Introduction

The oxidation of mesophase pitch, as the first step in microstructural stabilization after such flow processes as fiber-spinning or mesophase-injection, is essentially a process of oxygen diffusion into a reactive medium [1-5]. A variety of oxidation reactions are possible with the complex aromatic molecules that comprise mesophase pitches; most such reactions begin at or above 150°C [6-8]. This investigation focuses on the question raised by the work of Cornec et al. [9]: Can mesophase oxidation be conducted, under conditions of low temperature and elevated pressure, to achieve stabilization to useful depths, with benefits to carbonization yield, reduced process time, and properties of the carbon product?

An extended abstract [10] for the CARBON 2000 conference described our microstructural approach and showed that the use of temperatures as low as 150°C reduced the variety of active oxidation reactions and that pressures up to 100 psia (0.7 MPa) could increase the depth of stabilization as well as the oxygen uptake. Further results presented at the conference demonstrated that, for longer oxidation exposures at low temperatures, the depths of stabilization could be competitive with those obtained at the higher temperatures conventionally used for mesophase stabilization. This paper documents the latter observations and adds results for oxidation temperatures down to 130°C.

Experimental

The experimental method was developed in a study of the stabilization of an alkylbenene-based mesophase pitch produced by Mitsubishi Oil [11]. The naphthalene-based ARA24R pitch by Mitsubishi Gas-Chemical is the subject of the present investigation. Mesophase rods were extruded and thick filaments spun to obtain the fine fibrous microstructures illustrated by Fig. 1. Specimens were oxidized at pressures up to 100 psia and at temperatures in the range of 270 down to 130°C, then carbonized to 1150°C to “develop” the stabilized region of the cross sections. A sufficiently oxidized rim retains the fine as-spun microstructure, but less oxidized mesophase melts or coarsens sharply in microstructure, and can be blown from the interior of the rod or filament by pyrolysis gases.

Observations

Figure 2 illustrates, for thick filaments as well as mesophase powder, the effect of pressure in reducing the exposure time required for oxidation at 169°C to reach a stabilizing level of oxidation mass gain (OMG); a level of OMG = 0.06 has been quoted as sufficient to stabilize fine filaments [2]. As seen in Fig. 3, the effect of pressure on the oxidation mass gains of extruded rods is stronger at temperatures of 150 and 130°C; however without applying an oxygen pressure of 50 to 100 psia, stabilization would not be practical.

The depths of microstructural stabilization, for various conditions of pressure and temperature, are illustrated by Figs. 4 through 7. The boundaries between stabilized and coarsened microstructures are clear and consistent, and the depths of stabilization are readily measured by microscope reticle; these measurements are summarized for room pressure and for pressures near 100 psia in Fig. 8. Striking features of these plots are (1) the sharply limited growth of the stabilized rim at room pressure and high temperature, e.g. at 270°C, and (2) the increasing tilt of the growth curves at lower oxidation temperatures. At the lower temperatures, there is a delay time before oxidation makes its effect apparent in terms of a stabilized layer.

Discussion

Before considering further the patterns of stabilization depth, several points from the literature are relevant:

- Oxidation reactions at lower temperatures, below about 200°C, are generally limited to the liberation of water [6-8] and can be written: \( \text{O}_2(g) + \text{mesophase pitch} \rightarrow \text{oxidized pitch} + \text{H}_2\text{O}(g) \).
Thus one molecule of oxygen gives one molecule of steam, and these oxidation reactions are not very pressure-sensitive until pressure condenses the steam to liquid water.

- Using electron paramagnetic resonance, Singer and Mitchell [5] found that the oxidation of mesophase pitch below 150°C is reversible.

- Oxygen concentration profiles, determined by microprobe techniques applied to oxidized filaments [2,3,7,12,13], indicate that the oxygen gradient is steeper for higher oxidation temperatures, and that the oxygen content at the filament boundary increases with temperature.

- Micropores form at the exposed rim of mesophase that has been over-oxidized [6,14]. The superior strength of carbon filaments stabilized under moderate-temperature conditions [15] may be due to this effect.

The schematic diagram of Fig. 9 utilizes this information to describe the effects of temperature and pressure in terms of oxygen concentration profiles that are increasingly free of the effects of oxidation reactions as the exposure temperature is brought below 200°C. Thus oxidation at lower temperatures, enabled by relatively modest levels of pressure, offers a means of avoiding the effects of over-oxidation at the surface of a mesophase body or filament.

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References
Fig. 1. Transverse microstructures of extruded rods and thick filaments of the ARA24R mesophase pitch used in oxidation experiments. Crossed polarizers.

Fig. 2. Oxidation mass gains at 169°C for ARA24R mesophase pitch in the form of powder and filaments, as functions of oxygen pressure and exposure time.
Fig. 3. The effects of pressure on oxidation mass gains at 150 and 130°C.
Temperature: 170°C
Exposure time: 91.7 hours
Stabilized depth: 25.8 (±2.1) µm

Temperature: 270°C
Exposure time: 98.8 hours
Stabilized depth: 6.9 (±0.5) µm

Fig. 4. Extruded mesophase rods oxidized at room pressure, after carbonization to 1150°C.

Temperature: 220°C
Exposure time: 46.5 hours
Stabilized depth: 23.3 (±1.3) µm

Temperature: 270°C
Exposure time: 49.1 hours
Stabilized depth: 6.5 (±0.6) µm

Fig. 5. Thick mesophase filaments oxidized at room pressure, after carbonization to 1150°C.
Oxygen pressure: 14.7 psia
Exposure time: 46.5 hours
Stabilized depth: 13.6 (±1.4) µm

Oxygen pressure: 100 psia
Exposure time: 49.1 hours
Stabilized depth: 48.5 (±7.1) µm

Fig. 6. The effect of oxygen pressure on extruded mesophase rods oxidized at 170°C, after carbonization to 1150°C.

Oxygen pressure: 98 psia
Exposure time: 144 hours
Stabilized depth: 77 (±8) µm

Fig. 7. Extruded mesophase rods oxidized at 130°C, after carbonization to 1150°C.
Fig. 8. Depths of stabilization for extruded mesophase rods as a function of exposure time. Above, at room pressure. Below, at pressures near 100 psia.
Oxygen Diffusion into Pitch Rod

\[ C_{st} = \text{Oxygen content required for stabilization} \]

**Oxidation at high temperature, e.g., 250°C**

Many reaction sites, of varying reactivity

- \( t_1 \): oxygen profile established
  - steep oxygen gradient
- \( t_2 \): profile rises, \( d_{st} \) increases slowly
- \( t_3 \): profile rises, stabilization complete
  - rim is strongly overoxidized

\[ \overline{\text{excess oxidation}} \]

**Oxidation at low temperature, e.g., 150°C**

Fewer reaction sites

- \( t_1 \): gentle profile established, \( d_{st} = 0 \)
- \( t_2 \): profile rises, \( d_{st} \) suddenly increases
- \( t_3 \): stabilization complete, little overoxidation

Fig. 9. Schematic models of oxygen profiles at temperatures where oxidation reactions are dominant (above) and limited (below).