

LOW-TEMPERATURE OXIDATION STABILIZATION STUDIES OF AR-MESOPHASE PITCH

C. Rottmair¹, A. Volek¹, A. Jung¹, P.C. Chau², and B. Fathollahi²

¹*University of Erlangen-Nuremberg
Central Institute for New Materials and Processing Technology
Dr.-Mack-Str. 81, 90762 Fuerth, Germany*

²*University of California, San Diego
Chemical Engineering Group
La Jolla, CA 92093, USA*

Introduction

The oxidation of mesophase pitch by air or oxygen at 200 to 300 °C is a key step in stabilizing the flow-induced microstructures of as-spun filaments [1, 2] and the matrix of carbon-carbon composites [3, 4, 5]. Previous works have shown that oxidation stabilization at low temperatures improves the carbon yield and decreases the time required for in-depth stabilization [6 -10] measured the depth of stabilization in large diameter filaments by determining the local softening temperature using a micro thermal probe. They related the softening temperature to oxygen content by electron probe micro-analysis (EPMA). They observed greater depths of stabilization at lower oxidation temperatures. Drbholov and Stevenson [11], who studied oxidation stabilization of AR mesophase pitch at various temperatures, postulated that weight gain reactions have lower activation energies and predominate at lower temperatures and the weight loss reactions become more dominant at higher temperatures accompanied with release of CO and CO₂. Sufficiently stabilized samples were attributed to those having ester and anhydride crosslinks. Fanjul et. al. [12] examined the stabilization of AR mesophase using elemental analysis and FTIR in the temperature range of 200 °C to 300 °C. They reported a shift in peaks in the carbonyl stretching region, 1680 cm⁻¹ to 1800 cm⁻¹, to higher wavenumbers with increase in oxidation temperatures. Ketone and aldehydes peaks were observed at lower temperatures and an increase in intensity of ester and anhydride peaks at higher temperatures. Similar to Drbholov and Stevenson, they concluded that the increase in intensity of esters and anhydrides at higher oxidation temperatures leads to formation of cross-linked structures via condensation reactions.

Fathollahi et. al. [6] used a microstructural approach and showed that oxidation at temperatures as low as 130 °C and pressures up to 0.7 MPa could increase the oxygen uptake and the stabilization depth to as much as 80 μm. At temperatures as high as 270 °C, they observed the stabilization front to stop at a depth of about 7 μm regardless of exposure to oxygen for up to 100 h. Based on the microstructural observations, they inferred that high temperature oxygen uptake was restricted to regions close to the surface. In contrast, a more uniform oxygen gradient within the structure was attained at low temperatures [9, 10].

The main objective of this work is to examine the difference in oxidation stabilization at low and high temperature by means of analysis of functional groups of the oxidized mesophase. FTIR is used to analyze the chemical fineshift of the oxygen peaks in order to characterize the changes in functional groups, in particular the carbonyl groups, under different oxidation temperatures ranging from 130 °C to 270°C and with further heat treatment to 500 °C in inert atmosphere.

Experimental

Details of preparation of as-spun filaments and extruded rods from naphthalene-based ARA24R mesophase pitch with a softening point of 297 °C follows previously described procedures [6]. Thick as-spun filaments (~100 μm in diameter) were exposed to pure oxygen at ambient pressure and at selected temperatures between 130 °C and 270 °C for periods of up to 100 h. Selected oxidized specimens were further heat treated from the stabilization temperature up to 500 °C in inert atmosphere. Samples were removed from the furnace at 300 °C, 350 °C, 400 °C, and 500 °C for analysis by FTIR.

The oxygen distribution across filaments and rods was analysed using a JEOL LCXA 733 electron beam micro analyser equipped with five wavelength dispersive spectrometers. The samples were coated with gold. Semi-quantitative analyses for oxygen was performed at an acceleration voltage of 10 kV and probe current of 100 nA, dwell time 200 ms. The X-ray intensity obtained from a sample of B₂O₃ was used to standardize the oxygen content.

Results and Discussion

The EPMA measurements of oxygen distributions in 100- μm diameter filament at different oxidation temperatures and time are shown in Figure 1. At low exposure times there exists a steep oxygen gradient with increasing temperature of oxidation. At 270 $^{\circ}\text{C}$ and 25 h exposure time, the maximum oxygen content near the surface is about 7 wt.% and drops below 1 wt.% after a distance of 40 μm . At lower temperatures, the oxygen content at the outer region is lower; however the oxygen uptake level stays relatively uniform. At higher exposure times, the oxygen uptake at high temperatures eventually extends deep into the mesophase filament and a uniform oxygen profile is observed at 75 h. Fathollahi et. al. [6] observed the stabilization depth in identical thick filament oxidized at 270 $^{\circ}\text{C}$ not advancing beyond 7 μm at exposure time of up to 100 h. However, the EPMA data in Figure 1 show the relative oxygen content at 270 $^{\circ}\text{C}$ and 75 h and above to extend uniformly throughout the filament. Even at exposure time of 25h, high level of oxygen uptake is already extended well past 10 μm . While it is well recognized [11, 12] that anhydride and ester linkages are formed at higher temperatures and are contributing toward stabilization, the oxygen incorporation at 270 $^{\circ}\text{C}$ is incongruent with past results [6]. Our analytic method does not allow for a spatial resolution of the oxygen-bearing function groups, so the actual mechanism underlying microstructural stabilization probably remains unknown. The EPMA results and the measured depth of stabilization at 270 $^{\circ}\text{C}$ reported by Fathollahi et. al. indicate the level of oxygen uptake is not an absolute measure of stabilization in AR mesophase pitch. This is especially so considering that the reaction pathways leading to anhydrides and esters involve so-called carbon burnt off reactions that also contribute toward low carbon yields [10-12].

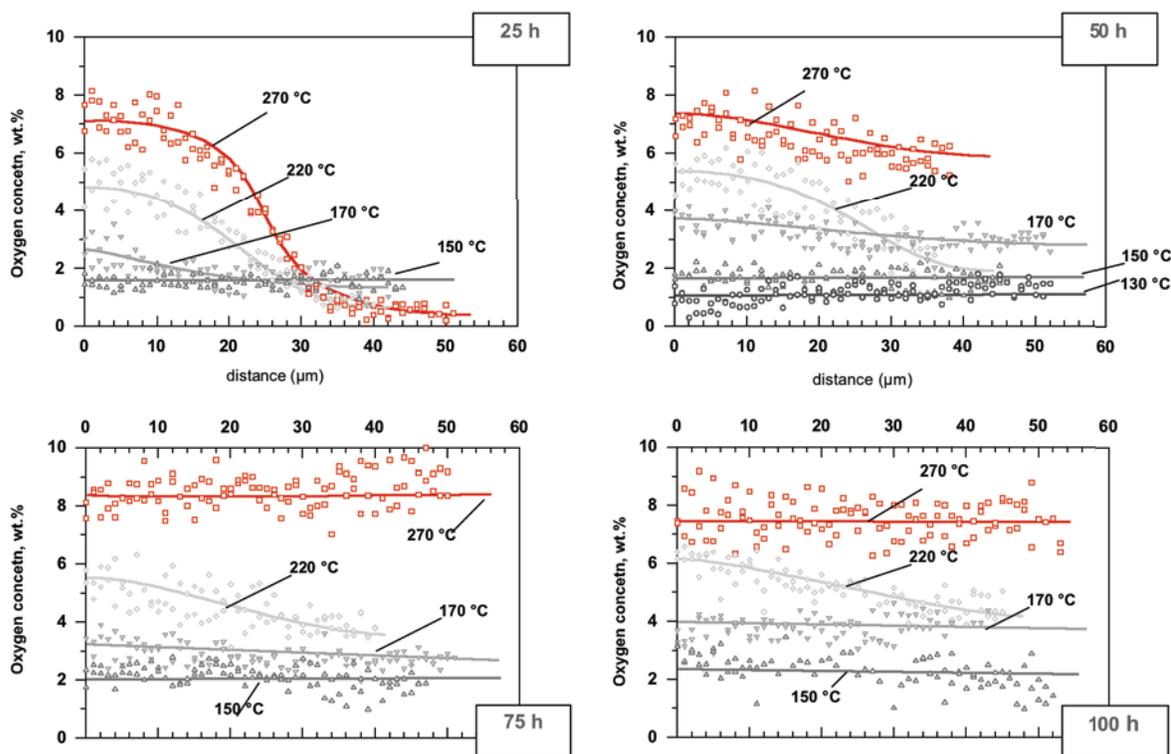


Figure 1. Oxygen distribution in thick filaments oxidized at different temperatures and exposure times.

The FTIR spectra for the mesophase filaments at oxygen exposure times of 25 h and 100 h are shown in Figure 2, where each spectrum is annotated with the oxidation temperature. The oxidized samples generally exhibit the addition of oxygen-bearing groups at around 1250 cm^{-1} , various C-O-C and O-C-O stretches, and 1700 cm^{-1} , carbonyl groups C=O stretching. The loss of aromatic C-H (700–900 cm^{-1} , and 3040 cm^{-1}) and aliphatic C-H (2900 cm^{-1}) is observed with increasing oxidation temperature and exposure time as reported previously [6, 10-12]. At lower oxidation temperatures and longer exposure times the carbonyl groups consists mostly of ketones and aldehydes. At higher temperatures and increasing exposure times, there is a shift to higher wavenumbers where ester and anhydrides functional groups are observed. At 270 $^{\circ}\text{C}$, the formation of esters and anhydrides lead to carbon burnoff reactions in the form of CO and CO₂. Drbholov and Stevenson [11] and Fanjul et. al. [12] suggested that the ester and anhydrides leads to formation of oxygen containing cross-links and

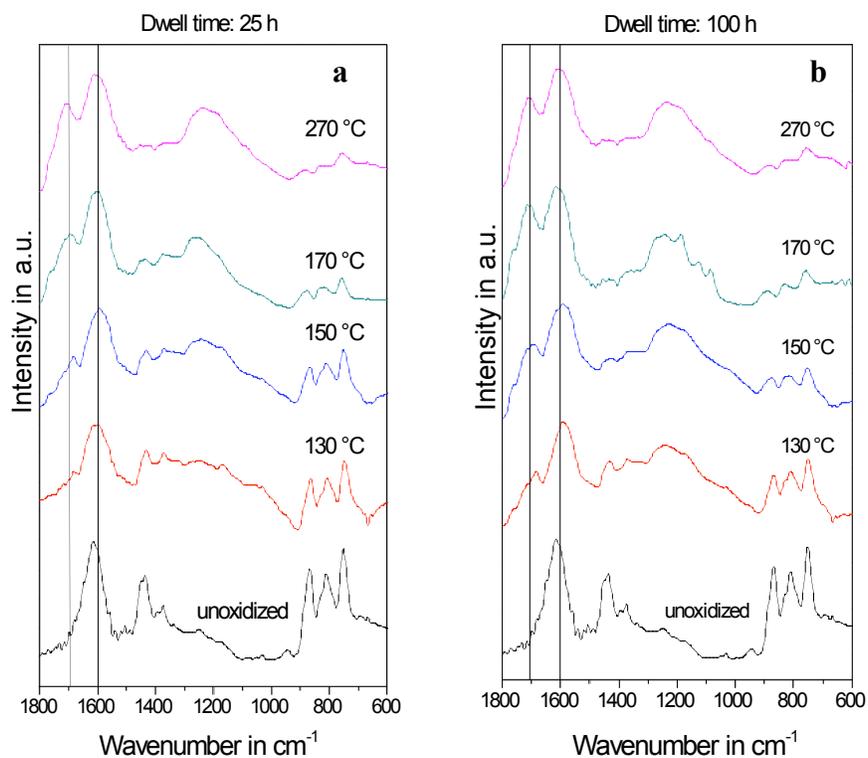


Figure 2. FTIR spectra for AR mesophase filaments oxidized at different temperatures and at exposure time of (a) 25h and (b) 100 h. The spectrum of the unoxidized sample is shown for comparison.

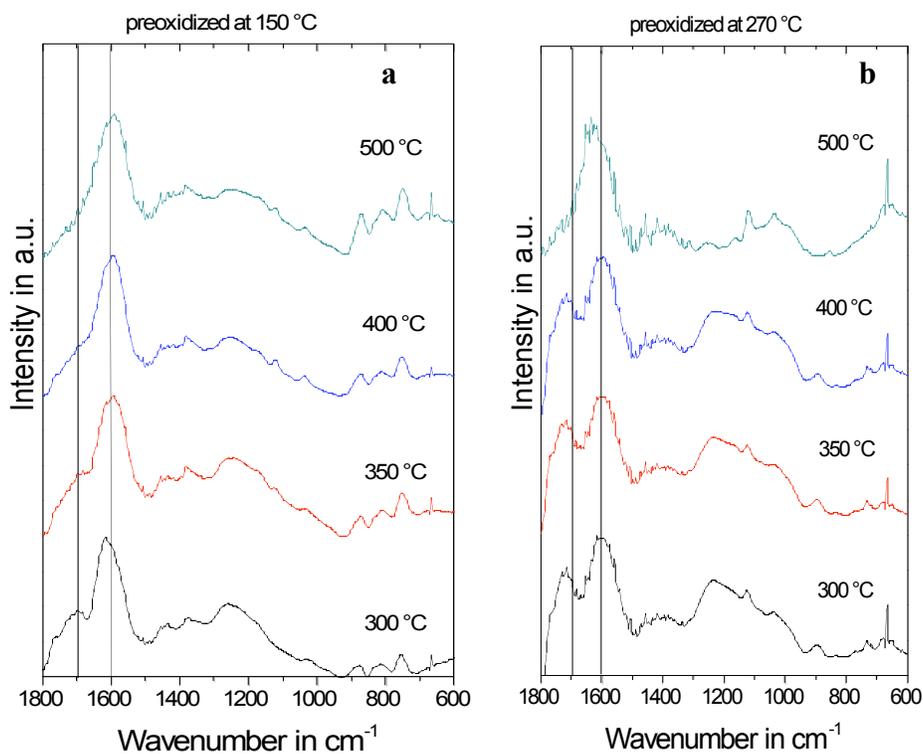


Figure 3. FTIR spectra of specimens removed at different stages of heat treatment to 500 °C in inert atmosphere. The AR mesophase filaments were initially oxidized at (a) 150 °C and (b) 270 °C for exposure time of 50 h.

subsequent stabilization. The results of Fathollahi et. al. [6] and the FTIR results in Figure 2 suggest that ester and anhydride may not be necessary for in-depth stabilization.

Figure 3 shows the FTIR spectra with heat treatment up to 500 °C of specimens oxidized at 150 °C and 270 °C for 50 h. The spectra of the sample stabilized at 150 °C show the carbonyl bands consisting mostly of ketones and aldehydes disappear at about 350 °C. In contrast, the carbonyl band at 270 °C is still present at the heat treatment temperature of 400 °C. The carbonyl bands have a peak intensity at about 1730 cm⁻¹ due predominantly to ester and anhydrides.

Conclusions

Together with previous stabilization studies [6], our results suggest that in-depth stabilization can be achieved more effectively using low temperature oxidation, under which weight gain reactions involving the formation of simpler aldehydes and ketones are more prominent. There is a clear shift from aldehydes and ketones to anhydrides and esters with increasing oxidation temperatures and exposure time. However, it is probable that stabilization can be achieved with a high enough density of aldehydes and ketones and the formation of anhydrides and esters are not necessary condition. Furthermore, the EPMA data of oxidized samples at 270 °C show a uniform uptake of oxygen at long exposure time even though previous results [6] of identical samples have shown the stabilization front not extending beyond 7 μm.

Acknowledgements

A financial grant of the Bavarian State Ministry of Sciences, Research and the Arts and the Objective 2 Funding of the European Union is gratefully acknowledged. The authors also thank BaCaTeC for financial support in initiating the exchange program between Friedrich Alexander University Erlangen-Nuremberg and University of California, San Diego. Finally special thanks to Dr. Qianqian Li for most valuable and stimulating discussions.

References

1. Otani S. Carbonaceous mesophase and carbon fibers. *Mol Cryst Liq Cryst.* 1981; 63: 249-46.
2. Singer LS. The mesophase and high-modulus carbon fibers from pitch. *Carbon* 1978; 16:408-15.
3. White JL, Sheaffer PM (1989). Pitch-based processing of carbon-carbon composites. *Carbon* 1989; 27:697-707.
4. Fathollahi B., Chau PC, White JL. Injection and stabilization of mesophase pitch in the fabrication of carbon-carbon composites. Part II. *Carbon* 2005; 43:125-133.
5. White JL, Gopalakrishnan MK, Fathollahi B. A processing window for injection of mesophase pitch into a fiber preform. *Carbon* 1994; 32:301-10.
6. Fathollahi B., Jones B., Chau, PC, White JL. Injection and stabilization of mesophase pitch in the fabrication of carbon-carbon composites. Part III. *Carbon* 2005; 43:143-151.
7. Singer LS. The mesophase and high-modulus carbon fibers from pitch. *Carbon* 1978; 16:408-15.
8. Lu YG, Wu D., Zha QF, Liu L. Skin-core structure in mesophase pitch-based carbon fibers: causes and prevention, *Carbon* 1998; 36:1719-1724.
9. Blanco C, Lu S, Appleyard SP, Rand B. The stabilisation of carbon fibres studied by micro-thermal analysis. *Carbon* 2003; 41:165-171.
10. Miura K, Nakagawa H, Hashimoto K. Examination of the oxidative stabilization reaction of the pitch-based carbon fiber through continuous measurement of oxygen chemisorption and gas formation rate. *Carbon* 1995; 33:275-82.
11. Drbohlav J, Stevenson WTK. The oxidation stabilization and carbonization of a synthetic mesophase pitch, part I: The oxidatative stabilization process. *Carbon* 1995; 33:693-711.
12. Fanjul F, Granda M, Santamaria R, Menendez R. Pyrolysis behavior of stabilized self-sintering mesophase. *Carbon* 2002; 41:413-422.