MESOPHASE PITCH AND MICRO-THERMAL ANALYSIS OF GRAPHITIC MATERIALS

B.Rand
Institute for Materials Research, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds, LS2 9JT, UK

The work of White and co-workers, Zimmer, Shaeffer and Fathollahi [1-6] has had a major impact on our understanding of the nature of mesophase pitch precursors, their controlling influence on the microstructure of carbonised and graphitised materials, and on the microstructure dependent properties of carbon-carbon composites. In this paper some recent studies of the microstructures and properties of mesophase based materials, inspired by the work of White *et al* and others, are summarised.

1. Microthermal Analysis as a tool for microstructural characterisation

Microthermal analysis in the atomic force microscope is a recent technique that is very useful for aspects of carbon science. In this technique, a special Wollaston thermal probe is used, which functions to gather both topographic and thermal information. In the thermal mode the probe acts as the heat source and detects the thermal response at the surface of the material under investigation. The instrument can be used to image according to the thermal properties of the material or to determine local information at specific positions on the surface. Details of the instrument and its application to the study of the softening behaviour of partially stabilised fibres and the thermal conductivity of C/C composites can be found in the papers of Blanco *et al* [7-9].

1.1 Stabilisation of mesophase structures

Oxidative stabilisation of mesophase pitch is an essential step in the maintenance of the preferred orientation induced in fibres and to control the carbonisation of pitch-derived matrices in C /C composites. In both cases the aim is to reduce fluidity, to prevent relaxation of shear and draw induced orientation in fibrous products and prevent boating when volatiles are released and 'lock in' the microstructure in the case of the C/C composites. There have been various studies of the stabilisation process, but there is little published on the changes to the rheological properties of the mesophase pitch brought about by the oxidation process

In order to follow the effect of stabilisation time and temperature on the softening behaviour of fibres, large diameter fibres (up to 150μm in diameter) were produced from Mitsubishi AR24 mesophase pitch. They were stabilised in oxygen for various times and temperatures. Polished transverse sections of the fibres were then examined by micro thermal analysis at various points along the radius of the fibre [7]. At each point the temperature was ramped up at constant heating rate and the vertical position of the probe monitored to assess the softening temperature at that point. In selected cases the oxygen content was also determined as function of fibre radius with a microprobe Cameca SX-50 fitted with 3 wavelength dispersive spectrometers used for all quantitative analyses and an Oxford microanalysis Division Link 10/55S EDS for reconnaissance and qualitative analysis. Figure 1 shows a typical example. The 100μm

fibre oxidised in oxygen at 180°C for 15h is only partially stabilised. The region at the centre of the fibre (1) has a softening point of about 280°C, virtually unchanged from the unoxidised fibre, whereas at point (6) near the surface of the fibre no softening is detected at all indicating that the fie is fully stabilised in this region. Thus, the softening profiles can be determined for various oxidation conditions as shown in Figure 2. An interesting observation resulting from the data in Figure 2 is that after 5 hours the profile at 200°C is more steep and penetrates further to the fibre than that at 160°C, but after 25 hours whilst the 200°C profile is still the steeper of the two, the centre of the fibre has still hardly changed. The 160°C profile on the other hand shows that the centre of the fibre is party stabilised and indeed it is possible to stabilise the fibre completely in a shorter time at the lower temperature. Such observations are of significance in the stabilisation of shaped systems.

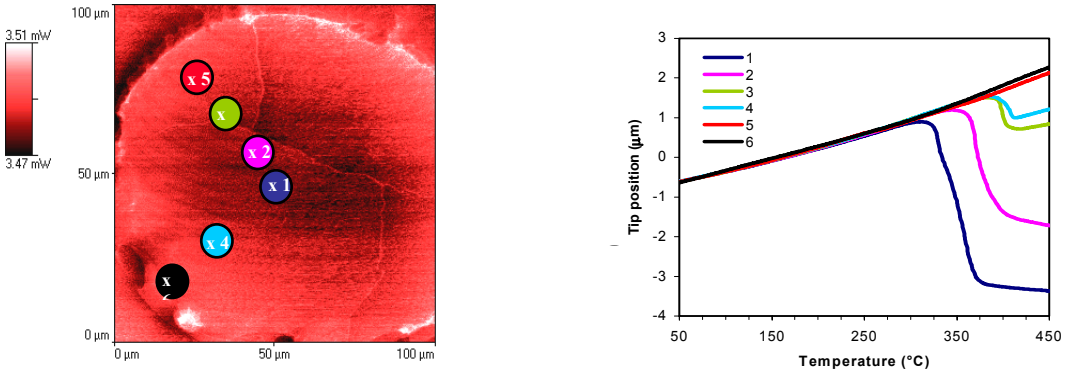


Figure1. Micro-thermal analysis data for a 100µm diameter mesophase-pitch fibre oxidised for 15h at 180°C in oxygen. The left hand micrograph is a thermal image; the dark regions are of lower thermal conductivity because they are of lower stabilisation degree. The right hand figure shows the softening behaviour at the various points indicated on the thermal image.

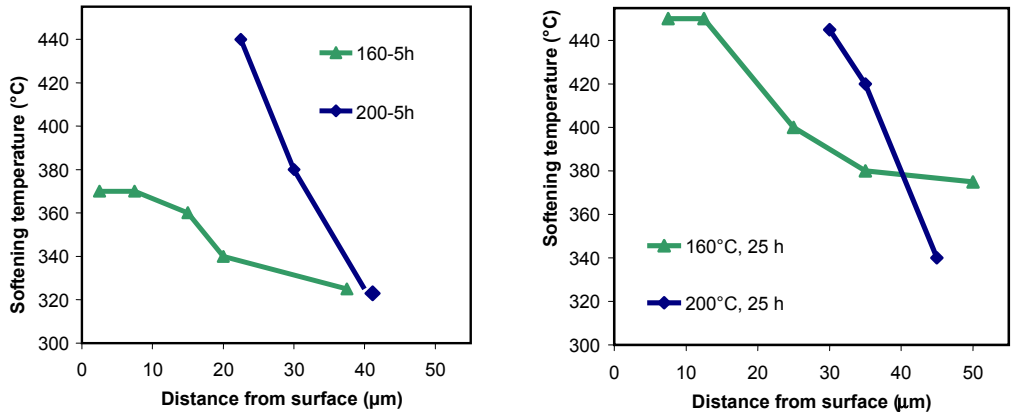


Figure 2. Softening temperature profiles for 100µm diameter mesophase-pitch fibres oxidised for 5 and 25h in oxygen at 160 and 200°C.

Microprobe results demonstrated a similar oxygen profile across the fibres and it was found that at the lower temperatures there was a linear relationship between the oxygen content and the softening temperature. However, at 200°C and for long times at 180°C the softening temperature increased more rapidly with oxygen content, indicating a change in the mechanism. It appears that at the higher temperature the oxygen diffusivity of the diffusion barrier formed at the outside of the fibre is lower than that of fibres oxidised at temperatures around 160°C. It is possible that the nature of cross links is different at the higher temperatures, possibly involving more C-C bonds than C-O-C linkages. Further work is required before a full understanding of this process will emerge.

1.2. Determination of the properties of mesophase and isotropic phases in two phase systems

The transformation from isotropic pitch to mesophase to carbon occurs with dramatic changes in chemical composition, molecular weight distribution and in rheological behaviour. The rheological changes are profound. Isotropic pitch is a glassy solid at low temperatures and shows Newtonian or near Newtonian flow character above the glass transition temperature, T_g. The mesophase displays significantly higher T_g and may show significant viscoelastic character above this temperature. Following the changes in T_g and viscoelastic character as the pitch transforms through the mesophase state has proved difficult. Rand and Benn [10] produced a 'Transformation diagram' by using hot centrifugation to separate the two phases whose properties could then be individually assessed. Figure 3 shows an example.

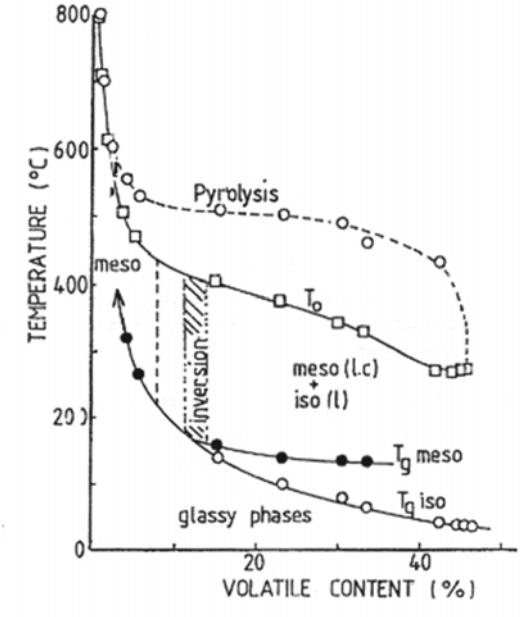


Figure 3. Pitch Transformation Diagram, showing the variation of glass transition temperatures with residual volatile content through the pyrolysis from isotropic pitch to mesophase to carbon. The two separate T_gs in the two phase region are shown.

The technique of microthermal analysis offers an easier approach to the determination of such diagrams obviating the need for physical separation of the two phases. The probe can be used to determine the local properties of each phase in a polished section. For example, Figure 4 shows thermal analysis results on a two phase pitch. Local

softening behaviour is shown for points within a mespophase sphere, identified as the more bright region in the thermal image (i.e. mesophase has thermal conductivity), and in the isotropic phase. The mesophase has significantly higher softening temperature. The technique does not locate precisely the glass transition temperature which is a little lower than the temperature located. Nevertheless, the method has great potential for following mesophase development and its comparison with the isotropic phase [9].

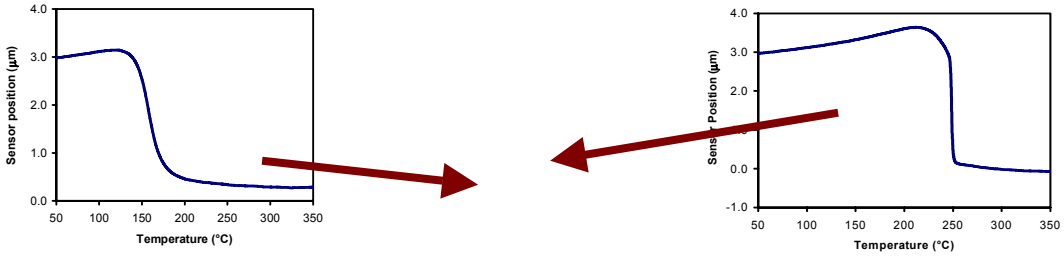
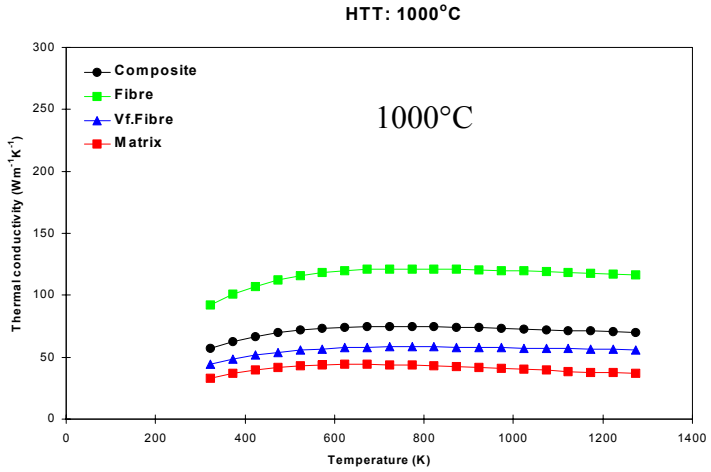


Figure 4. Microthermal analysis of two phase pitch showing the different softening behaviour of the mesophase sphere and the isotropic phase.



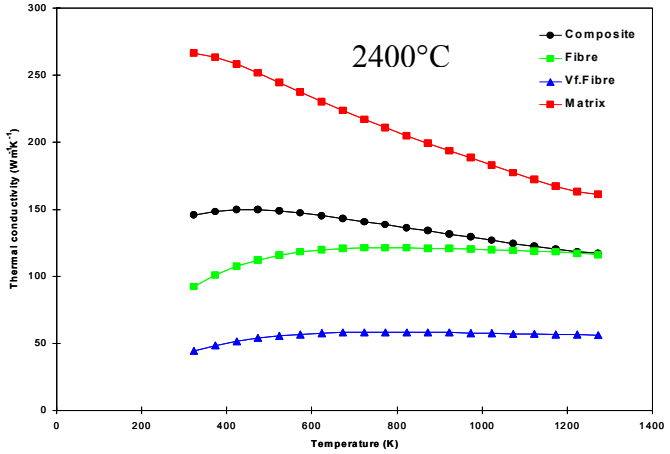


Figure 5. Thermal conductivity in the fibre direction of 1D C/C composites as a function of measurement temperature, compared with the measured values of the fibre and calculated values of the matrix for two HM PAN-based fibre/mesophase pitch matrix composites heat treated to 1000ºC (top) and 2400ºC (bottom).

1.3. Thermal imaging of Carbon-Carbon composites [8]

Although the mechanical properties of carbon-carbon composites are dominated by those of the fibres and controlled to a large extent by the fibre architecture, e.g. cloth, staple fibre, the same does not necessarily apply to the transport properties which are may well be dominated by the phase of greatest conductivity. For example, in graphitised composites with PAN-based fibres and CVD or pitch derived matrices the thermal conductivity of the matrix may be much the greater, since the fibres are non-graphitising. This is illustrated in Figure 5, which shows thermal conductivity data along the fibre direction for two 1D composites with high modulus PAN-based fibres and pitch-based matrix. One has been heat-treated to 1000°C and the other to 2400°C. The fibres had experienced higher temperatures during manufacture and so their thermal conductivity, previously measured, is not expected to change during these heat-treatment procedures. The thermal diffusivity of the composites was measured, along the fibre direction and transversely, by Li and Taylor [11] using the laser flash method. Using conventional mixture rules the conductivity of the matrix phase was estimated at each measurement temperature. The fibre at room temperature has a thermal conductivity of 90 $Wm^{-1}K^{-1}$. After a heat treatment to 1000°C the conductivity of the matrix is less than half that of the fibres, but after the high temperature treatment the situation is reversed with the matrix displaying conductivity three times that of the fibres. Even higher conductivities in the matrix are to be expected when higher graphitisation temperatures are employed. These differences ought to be observable by thermal microscopy and that is shown clearly in the two micrographs displayed in Figure 6.

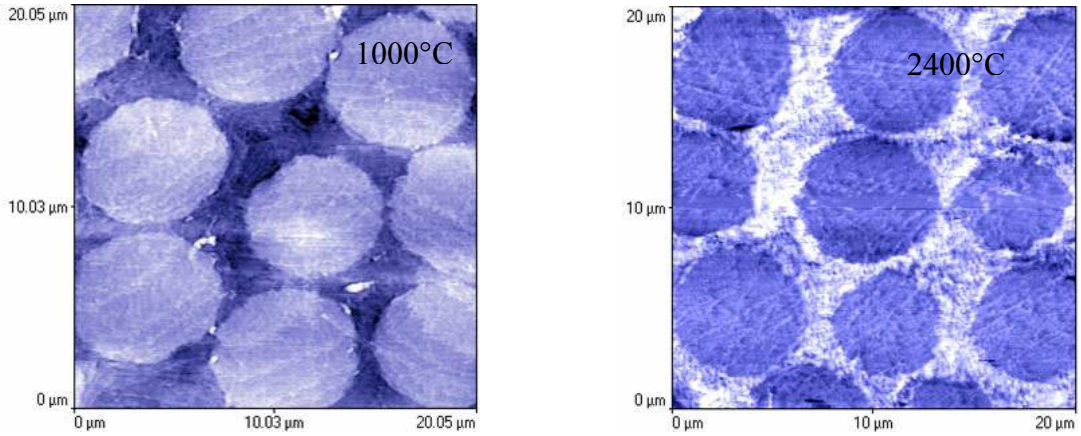


Figure 6. Thermal images of the 1000 and 2400°C C/C composites. The degree of brightness reflects the relative thermal conductivity.

Even non-graphitising precursors may show preferred orientation around the fibres in C/C composites and Figure 7 shows that the thermal conductivity of the matrix may be really quite high due to such an effect. The thermal conductivity data determined by Li and Taylor [11], as outlined above, show that at room temperature the matrix may display a conductivity of $130Wm^{-1}K^{-1}$, significantly higher than that of the fibre. The thermal image in the figure shows that this is due to the effect of a narrow oriented region around the fibres and that further away from the fibres where the matrix is not so

well oriented, it displays quite low thermal conductivity. Clearly the conductivity in the oriented region around the fibres must be much higher than the average value assessed from the laser diffusivity results. These results demonstrate the value of the thermal microscopy technique. The probe used in the results reported here had a resolution limited to about 1µm, but recently probes have been developed that reach into the nanoscale region and there are attempts to make the technique more quantitative.

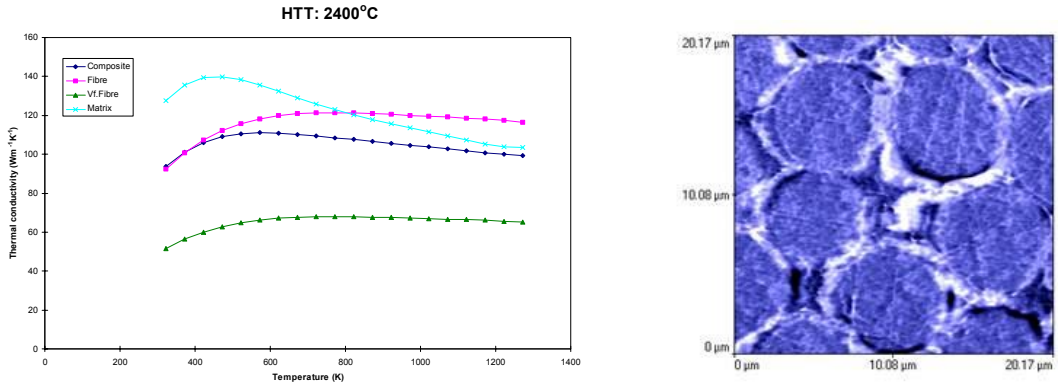


Figure 7. a) Thermal conductivity data in the fibre direction for a 1D C/C composite, the corresponding fibres and calculated values for the matrix. The fibres are High modulus PAN-based and the matrix is derived from a phenolic resin.
b) The corresponding thermal image showing regions of high conductivity in the matrix adjacent to the fibres.

References

1. Zimmer, JE and White, JL, “Disclination structures in the carbonaceous mesophase”, in *Advances in Liquid Crystals,* vol.5, Pub. Acadmemic Press, New York (1982), p157.
2. White, JL and Sheaffer, PM, Carbon **27**, (1989) p697
3. Zimmer, JE and White, JL, Carbon, **21**, (1983) p323
4. Zimmer, JE and White, JL, Mol. Cryst.Liq. Cryst., **38**,(1977) p177.
5. White,JL, Gopalakrishnan, MK, Fathollahi, BA, Carbon, **32**, (1994) p301
6. Fathollahi, B, Jones, B, Chau, PC and White, JL, Ext. Abstr. Carbon 2000, Berlin 2000, p259.
7. C. Blanco, S.Lu, S.P. Appleyard and B.Rand “The stabilisation of carbon fibres studied by micro-thermal analysis”, Carbon, **41**, 165-171 (2003).
8. C.Blanco, S.P. Appleyard and B.Rand, “Study of carbon fibres and carbon-carbon composites by scanning thermal microscopy”, *J. Microscopy,***205**, 21-32 (2002)
9. C. Blanco, S.Lu, S.P.Appleyard and B.Rand, “Micro-thermal analysis as a technique for in-situ characterization of the softening behaviour of the isotropic phase and mesophase in thermally treated pitches”, *Carbon ,***40**, 132-135 (2002).
10. M. Benn, B. Rand and S. Whitehouse. "Transformation diagrams for a number of pitches". Extended Abstracts of the 17th Biennial American Carbon Conference, Lexington, Kentucky, June 1985, pp 159-160.
11. Li,Q and Taylor, R, unpublished results, private communication.