STUDYING THE STABILISATION OF CARBON FIBRES BY MICRO-THERMAL ANALYSIS

C. Blanco, S. Lu, S.P. Appleyard and B. Rand
Department of Materials, University of Leeds, Leeds LS2 9JT, UK.

Introduction

Micro-thermal analysis is a relatively new technique that combines the imaging capabilities of atomic force microscopy with the physical characterisation capabilities of thermal analysis. The origin of the technique is scanning thermal microscopy (SThM), a form of contact atomic force microscopy (AFM) in which the tip is replaced by a miniature temperature probe which provides the heat source and also provides the means to measure the thermal response. Both "topographic" and "thermal" images are obtained and a particular area of any of these images may then be selected and subjected to local thermal analysis, obtaining information similar to a thermomechanical analysis experiment [1, 2].

The aim of this study is the application of micro-thermal analysis to the study of the stabilisation process of mesophase pitch-based carbon fibres.

Experimental

Pitch fibres were prepared by melt extrusion from naphthalene derived mesophase pitch ARA24. As-spun fibres (~100 μm diameter) were exposed to oxygen at temperatures of 180°C and 160°C for different times (up to 100 h). The samples were then mounted vertically in resin and polished using the same procedure as for optical microscopy examination. Cross-sections of the fibres were then studied by micro-thermal analysis.

The micro-thermal analysis apparatus is commercially available (Thermomicroscopes) and comprises an atomic force microscope fitted with a Wollaston thermal probe (Figure 1). The probe forms part of a Wheatstone's bridge circuit and provides the heat source and also detects the thermal response. "Topographic images" can be obtained in a similar way to conventional AFM. At the same time, the variable electrical current required to maintain the thermal tip at a given temperature as it scans across the sample is used to construct a "thermal image". A particular area of any of these images may then be selected and subjected to local thermal analysis. The thermal tip is brought into contact with the chosen area and its temperature is increased linearly with time. Any change in its vertical position will be detected if the material beneath the tip softens, thus providing information similar to a thermomechanical analysis experiment. Because of the small size of the heating element and of the amount of material involved, heating rates can be as fast as 20°C s^{-1}. The area affected by the measurement has been reported to be ~ 3-5 μm [2]. The analyses in this study were performed with an applied force of 40 nN, increasing the temperature from 30 to 450°C at a heating rate of 10°C s^{-1}. Because the maximum temperature of the micro-thermal analysis is limited to 450°C, thermal transitions occurring at higher temperatures can not be detected. Therefore, it is assumed in this study that regions that do not show softening up to 450°C correspond to stabilised areas.

Results and discussion

Figure 2a shows the thermal image obtained for a fibre after exposure to oxygen at 180°C for 15 h. Lighter colours in the images indicate areas where more heat is dissipated from the tip, whereas darker colours correspond to less dissipation of heat. The image in Figure 2a shows the outer region of the fibre in lighter colour (similar to those of the resin in which the fibre is embedded), the colour becoming darker towards the core of the fibre. This pattern was observed for most of the fibres studied, however the extension of the central darker region decreased with increasing the time of exposure to oxygen. Therefore, this region could be related to the non-stabilised region of the fibre.

Local thermal analyses performed in selected regions of the fibre can provide significant additional information about the extent to which the stabilisation reaction has taken place. Figure 2b shows the curves obtained for the thermal analyses performed in different regions of the fibre (the locations are marked in the image in Figure 2a). The central region of the fibre (location 1) softens at 325°C, which is the same temperature obtained with this technique for the parent pitch ARA24. This means that the central region of the fibre has not been affected by the exposure to oxygen. Moving towards the surface, the softening temperature increases progressively, to 350°C at 35 μm from the surface (location 2) and 400°C at 20 μm (locations 3 and 4). Areas closer to the surface (location 5 at 12 μm and location 6 at 5 μm) do not soften below 450°C, which indicates that these regions have been stabilised. As the softening temperature decreases from the surface to the core of the pitch fibre, the depth penetrated

by the tip increases accordingly. The results demonstrate that the stabilisation process is diffusion controlled. EDX analysis demonstrates that the oxygen content decreases towards the centre of the fibre.

In each of the temperature series studied, 180°C and 160°C, the extension of the stabilised region increased with increasing time of treatment. However, a different behaviour was observed for each temperature. At 180°C, there was a progressive increase in the stabilised depth and the fibres became fully stabilised after 75 h of treatment. However, at 160°C the stabilisation was significantly slower for the initial stages of the treatment but became faster for intermediate times of treatment (25-50 h). This behaviour could be due to the formation of a surface diffusion barrier produced by a rapid initial oxidation at higher temperatures [3]. Work continues to quantify the diffusion gradients at different temperatures.

Conclusions

Micro-thermal analysis has been proven to be a very promising technique for the study of the stabilisation process of pitch fibres. It has uniquely allowed measuring and monitoring the change in softening behaviour from the surface to the core of the fibre, as a function of the degree of stabilisation. It has also been possible to determine the depth of the stabilised region potentially enabling the kinetics of the stabilisation process to be studied.

Acknowledgements

C. Blanco thanks EU for a postdoctoral Marie Curie Fellowship (HPMF-CT-1999-00233).

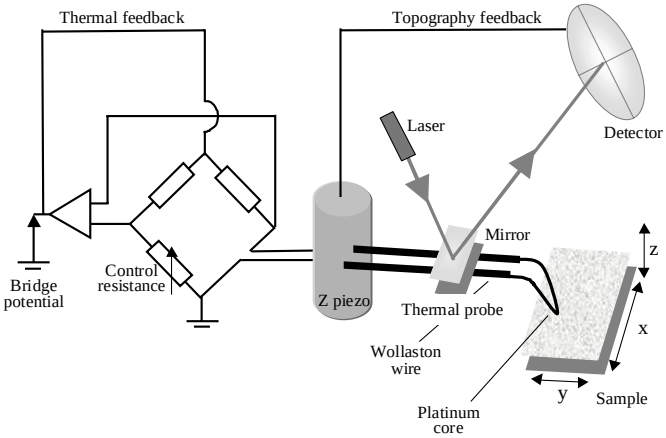

Figure 1.- Schematic diagram of the micro-thermal analyser.

References

1. Hammiche A, Pollock HM, Song M and Hourston DJ. Sub-surface imaging by scanning thermal microscopy. Meas. Sci. Technol. 1996; 7: 142-150.
2. Price DM, Reading M and Lever TJ. Applications of micro-thermal analysis. Journal of Thermal analysis and calorimetry 1999; 56: 673-679.
3. Lin SS. Oxidative stabilization in production of pitch based carbon fibre. SAMPE Journal 1991; 27: 9-14.

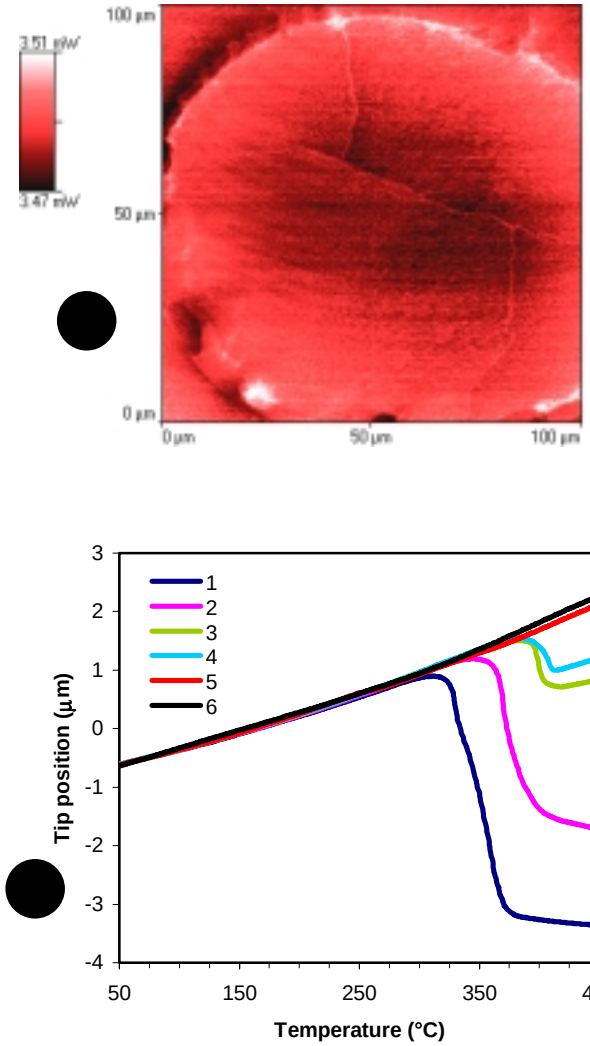

Figure 2.- A) Thermal image of fibre after exposure to oxygen at 180°C for 15 h; B) Local thermal analysis in different areas of the fibre.