

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

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## Introduction

Injection of a low viscosity mesophase pitch into CVD-rigidized preforms can be an effective approach for fabrication of carbon-carbon composites [1-5]. Here, flow-induced microstructures are stabilized by oxidation such that upon carbonization, the fibrous carbon needles running through the flow channels are retained.

While the injection method is effective in making highly densified materials with controlled microstructure, it is not without limitations. The method is best applied to well-defined geometries such as aircraft brakes, and the use of rigidized preforms is preferred in order to resist compaction under injection pressure.

The Air Force Research Laboratory has developed a rapid, low cost impregnation process that can be used to rigidize preforms or for further densification of C/C composites [6]. The Air Force impregnation method is based on the mesophase pitch synthesis process advanced by Mochida and co-workers [7]. The principle behind the impregnation strategy is that pure wetting monomer mixed with a catalyst can easily penetrate a fiber bundle or pore space in a preform by capillary forces. Once the preform is completely filled, in-situ polymerization of the monomer leads to formation of mesophase and hardening to coke.

In this paper, the microstructures of mesophase formation in bulk and within preforms were examined at various stages in the temperature range critical to mesophase formation and hardening. Results of multiple cycle in-situ transformation are also compared with impregnation using fully transformed mesophase pitch and will be presented at the conference.

## Experimental

All transformation and impregnation experiments follow the approach described by White *et al.* [8, 9]. The pyrolysis chamber consists of a cylindrical aluminum block with

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14. ABSTRACT

**Injection of a low viscosity mesophase pitch into CVD-rigidized preforms can be an ineffective approach for fabrication of carbon-carbon composites [1-5]. Here, flow-induced microstructures are stabilized by oxidation such that upon carbonization, the fibrous carbon needles running through the flow channels are retained. While the injection method is effective in making highly densified materials with controlled microstructure, it is not without limitations. The method is best applied to well-defined geometries such as aircraft brakes, and the use of rigidized preforms is preferred in order to resist compaction under injection pressure. The Air Force Research Laboratory has developed a rapid, low cost impregnation process that can be used to rigidize preforms or for further densification of C/C composites [6]. The Air Force impregnation method is based on the mesophase pitch synthesis process advanced by Mochida and co-workers [7]. The principle behind the impregnation strategy is that pure wetting monomer mixed with a catalyst can easily penetrate a fiber bundle or pore space in a preform by capillary forces. Once the preform is completely filled, in-situ polymerization of the monomer leads to formation of mesophase and hardening to coke. In this paper, the microstructures of mesophase formation in bulk and within preforms were examined at various stages in the temperature range critical to mesophase formation and hardening. Results of multiple cycle in-situ transformation are also compared with impregnation using fully transformed mesophase pitch and will be presented at the conference.**

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four slots machined precisely for the tight fitting of aluminum test tubes. The entire chamber was wrapped in a clamp-shell heater and surrounded by insulating material, but in a design that facilitated expedient intermittent sample removal.

In each run, 5 to 10 g of naphthalene (Aldrich Chemicals, 99% purity, Cat. No. 147141) was mixed thoroughly with 5 wt%  $\text{AlCl}_3$  (Aldrich Chemicals, 99% purity, Cat. No. 237051) in a mortar before being placed in the aluminum tubes. For in-situ transformation and impregnation studies, a small cube of preform (about 7.5 mm  $\times$  7.5 mm  $\times$  15 mm or 18 mm  $\times$  18 mm  $\times$  15 mm) was also placed in the tube such that it was submerged once the naphthalene had melted.

The temperature was raised with a constant ramp varying between 30  $^\circ\text{C}/\text{h}$  to 80  $^\circ\text{C}/\text{h}$  to the desired set point, which ranged from 300  $^\circ\text{C}$  to 480  $^\circ\text{C}$ , at which point the temperature was held constant for various periods up to 3 h long. Samples were removed at various time intervals and quenched at room temperature. The sample tubes with their entire content were mounted and sectioned to provide a full vertical profile for subsequent polishing. The microstructures of polished sections were examined by polarized-light micrography.

Impregnation experiments were also performed using fully transformed mesophase pitch. 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  $^\circ\text{C}/\text{h}$  to a set point of 340  $^\circ\text{C}$ . After a 2.5 h hold, the quenched samples were oxidized and carbonized. After carbonization to 1150  $^\circ\text{C}$ , specimens were cut to expose the innermost section and embedded in epoxy before a series of polishing for microscopic analysis.

## Results and Discussions

The formation of mesophase microstructures starting with naphthalene and  $\text{AlCl}_3$  catalyst follows the common pattern of transformation from isotropic pitches to nucleation of Brooks-and-Taylor (B-T) spherules, and subsequent coalesced structures [10]. Anisotropic mesophase spherules precipitation and formation were observed for the sample at 345  $^\circ\text{C}$  with a heating rate of approximately 40  $^\circ\text{C}/\text{h}$  (Fig.1). The spherules had a large size distribution, ranging from a few microns to approximately 50  $\mu\text{m}$ . Moreover, larger spherules were collected at the bottom of the tube and began coalescing to form bulk mesophase (Fig.1). As pyrolysis progressed, the spherules grew and coalesced to produce large regions of bulk mesophase. In addition to regions of coalesced mesophase consisting of coarse, fibrous, and lamellar microstructure, stringy coalescence was also evident for the sample taken at 475  $^\circ\text{C}$ . Under polarized-light microscopy, the stringy coalescence was an array of small spherules having fine structure of extinction contours with less rearrangement than the coarse microstructure. These fine structures were random and appear to be isotropic.

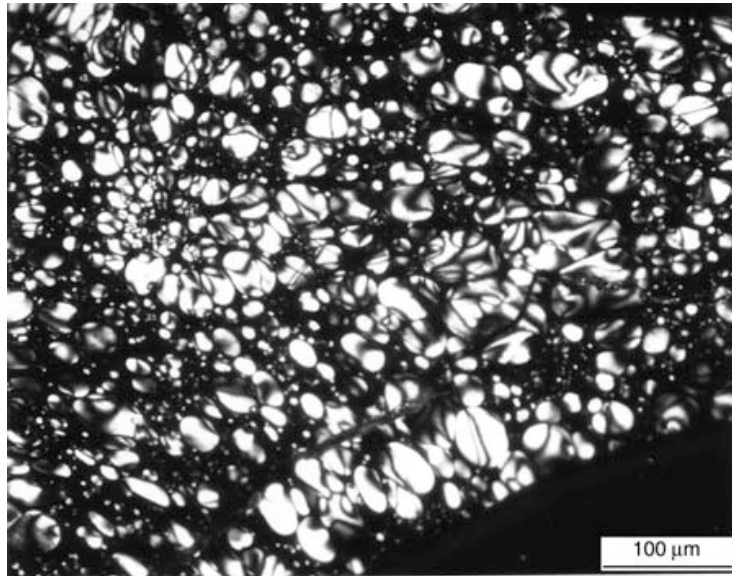
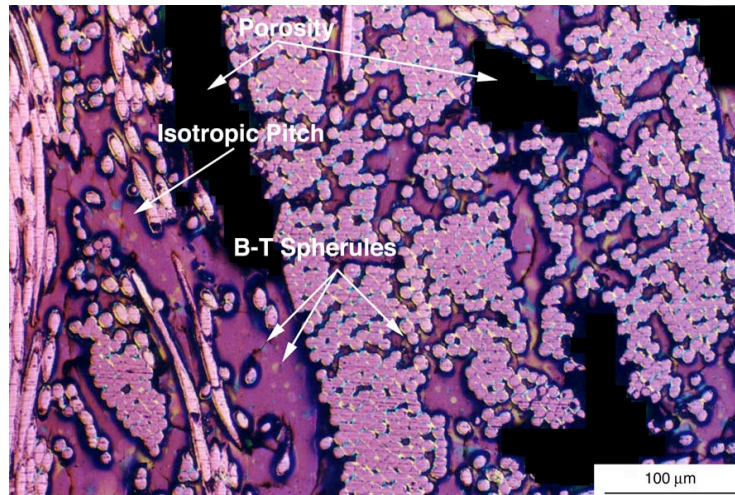


Fig. 1. Polarized-light micrograph of mesophase spherules in a specimen pyrolyzed to 345 °C at a heating rate of approximately 40 °C/h.

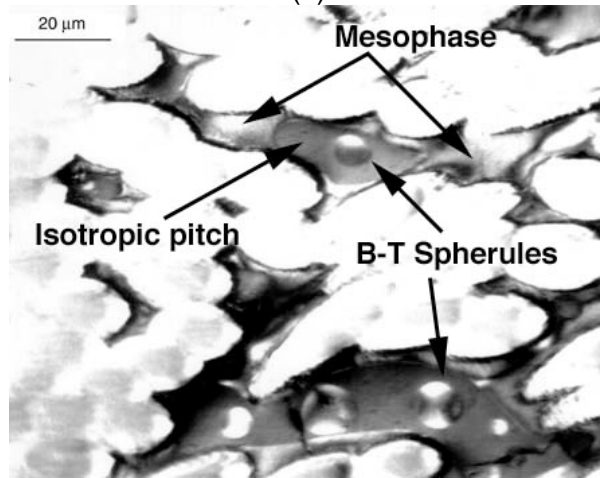
The impregnation and in-situ mesophase transformation with non-woven preform was examined under various heating profiles in soft and CVD-rigidized preforms. The preform consists of mat plies that are laid up in a regular rotational pattern from ply to ply. The principal flow channels lie between the bundles as well as along the paths imposed by the needling.

At the early stage of heat treatment, the naphthalene and  $\text{AlCl}_3$  catalyst mixture has low enough viscosity such that it can infiltrate the fiber bundles and the flow channels. Without applying pressure, the penetration with the wetting monomer is achieved by capillary forces. Figure 2a illustrates the formation and precipitation of mesophase spherules with the sample taken at 350 °C, using a heating rate of 40 °C/h. As expected, the mesophase layers are aligned normal to the isotropic pitch and parallel next to the carbon filament or CVD surface [10]. The formation of mesophase spherules within fiber bundles was well observed under higher magnification as shown in Fig. 2b. After 1 h of hold time at 475 °C, most mesophase spherules had coalesced to form carbonaceous mesophase (Fig. 2c).

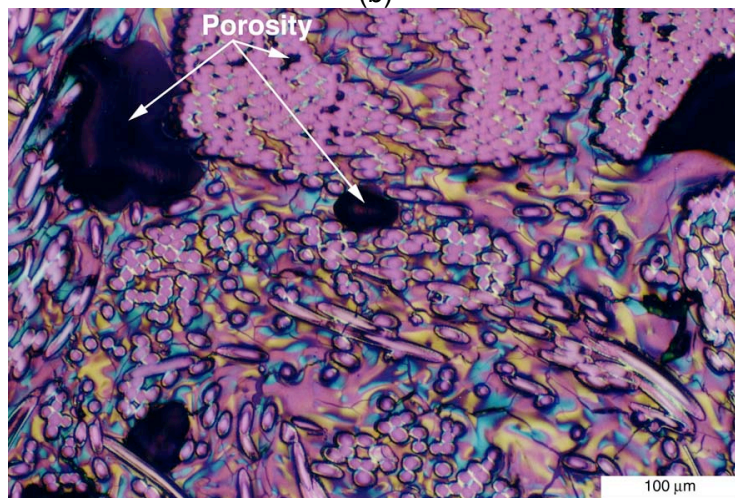
Multiple impregnation cycles with naphthalene and with AR mesophase were applied to study the densification of the preform. Table 1 summarizes the density data. After the 1<sup>st</sup>-cycle of impregnation with naphthalene, micrographic observations for both the inner and the outer regions of the preform were similar, indicating that the impregnation was uniform. The micrographs of Fig. 3 were taken of the inner region after 3<sup>rd</sup>-cycle



(a)



(b)



(c)

Fig. 2. The mesophase formation within a CVD-rigidized preform cube; (a) B-T spherules observed at 350 °C with 0 holding time, and (b) formation of B-T spherules in tightly packed fiber bundles. (C) fully transformed at 475 °C with 1 h of holding time.

Table 1. Variation of weight gain and density at increasing impregnation cycle with naphthalene-catalyst mixtures (above) and AR mesophase pitch (below). The impregnation experiments were conducted at ambient pressure.

Number of cycle	Weight gain <sup>a</sup> %		Bulk density <sup>b</sup> g/cm <sup>3</sup>	Density gain <sup>b</sup> %	Incremental density gain <sup>b</sup> %
	I	C			
0			0.42		
1	191.1	163.0	1.11	163	163
2	26.3	23.7	1.38	225	23.7
3	6.7	5.5	1.45	243	5.5
4	3.9	3.3	1.50	254	3.27
5	2.4	2.0	1.53	261	1.96

<sup>a</sup>Weight gain data reported after impregnation, I, and carbonization, C.

<sup>b</sup>Density data reported after carbonization to 1150 °C at heating rate of 3°C/min.

Number of cycle	Weight gain <sup>a</sup> %		Bulk density <sup>b</sup> g/cm <sup>3</sup>	Density gain <sup>b</sup> %	Incremental density gain <sup>b</sup> %
	I	C			
0			0.4		
1	213	181	1.19	180	200
2	28.8	23.6	1.47	247	23.6
3	9.5	7.6	1.58	273	7.6

Specimens stabilized at 170 °C and 0.7MPa for 25 hours before carbonization to 1150 °C

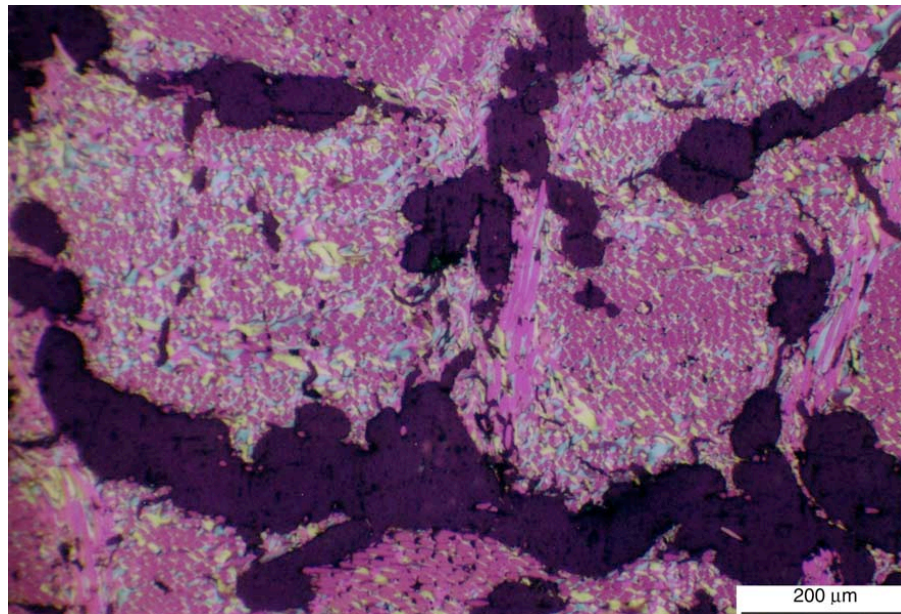
impregnation. The fiber bundles are well filled but the large pores and the flow channels remain unfilled. The high magnification micrograph (Fig. 3b) illustrates the mesophase microstructures in the fiber bundles to be dominated by the sheath effect [10].

The extent of impregnation with AR mesophase decreased from the outer to the inner region, likely the result of the higher viscosity of AR mesophase. The flow channels appeared to be mostly filled in the outer region. Low-temperature oxidation stabilization [5] 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 impregnation process.

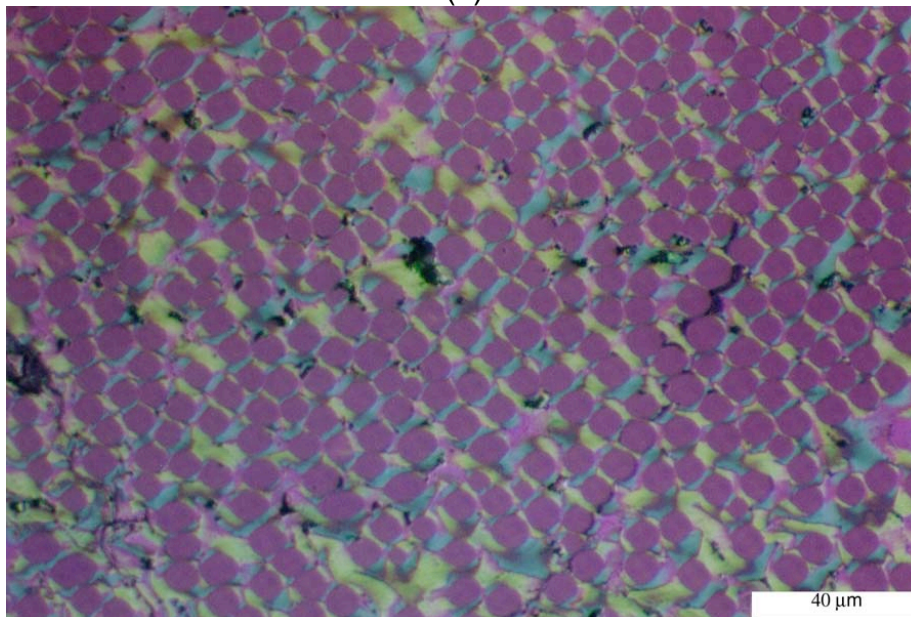
## Conclusions

Impregnation with a wetting monomer and catalyst mixture followed by in-situ transformation process is a rapid and cost-effective approach for fabrication of C/C composites of odd shapes and large sizes. The impregnation is efficient in filling tightly packed fiber bundles but not large open channels. In fabrication of C/C composites for aircraft brakes by the injection and stabilization process, one impregnation cycle can be

applied as a low-cost alternative to rigidization of the preforms by CVD. In addition, impregnation can be applied as a final rapid densification step in order to reach higher composite densities.



(a)



(b)

Fig. 3. Mesophase microstructure after third-cycle impregnation with naphthalene-catalyst mixture. (a) Low-magnification micrograph on the inner regions of the preform. (b) High-magnification view of the well-filled fiber bundles.

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