

INVESTIGATION OF PITCH STABILISATION USING PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Introduction

Oxidative stabilisation of mesophase pitch is well known to severely limit the dimensions of artifacts formed from it or, for slightly larger artifacts, to be time-consuming and costly (Gallego, Edie, Nysten, Issi, Treleven, and Deshpande, 2000). Control and understanding of this step is of very great interest in the production of highly oriented graphitisable material as it could lead to a dramatic reduction in production costs. The mechanism of such stabilisation is thought to involve oxygen cross-linking but its exact nature is still not fully understood (Drbohlav and Stevenson, 1995). Analytical pyrolysis methods such as pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) are ideal for investigating the structure of macromolecular polymeric materials (Jones, Ross and Williams, 2006). Strong inferences regarding pitch structure and composition can be drawn from the identification and quantification of hydrocarbon fragments evolved during pyrolysis of pitch. Py-GC-MS is therefore ideally suited to identification of structural changes occurring in the pitch during oxidative stabilisation. In addition, the use of reactive gas Py-GC-MS offers a method for performing oxidative stabilisation of the pitch on an analytical scale.

A series of oxygen-treated mesophase pitch samples with a range of potentials for stabilisation following further heat treatment (as demonstrated by softening point behavior) have been characterised using Py-GC-MS. This technique was used to identify and quantify volatile species evolved upon pyrolysis of the series of samples. Identification of the oxygen containing fragments has shed light on the nature of the oxygen functionality within the oxygen-treated pitch and therefore helped to elucidate the mechanism of the stabilisation process.

Experimental

Melt-spun Mitsubishi AR-MP mesophase pitch tape samples have been characterised both “as-spun” and following treatment in pure oxygen under a range of heat treatment regimes, summarised in Table 1. Py-GC-MS analysis was performed on a CDS 5000 series pyrolyser connected to a Shimadzu 2010 GC-MS. The samples of oxygen-treated tape (2 mg) were pyrolysed at 1000 °C in He at a ramp rate of 20 °C / ms with a hold time of 20 s. The products were separated on an RTX 1701 60 m capillary column, 0.25 mm i.d., 0.25 µm film thickness, using a temperature program of 40 °C, hold time 2 minutes, ramped to 250 °C, hold time 30 minutes, column head pressure of 30 psi at 40 °C. Simulation of the stabilisation process was performed in reactive pyrolysis mode in 100% O₂ at 240 °C with a dwell time of 300 minutes and a ramp rate of 1 °C / min. The volatile species evolved during the oxidation were collected onto a Tenax trap and subsequently desorbed and analysed by GC-MS. Samples stabilised using oxidative pyrolysis were further analysed upon pyrolysis at 1000 °C in He in the same way as the O₂-treated samples.

Table 1. Conditions for oxygen pre-treatment of mesophase pitch and resulting compositional data prior to its Py-GC-MS characterisation

Temperature (°C)	Time (hrs)	H / C Ratio	O / C Ratio
160	5	0.58	0.05
160	25	0.50	0.11
240	5	0.51	0.12
240	25	0.39	0.24
300	5	0.49	0.08
300	25	0.36	0.32

Results and Discussion

The Py-GC-MS of oxygen-treated mesophase pitches show a significantly different fingerprint to that from the “as spun”, i.e. green, pitch. The products from pyrolysis of the green pitch at 1000 °C are shown in figure 1a. The products include aromatic fragments consisting of between one and four fused rings, as expected, with a significant presence of alkyl (principally methyl) substituted content. No oxygenated species are evolved. In contrast, an example of the pyrolysis products from an oxygen-treated (25 hours at 240 °C) pitch sample is shown in figure 1b. This indicates a significantly different fragmentation pattern dominated by oxygen-containing hydrocarbons and a significant reduction in alkyl aromatics. Carbon yields can be estimated from Py-GC-MS and show a clear increase with oxidative treatment in comparison with the green pitch. Of particular interest is the fragment eluting at 35 minutes, identified by mass spectrometry as phthalic anhydride. The abundance of this fragment appears to increase with both stabilisation temperature and time. This correlates not only with an increase in O / C ratio but also with the degree of stabilisation potential in the various oxygen-treated pitches (as established by softening point behaviour). The naphthalene analogue of phthalic anhydride is also present. Additional oxygenated analogues include benzoic acid and phenol as well as a number of ether containing fragments. Generation of acetic acid implies the presence of acetyl groups in the stabilised matrix.

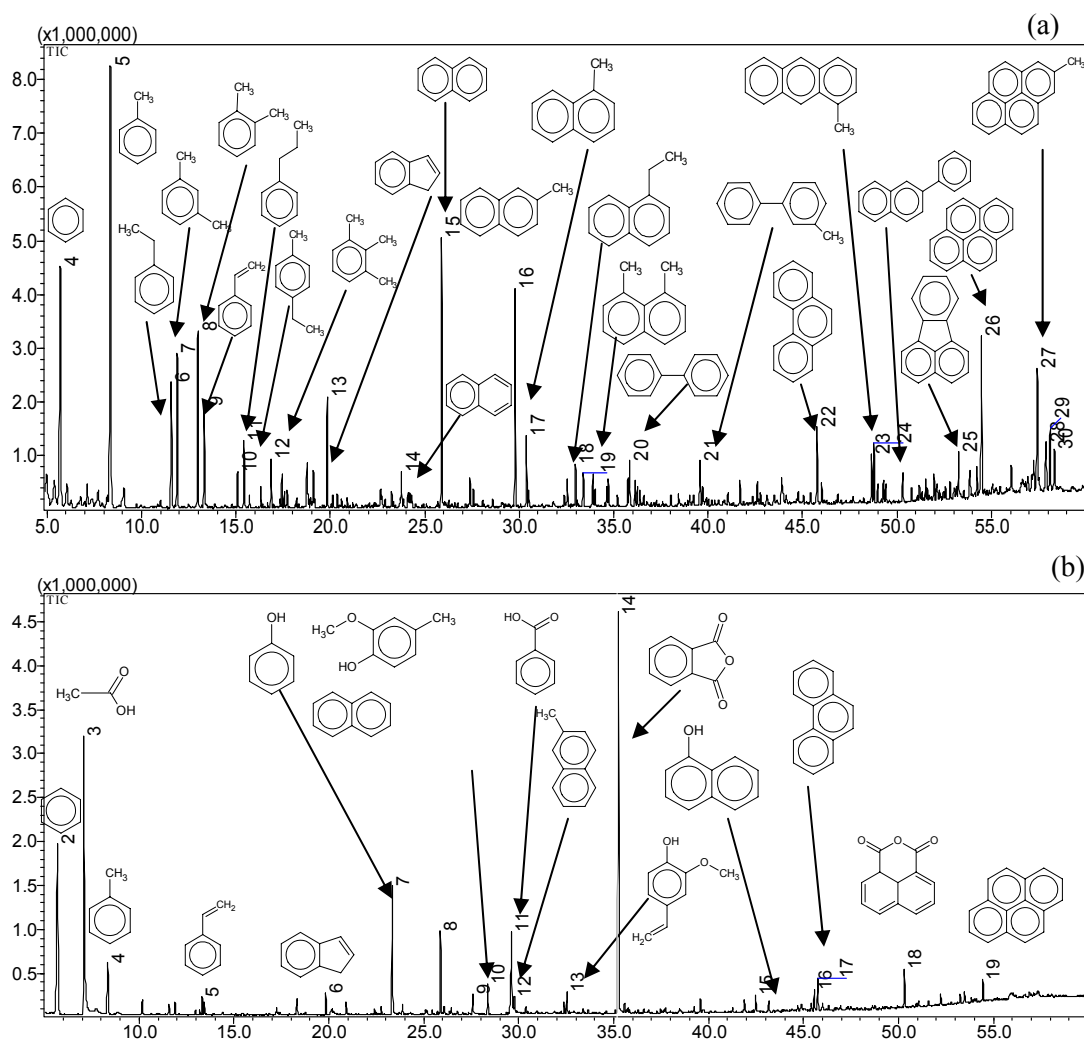


Figure 1: Fragment retention time in minutes (x-axis) vs. abundance (y-axis) results from Py-GC-MS at 1000°C of mesophase pitch tape; (a) green and (b) treated in oxygen at 240°C for 25 hours.

Operation of Py-GC-MS in reactive gas mode allows a simulated oxidative treatment to be carried out on an analytical scale. The oxidative treatment can be performed on small samples of mesophase pitch-based tape or powder held in a quartz tube under 100% O₂ or air. An advantage of analytical stabilisation is that the volatiles liberated during the stabilisation process itself can be observed and a parametric analysis of stabilisation conditions can easily be performed. The extent of stabilisation can be measured by a number of methods; firstly by the appearance of oxygenated volatile fragments desorbed from the Tenax trap at the end of the oxidative treatment, secondly by the carbon yield of the tape upon further pyrolysis at 1000°C and thirdly by the appearance of the carbon tape upon subsequent pyrolysis at 1000 °C (i.e. whether its shape is retained). Figures 2a and 2b show the volatile products from analytical scale oxidative pyrolysis of a green tape at 240°C for 5 hours and from the subsequent pyrolysis of the resulting tape at 1000°C, respectively. The heating rate of 1 °C / min. employed during stabilisation is comparable to the conditions used in the off-line oxygen-treatment. A carbon tape which had undergone oxidative treatment at 240°C for 25 hours did not soften upon analytical pyrolysis at 1000°C whereas green or insufficiently stabilised tape softens in the quartz tube and does not maintain its shape. In addition, oxygenated species similar to those observed from the pitch that was oxidatively treated off-line are present. However, there are also a number of lighter fragments that were not previously observed.

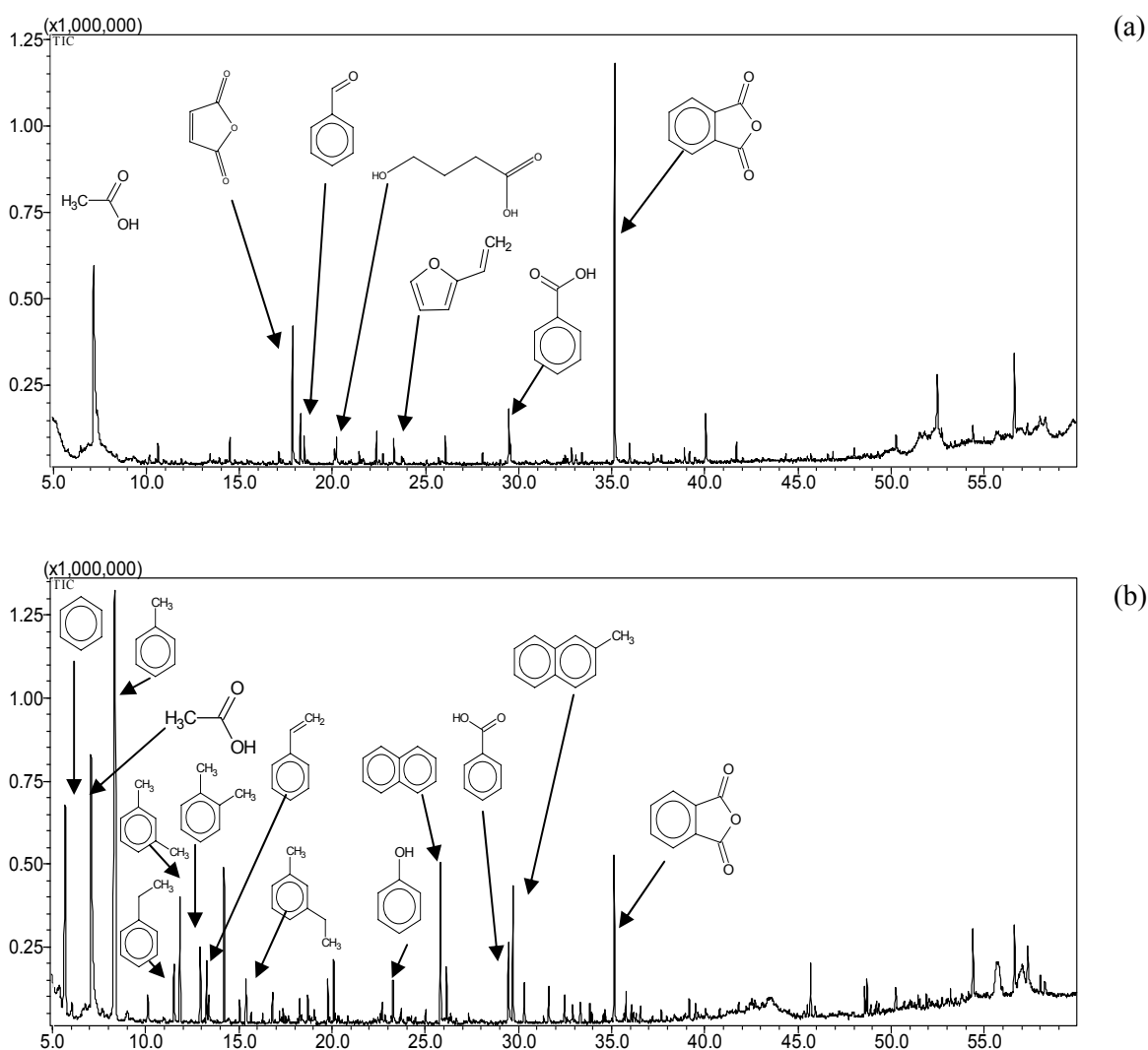


Figure 2. Fragment retention time in minutes (x-axis) vs. abundance (y-axis) results from Py-GC-MS of (a) green tape in reactive mode at 240 °C for 5 hours in 100% O₂ and (b) the resulting stabilised tape in pyrolysis mode at 1000°C.

Consideration of the combination of observed oxygenated species evolved during analytical stabilisation together with the pyrolysis products from the green pitch and stabilised tape provides insight into the functionality of oxygen incorporation during oxidative stabilisation and possible mechanistic routes. Firstly, it is clear that significant quantities of alkyl substituted polycyclic aromatic hydrocarbons (Alkyl-PAH) are present in the green pitch. These alkyl sites are thought to be oxidised first, forming aldehyde and carboxylic acid groups. Both of these analogues are observed for benzene. Secondly, it is proposed that these groups form anhydride linkages that can either link larger polycyclic aromatic hydrocarbon (PAH) moieties or form smaller fragments such as phthalic anhydride and its naphthalene analogue (both observed). These smaller anhydride-containing fragments may form linkages via reaction with phenolic fragments to form esters. The observation of maleic anhydride is significant and this may form via oxidation of butene or benzene, although normally this reaction occurs catalytically, or alternatively via pyrolytic degradation of acid anhydrides. What is certain is that anhydride linkage formation is key to the stabilisation process, in agreement with the work reported by Drbohlav and Stevenson (1995).

Conclusions

Py-GC-MS is a useful technique for studying the nature of oxidative treatment of mesophase pitch and identifies a range of oxygenated fragments that can be attributed to the reaction pathways during stabilisation. A correlation was observed between the evolution of oxygenated fragments and the degree of stabilisation potential in the pitch (as defined by softening point behaviour). This may represent an important, and possibly commercial, diagnostic application of the Py-GC-MS pitch characterisation technique. Py-GC-MS in reactive mode in oxygen enables stabilisation to be performed on an analytical scale, producing further evidence for the proposed stabilisation mechanism. The methods which have been developed in this work are capable of screening pitch samples, investigating stabilisation reaction pathways and optimising the conditions for oxidative treatment.

Acknowledgement

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