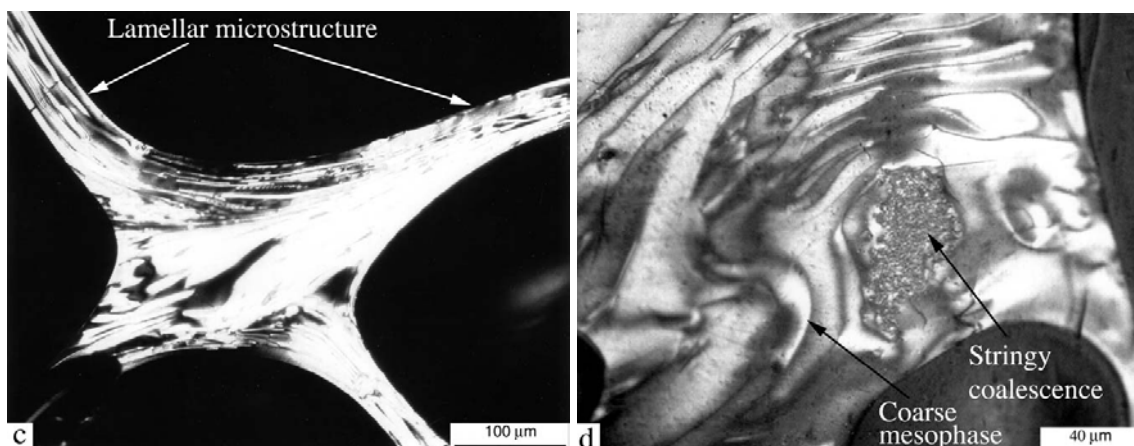


Fig. 1. Polarized-light micrograph of bulk mesophase formation in specimens pyrolyzed to 475 °C at a heating rate of 80 °C/h: (a) spherule formation in quenched sample removed at 350 °C; (b) the formation of microstructures by bubble percolation, 400 °C; (c) higher magnification showing the lamellar microstructure; (d) an island of stringy coalescence captured within coarse microstructure, 475°C.

For the specimen removed at 400 °C, less than 5 vol % of mesophase spherules was observed. The coarse, fibrous, and lamellar microconstituents were clearly evident as illustrated in Figs. 1b and 1c. The fibrous microstructure was produced by uniaxial stretching, and the lamellar microstructure observed in bubble walls resulted from biaxial deformation during growth of gas bubbles [13]. Islands of untransformed isotropic phase containing strings of mesophase spherules were observed deep within bulk mesophase (Fig. 1b). Eventually, the flow of bulk mesophase due to bubble percolation was blocked by hardening as viscosity increased with the extent of mesophase pyrolysis. At this point, the mesophase microstructure was locked in and further heat treatment would lead to formation of shrinkage cracks and sharpening of the folded mesophase layers. With this process, the carbon yield after heat treatment to 475 °C and hold time of 3 h was between 25% and 30%.

In addition to regions of coalesced mesophase consisting of coarse microstructure, stringy coalescence was evident for the subsequent sample removed at 475 °C (Fig. 1d). Under polarized-light microscopy, the stringy coalescence was an array of small spherules having a fine structure of extinction contours with less rearrangement than the coarse microstructure. These fine isotropic structures without long range preferred orientation might result from the spherules being in contact with little or no coalescence [14]. Similar structures were observed by White *et al.* [8, 9] during pyrolysis of coal-tar and petroleum pitches. They suggested that the stringy coalescence can form if nucleation of spherules occurs more rapidly before their growth and coalescence. More recently Fernandez *et al.* [15] also observed these fine-textured microstructures in unwashed cokes during the pyrolysis of anthracene oil with 10% wt. AlCl₃. They suggested that the catalyst in unwashed material causes rapid pyrolysis leading to increased viscosity, which in turn reduces the deformation of the coalesced spherules.

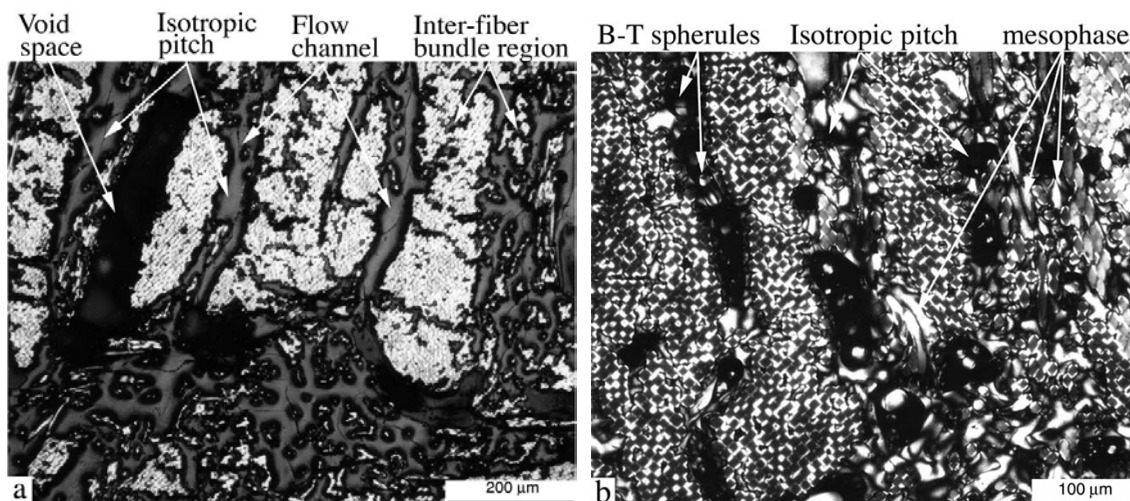
Bulk mesophase transformation under an applied pressure of 0.7 MPa revealed the same general observation of spherule nucleation, growth, and coalescence during pyrolysis. Under elevated pressure, higher yields of mesophase, consisting predominantly of coarse microstructures, were observed. However, undesirable stringy coalescence was also found to occur more frequently under high pressure.

3.2. In-Situ Mesophase Transformation Within Preforms

At the early stage of heat treatment, the naphthalene and catalyst mixture constitutes a very low viscosity wetting solution. The viscosity of naphthalene at 100 °C is 0.76cP [16], much lower than that of pitch-like material. Hence, the mixture can easily and uniformly infiltrate the fiber bundles and the flow channels by capillary forces without applied pressure. The wetting behavior of the isotropic liquid was similar for both the PAN filaments and the ones coated by CVI. As shown in Fig. 2a, most of the main flow channels were filled with an intermediate isotropic phase at 325 °C. No mesophase spherules had yet formed at this stage, which was arrived using a heating rate of 80 °C/h and without holding time. As either the temperature or the holding time increased, polymerization of the aromatic molecules led to nucleation and growth of mesophase spherules.

The formation and precipitation of mesophase spherules in the flow channels is illustrated with the sample taken at 350 °C in Fig. 2b; and the presence of mesophase spherules within fiber bundles was evident under higher magnification, as shown in Fig. 2c. Both isotropic and mesophase pitches wet the CVI-coated filaments. As expected, the mesophase layers were aligned normal to the isotropic pitch and parallel next to the carbon filament or CVI surface [13]. This image clearly shows that the mesophase transformation within a fiber bundle is similar to those observed in the bulk phase.

As the temperature increased to 475 °C, mesophase transformation was mostly completed. After 1 h of holding at 475 °C, most mesophase spherules had coalesced to form coarse carbonaceous mesophase; however, a few regions of stringy coalescence within fiber bundles were also observed (Fig. 2d). Figure 2e provides a low-



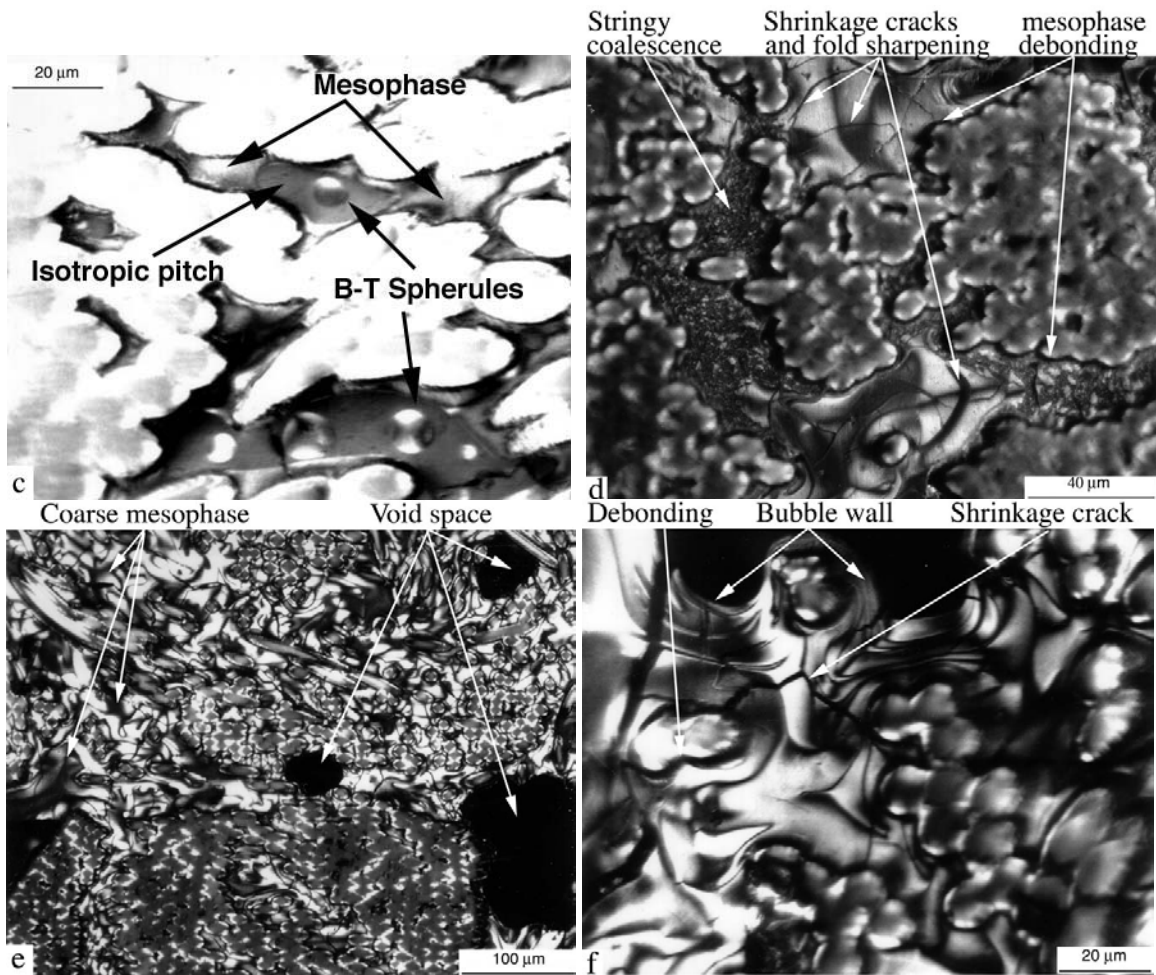


Fig. 2. The mesophase formation within a CVI-rigidized preform cube: (a) formation of an isotropic phase at 320 °C; (b) B-T spherules observed at 350 °C with zero holding time; (c) formation of B-T spherules in tightly packed fiber bundles; (d) stringy coalescence after 1 h holding at 475 °C; (e) fully transformed structures after 1 h holding at 475 °C; (f) higher magnification view of (e).

magnification view of the pyrolyzed preform along a vertical section near the innermost region. The hardened mesophase was mostly retained within the fiber bundles and the regions in between. The major void spaces were observed in the flow channels where the nucleation and growth of gas bubbles tend to take place. The high-magnification micrograph (Fig. 2f) shows the bloating of the mesophase matrix and the formation of the bubble wall microstructure. The bloating not only led to formation of voids but also forced the matrix into the surrounding regions or expelled it from the preform. An extensive network of shrinkage cracks was observed within the coarse mesophase matrix upon cooling due to thermal expansion mismatch between the matrix and the filaments.

3.3 Densification of Soft Preforms in Multiple Cycles

3.3.1. Naphthalene and Aluminum Chloride Catalyst

The increase in weight gain and apparent density through five impregnation cycles with naphthalene and AlCl_3 catalyst is summarized in Table 1. The apparent density of the composite increased with each impregnation cycle, although the incremental change in density decreased rapidly in cycles three through five. The largest weight gain and incremental density gain were achieved in the first and second cycles, where the molten naphthalene easily penetrates the fiber bundles and the small inter-fiber bundle regions. After two cycles, these regions were well filled with the transformed mesophase. The decrease in weight gain and density change beyond the second-cycle can be attributed to the incremental filling of the void spaces within the flow channels. The volume filling efficiency after each impregnation and carbonization cycle was, we estimated, based on the expressions reported by Matinos et al. [3] and Rellick [17]. The decrease in porosity after each cycle was calculated from the measured bulk density of the composite after carbonization, the starting void fraction of the dry perform, and the fiber and the mesophase coke densities. The density value used for the fiber and transformed mesophase heat treated to $1150\text{ }^\circ\text{C}$ was 1.62 g/cm^3 and 1.90 g/cm^3 , respectively. The filling efficiencies were approximately 49% and 14%, respectively, during the first two cycles; and afterward, the efficiency fell below 5%. Hence, the filling of the larger void spaces required multiple cycles in order to reach higher composite densities.

Table 1. Change in weight gain and density in different impregnation cycles with naphthalene-catalyst mixture at ambient pressure.

Number of cycles	Percent weight gain ^a		Bulk density ^b g/cm ³	Percent incremental density gain
	I	C		
0			0.42	
1	191.1	163.0	1.11	147%
2	26.3	23.7	1.38	24%
3	6.7	5.5	1.45	5.1%
4	3.9	3.3	1.50	3.4%
5	2.4	2.0	1.53	2.0%

^a Weight gain measured after impregnation, I, and carbonization, C.

^b Density measured after carbonization to $1150\text{ }^\circ\text{C}$.

Micrographs from the innermost regions of carbonized specimens from the different impregnation cycles are presented in Fig. 3. This set of specimens was pyrolyzed to $475\text{ }^\circ\text{C}$ and held at constant temperature for 3 h. Figure 3a clearly indicates that large void space remained in the main flow channels after one cycle of impregnation, although the fiber bundles appear to be well filled with mesophase (Fig. 3b). The mesophase microstructure in the bundles was determined by the sheath effect such that the alignment of the mesophase layers led to formations of $-\pi$ and -2π disclinations [13]. As compared to the CVI-coated filaments (Fig. 1f), there appeared to be good bonding between the filament and the mesophase matrix. The micrographs from the third-cycle impregnation (Figs. 3c and 3d) show filling of the shrinkage cracks and most of the inter-fiber bundle regions. There also appears to be a buildup of matrix within the larger flow channels. The image from the fifth-cycle (Fig. 3e) illustrates the complete filling of the inter-fiber bundle region and the still slow, gradual (or incremental) filling of the larger void space.

The preform can further be densified with additional impregnation cycles as long as the void space remains open. At this stage, the effect of matrix bloating, pitch expulsion from the flow channels, and the low carbon yield become increasingly more dominant, as indicated by the small incremental gain in density beyond the third cycle.

Applying modest pressures during pyrolysis was observed to improve the densification efficiency. Under 0.7 MPa, the densities of the composite after the first and second cycle were each around 1.2 and 1.47 g/cm³. These values were approximately 8% higher than those densities measured at room pressure. Figure 3f shows the innermost section of a carbonized specimen after the third-cycle impregnation. The bulk density of the specimen was measured to be 1.63 g/cm³, and the filling appears qualitatively to be similar to the impregnation after five cycles at ambient pressure.

3.3.2. *AR Mesophase Pitch*

Impregnation with a low-viscosity fully transformed AR mesophase pitch was conducted for comparison. The impregnation of soft preforms was conducted at an upper temperature limit of 350 °C in order to avoid thermal degradation of the AR mesophase pitch [18]. The viscosity at 350 °C was about 10⁴ cP [19, 20], significantly greater than that of naphthalene. As a result, the pitch cannot penetrate uniformly larger samples under ambient pressure. Hence, all impregnation runs using AR pitch necessarily required the use of the smaller 8 mm-sized preforms.

Weight gain and density values after each impregnation cycle are summarized in Table 2. The density of the composite rose to about 1.47 g/cm³ after two cycles, as compared with three cycles in Table 1. The key difference appears to be the slightly higher incremental density gain achieved during the first cycle. The density gain dropped back to 24% in the second cycle. In terms of filling efficiency, we estimated that it was about 55% during the first cycle, and lowered to 15.5% during the second cycle. Even at the third cycle, the incremental density gain was 7.5%, and the filling efficiency was approximately 9%. The composite achieved a density of 1.60 g/cm³ after the third cycle. While these figures appear much more attractive than using naphthalene in-situ transformation, we need to remember that the AR mesophase impregnation is applicable to only very small perform samples.

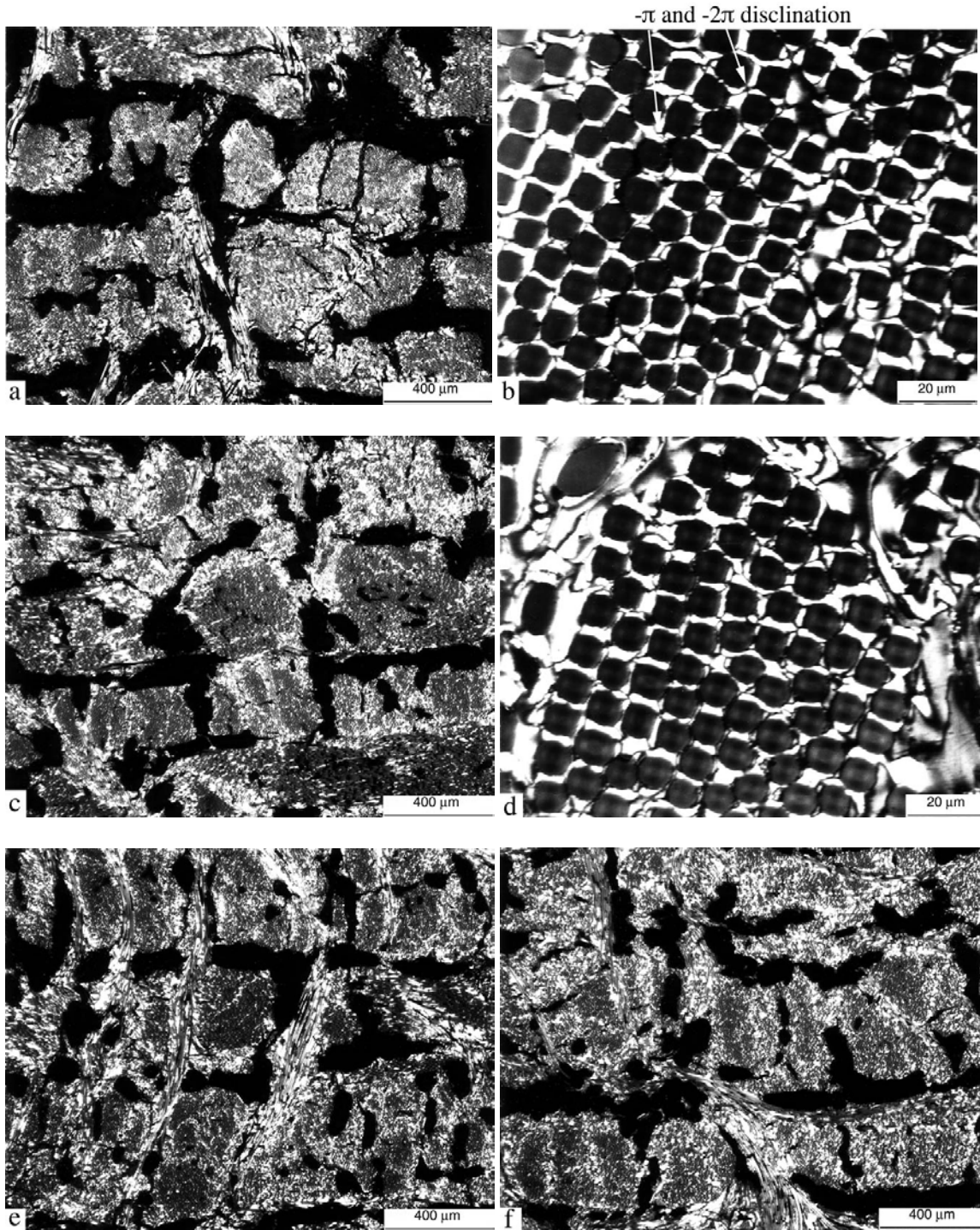


Fig. 3. Mesophase microstructure of the innermost region in specimens pyrolyzed and carbonized at ambient pressure: (a) after the first cycle impregnation; (b) higher magnification view of (a); (c) after the third cycle; (d) higher magnification view of (c); (e) after the fifth cycle; (f) after the third cycle impregnation and transformation under 0.7 MPa

Table 2. Change in weight gain and density in different impregnation cycles with AR mesophase pitch at ambient pressure.

Number of cycles	Percent weight gain ^a		Bulk density ^b g/cm ³	Percent incremental density gain
	I	C		
0			0.42	
1	213	181	1.19	183%
2	28.8	23.6	1.47	24%
3	9.5	7.6	1.58	7.5%

^a Weight gain measured after impregnation, I, and carbonization, C.

^b Density measured after carbonization to 1150 °C.

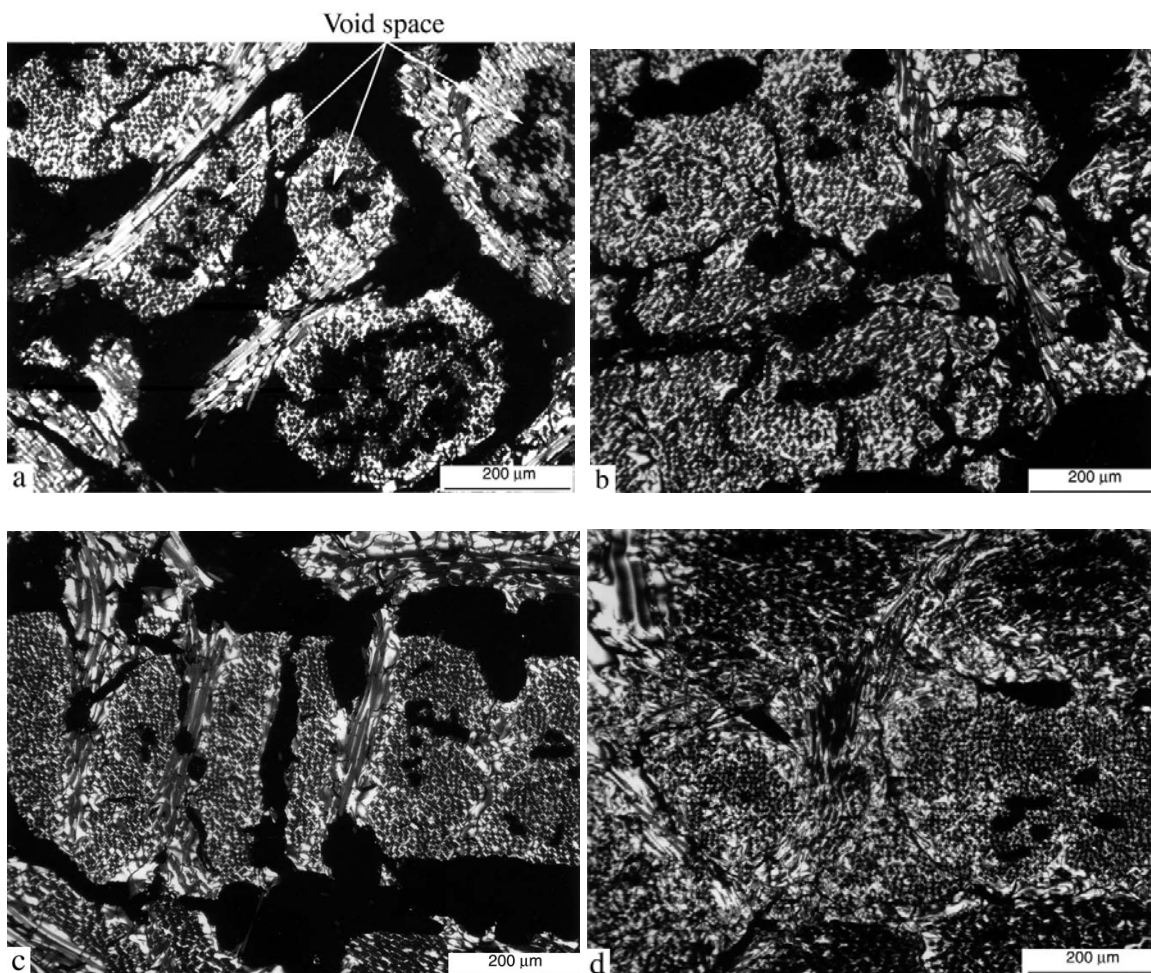


Fig. 4. Microstructure of stabilized and carbonized specimens impregnated with AR mesophase: (a) after the first cycle, inner region; (b) first-cycle, outer region; (c) third-cycle, inner region; (d) third-cycle, outer region.

Micrographic observations of the inner and outer regions after the first cycle are shown in Figs. 4a and 4b, respectively. The extent of mesophase penetration decreases

from the outer edge to the center of the preform, resulting in a non-uniform filling of the preform cube. In Fig. 4a, the inter-fiber bundle regions and the flow channels remain largely unfilled. With an additional impregnation cycle the pathways for penetration of mesophase to the inner regions become filled. After the third-cycle impregnation the flow channels in inner region remain unfilled, whereas they are mostly filled in the outer region (Fig. 4c and 4d). Significant blockage of access channels at the outer edge will significantly limit the access of mesophase to the innermost regions in the subsequent impregnation cycles.

Low-temperature oxidation stabilization [10] of the impregnated mesophase matrix was effective in retaining the mesophase during the carbonization. Consequently, the density of specimens impregnated with AR mesophase was higher than the preforms densified by in-situ transformation process. Nonetheless, one needs to recognize that the viscosity of the AR mesophase is much higher than that of molten naphthalene, and it is limited in in-depth penetration at ambient pressure [21]. One may consider raising the temperature. However, higher impregnation temperatures will approach the thermal stability of the AR mesophase leading to formation of bubbles.

Conclusions

Impregnation with a wetting monomer and catalyst mixture followed by in-situ transformation can be a relatively rapid and cost-effective approach for fabrication of C/C composites of non-uniform shapes and large geometries. The naphthalene catalyst mixture easily penetrates the carbon preform at ambient pressure, thereby producing a uniformly densified composite. The impregnation is efficient in filling tightly packed fiber bundles but not large open channels. Multiple impregnation cycles are required in order to fill the large void spaces.

With consideration of the different merits of in-situ transformation and mesophase injection, it may be fruitful to explore at the next stage an integrative approach that utilizes both processes at different cycles. For example, an initial impregnation cycle can be applied as a low-cost alternative to CVI-rigidization. This is followed by a small number of injection cycles. Toward higher density ranges, impregnation can be applied as final rapid densification steps.

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