

SURFACE ANALYTICAL CHARACTERISATION OF THE OXIDATIVE STABILISATION PROCESS IN MESOPHASE PITCH-BASED CARBON TAPES

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Introduction

Carbon fibres and tapes are perhaps the most successful carbon product to be commercialised in the past 35 years (Edie, 1998). Their industrial importance arises from their unique properties. Carbon fibres / tapes exhibit high specific strength and stiffness combined with low weight. Indeed, some fibres / tapes possess properties superior to steel whilst being up to 70% lighter (Donnet, 1984). It is well known that the oxidative stabilisation step, whilst essential in the production of typical pitch-based carbon fibres / tapes is costly and time consuming. Control and understanding of this step is critical and is therefore of significant interest for the production of pitch-based carbon products as it could lead to a dramatic reduction in costs. This study employed X-ray photoelectron spectroscopy (XPS) as an analytical technique in order to track the chemical changes that occur during this stabilisation process.

Experimental

Highly orientated mesophase pitch-based carbon tapes approximately 1mm wide and 10 μ m thick were manufactured from naphthalene-derived synthetic mesophase pitch (AR-MP-H ex Mitsubishi Gas Chemical Corporation) via melt extrusion through a slit-shaped die and wound onto a drum. The mesophase pitch contains 100% anisotropic content with a softening point of 237°C. The mesophase pitch-based carbon tapes were then treated in an oxygen atmosphere at various temperatures (between 160-300°C) for various durations (5 or 25 hrs). X-ray photoelectron spectroscopy (XPS) analysis was performed on the resulting samples using an ESCLAB 250 XPS. Analysis of the tapes after the various oxygen treatment conditions was also carried out via CHNO elemental analysis and TGA-FTIR.

Results and Discussion

Figure 1 shows XPS survey scans for samples of mesophase pitch-derived tapes following exposure to oxygen for various temperatures and times. The spectra all show an intense carbon peak at ca. 285 eV and the samples which have been oxidised also show an oxygen peak at ca. 533 eV. The intensity of this peak is observed to correlate with oxidation time and temperature. In the case of the spectra in figure 1, samples (a) and (b) represent two extremes of the oxidative stabilisation conditions and much greater oxygen uptake is observed in figure 1 (b) owing to the greater oxidation time and temperature. This increased oxygen content is confirmed by CHNO chemical analyses as shown in table 1. The green and graphitised samples exhibit the lowest intensity oxygen signals in their spectra. However, these low-intensity signals are likely to be as a result of surface oxidation via chemisorption of oxygen. It should also be noted that no nitrogen signals are detected in the spectra for any of the tapes spun from the Mitsubishi AR-MP-H mesophase pitch regardless of the treatment that they have undergone.

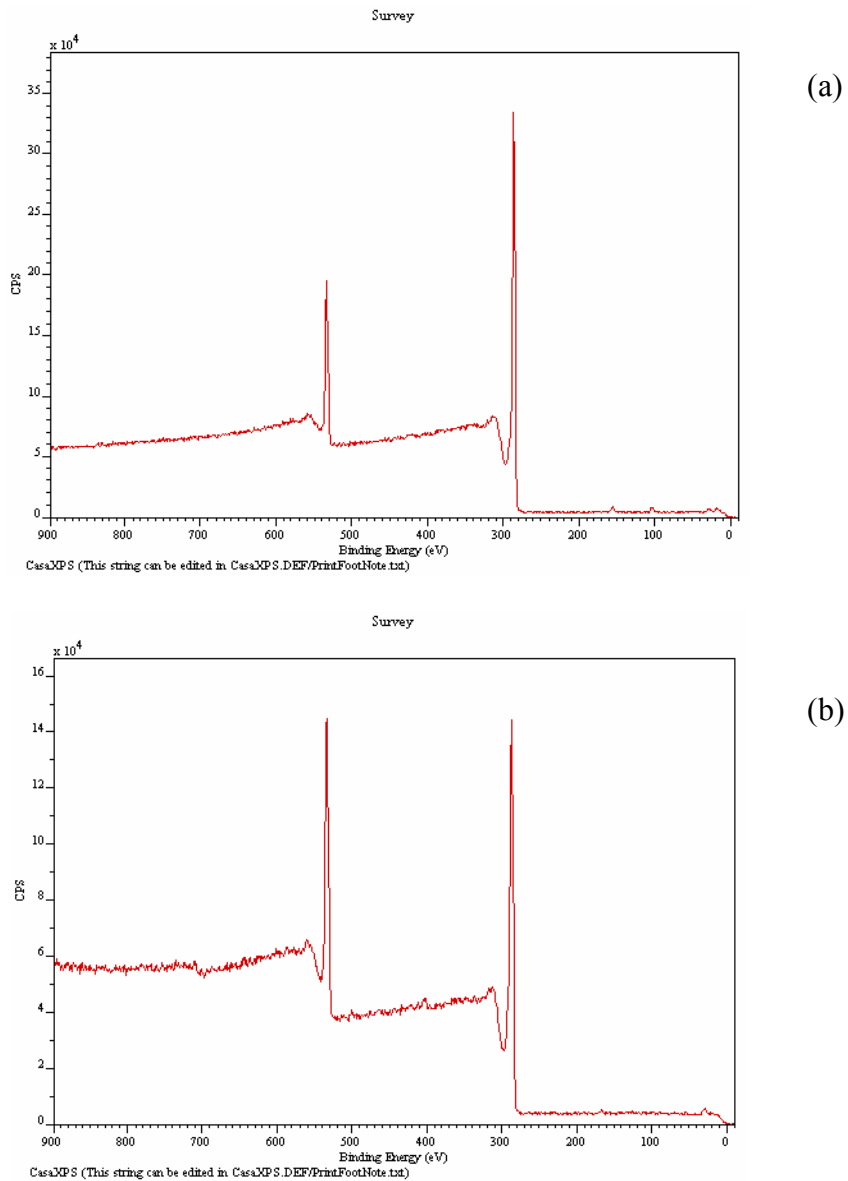


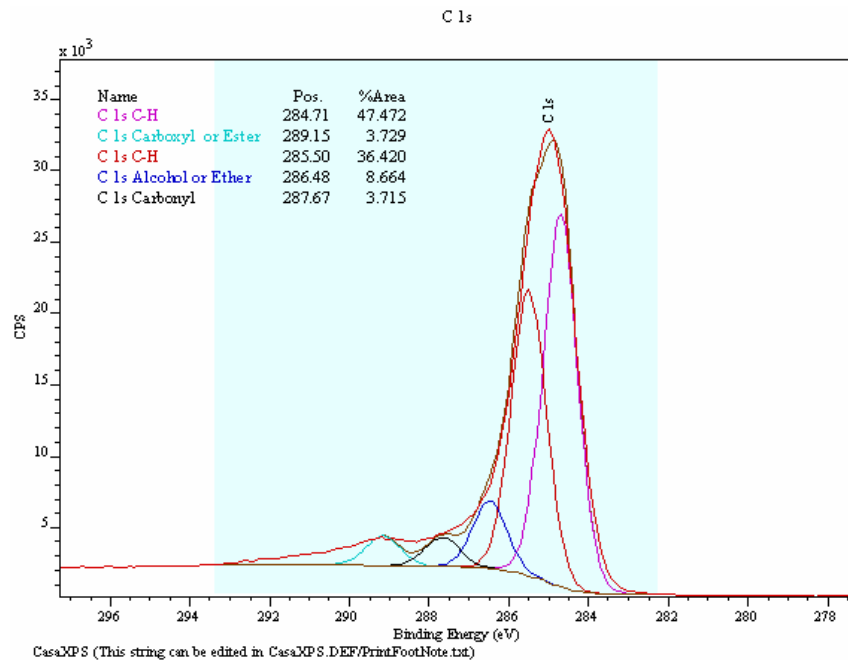
Figure 1. Overall spectral survey scans for samples of mesophase pitch-derived tapes following exposure to oxygen for various temperatures and times: (a) after 5hrs at 160°C and (b) after 25hrs at 240°C.

Table 1. CHNO analysis of mesophase carbon tapes which have experienced various oxidation conditions. (T/N means trace or negligible quantity).

	N	C	H	O	Total
Green Tape	T/N	94.75	5.40	T/N	100.15
160°C 5hrs O₂	T/N	90.33	4.38	5.68	100.38
160°C 25hrs O₂	T/N	82.65	3.50	12.45	99.90
200°C 5hrs O₂	T/N	81.70	3.48	13.58	98.35
200°C 25hrs O₂	T/N	72.80	2.38	23.10	97.30
300°C 5hrs O₂	T/N	73.78	2.46	21.55	96.00
300°C 25hrs O₂	T/N	68.35	2.00	25.65	99.55

Figure 2 shows the curve-fitted C1s region of the XPS for mesophase pitch-based tapes which were oxidised to varying degrees. These spectra were curve-fitted in order to identify the functional groups present in the samples based upon the various characteristic binding energy ranges corresponding to the chemical shift for each surface functional group. The various types of oxygen-containing functional groups which form on the fibre surface can be classified into “Oxide 1, 2, 3 and 4”, based upon chemical shifts of the C1s component peaks above the main graphitic peak of about 1.5, 3.0, 4.5 and 6.1 eV, respectively (Xie, Wang, Franklin and Sherwood, 1992). The main graphitic peak can be seen around 285 eV. The oxides present include: Oxide 1: alcohol (C-OH) and / or ether (C-O-C) groups (286.9 – 286.7 eV), Oxide 2: carbonyl (C=O) groups (288.0 – 288.1 eV), Oxide 3: carboxyl (COOH) or ester (COOR) groups (289.0 – 289.4 eV) and Oxide 4: carbonate (CO₃⁻) groups (291.0 – 291.1 eV). (All corrected for carbon at 285.0 eV, Gardener, Singamsetty, Booth and He, 1995).

As the degree of oxidative stabilisation of the samples increases with time and temperature, the composition of the oxidised C1s peak area changes and provides information on the proportions of functional groups present on the surface of the mesophase pitch-derived tapes (table 2). The most significant changes in the contributions from the various classes of oxygen-containing species can be seen in those samples which have experienced the highest oxidative stabilisation temperature of 300°C, the most significant increase being in the abundance of Oxide 2 and Oxide 3, accompanied by a considerable decrease in Oxide 1 concentration. It is also interesting to note that those samples which underwent a more optimal stabilisation (i.e. successful thermosetting whilst retaining high carbon yield) at low to moderate temperature (160°C / 240 °C) show very little difference between each other in terms of the abundances of the various oxides. The corollary to this is that the tapes oxidised at the highest temperature undergo excessive and undesirable surface oxidation. This leads to a reduced carbon yield upon carbonisation owing to increased CO and CO₂ production, as was observed using TGA-FTIR. Another example of undesirable excessive surface oxidation can be seen in the formation of “skin-core” structure. At elevated oxidation temperatures the tapes are successfully stabilised only to a depth of about 2-3µm from the surface, leaving the tape core unstabilised and thermally softenable. Formation of skin-core structure was confirmed using AFM micro-thermal analysis profiling to investigate sample softening point vs. probe position across a cross section of the tape. (EPMA was also carried out in an attempt to correlate this profile with oxygen content but the results were unreliable due to the high oxygen content in the mounting resin).



(a)

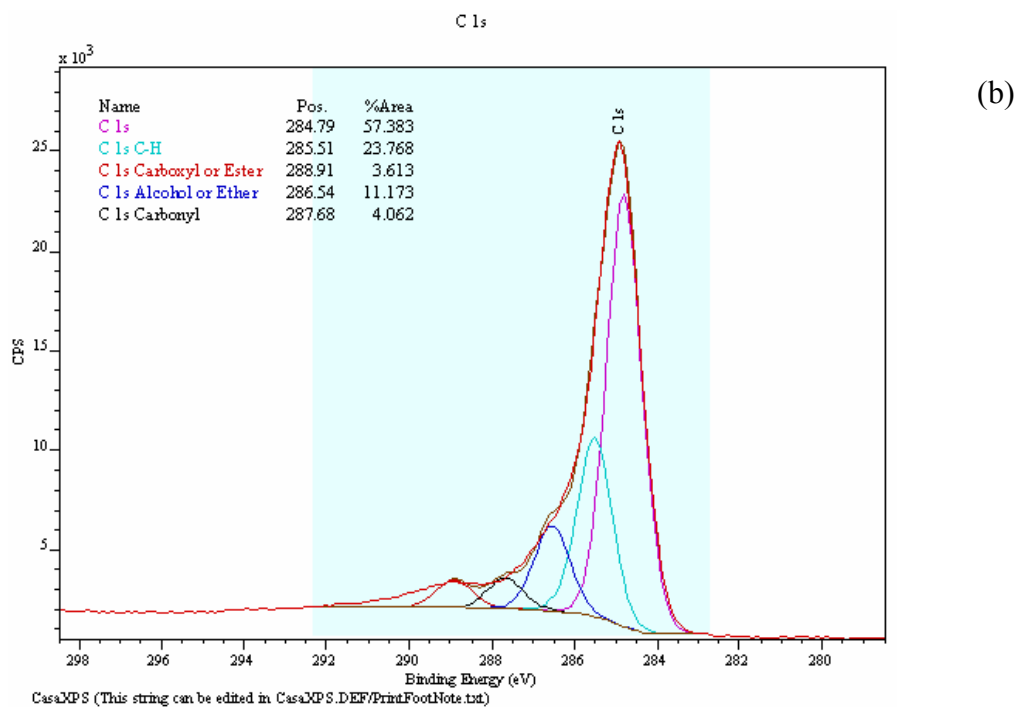


Figure 2. XPS C1s region scan for samples of mesophase pitch-derived tapes stabilised over various temperatures and times: (a) treated in O₂ for 5hrs at 160°C, (b) treated in O₂ for 25hrs at 240°C

Table 2. Relative concentrations of C1s carbon-oxygen functional groups for mesophase pitch-based tape samples stabilised under various conditions. Oxide 1 corresponds to alcohol and / or ether groups, Oxide 2 to carbonyl groups, Oxide 3 to carboxyl and / or ester groups and Oxide 4 to carbonate groups.

Sample	Oxide 1	Oxide 2	Oxide 3	Oxide 4
Green Tape	100	n/a	n/a	n/a
160°C 5hrs O ₂	83.89	8.66	3.72	3.72
160°C 25hrs O ₂	83.58	8.51	4.29	3.6
240°C 5hrs O ₂	80.59	9.64	5.01	4.75
240°C 25hrs O ₂	81.15	11.17	4.06	3.61
300°C 5hrs O ₂	28.58	28.46	28.23	7.99
300°C 25hrs O ₂	35.21	42.85	16.11	5.82

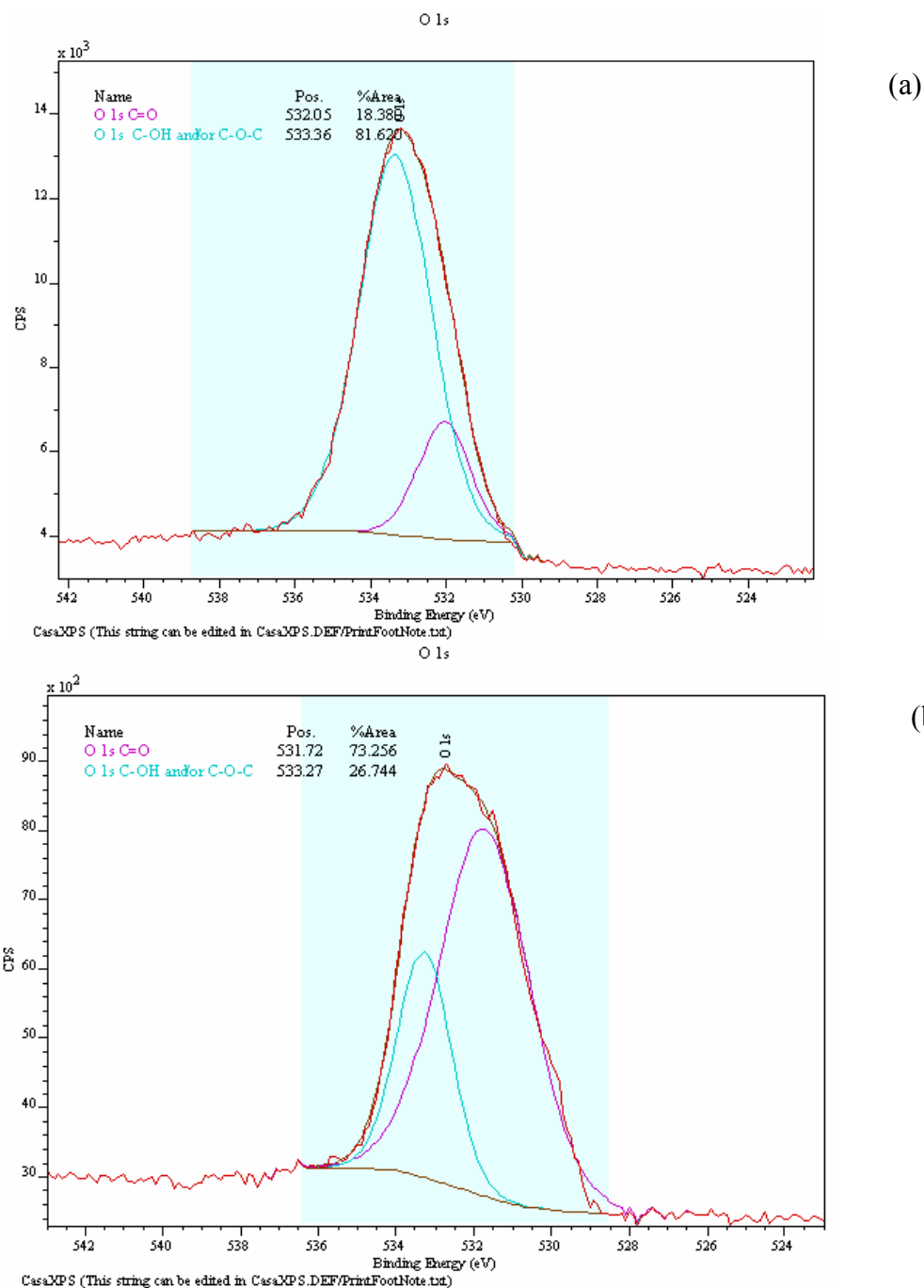


Figure 3. XPS O1s region scan for samples of mesophase pitch-derived tape (a) oxidised in O₂ for 5hrs at 160°C and (b) oxidised in O₂ for 25hrs at 240°C.

In the same way as for the C1s peaks, the O1s spectral region can be separated into three corresponding functional groups based on previous work carried out by Xie and co-workers (Xie et al., 1992). The three constituent peaks (figure 3) can be attributed to carbonyl (C=O) groups (531.6 - 532.0 eV), alcohol (C-OH) and / or ether (C-O-C) groups (533.2 - 533.5 eV) and chemisorbed oxygen and / or adsorbed water (535.8 - 536.2 eV) (All corrected for carbon at 285.0 eV). Upon examination of how the O1s functionality changes with stabilisation condition, it can be seen that, with increasing time and temperature up to 240°C, an increase in the proportion of carbonyl content is evident (figure 4). This

increase in carbonyl group concentration, which emerges in the XPS O1s region, can be attributed to ketone, ester and carboxyl groups (Gardner et al., 1995). For those tapes which were oxidised at 300°C, a different pattern can be seen. In this case, no carbonyl groups are detected and the majority of the surface functionality remains in the form of alcohols and / or esters. However traces of chemisorbed oxygen and / or adsorbed water can be detected and, again, the intensity of this signal increases with oxidation time. This increase can also be seen in the weight loss patterns of tapes when they are carbonised since those oxidised at the higher temperatures show a significant weight loss at about 100°C which is attributed to the removal of adsorbed water and this is also evident in TGA-FTIR data. It is clear from the results that stabilisation at elevated temperatures not only suppresses carbonyl group formation but also leads to increased levels of undesirable surface oxidation with correspondingly reduced ultimate carbon yield for the mesophase pitch-based carbon tape.

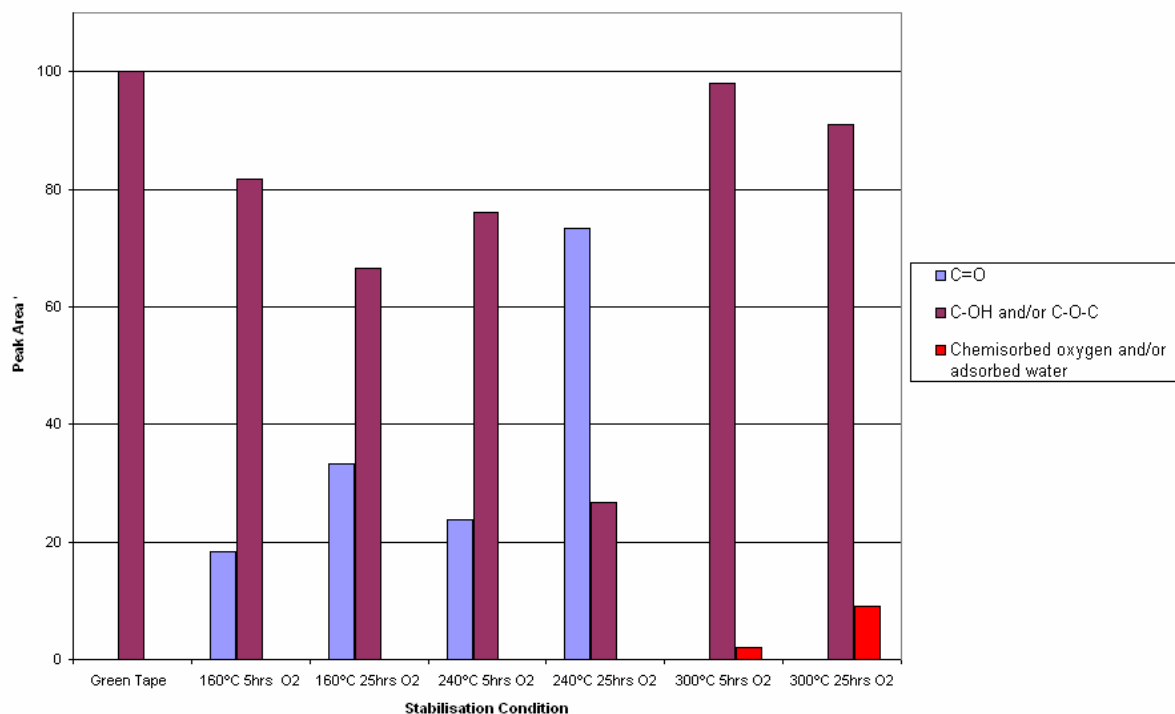


Figure 4. The relative concentrations of carbon-oxygen functional groups within each sample based on O1s XPS curve-fitting results.

(N.B. Absolute comparisons of functional group concentrations *between* samples are **not valid**)

It has long been known that the valence band is highly sensitive to chemical changes which can take place in the surface of the carbon tapes. Valence band spectra are used to investigate the change in separation between the O2s and the C2s peaks. In previous work the O2s – C2s peak separation in the valence band structure has been calculated and found to follow the sequence C-OH < C=O < C-O-C (Gardner et al., 1995). Using this sequence, determination of the dominant carbon-oxygen functionality becomes possible, whereas alcohols and ethers can not be distinguished using their C1s and O1s peaks. The valence band spectra (figure 5) show that, as the stabilisation temperature and time increase up to 240°C, the O2s – C2s peak separation increases. This is consistent with preferential development of carbonyl and ether groups and a reduction in the concentration of alcohol groups. This sequence is in keeping with previous work carried out by Gardner and co-workers, in which PAN-based fibres were exposed to aqueous nitric acid at various temperatures (Gardner et al., 1995). For the higher stabilisation temperature (300°C), the opposite applies. After the initial 5 hours, the valence peak separation can be seen to increase indicating

the formation of ether groups but after longer periods this separation reduces, pointing to a predominance of alcohol groups and suggesting no carbonyl formation.

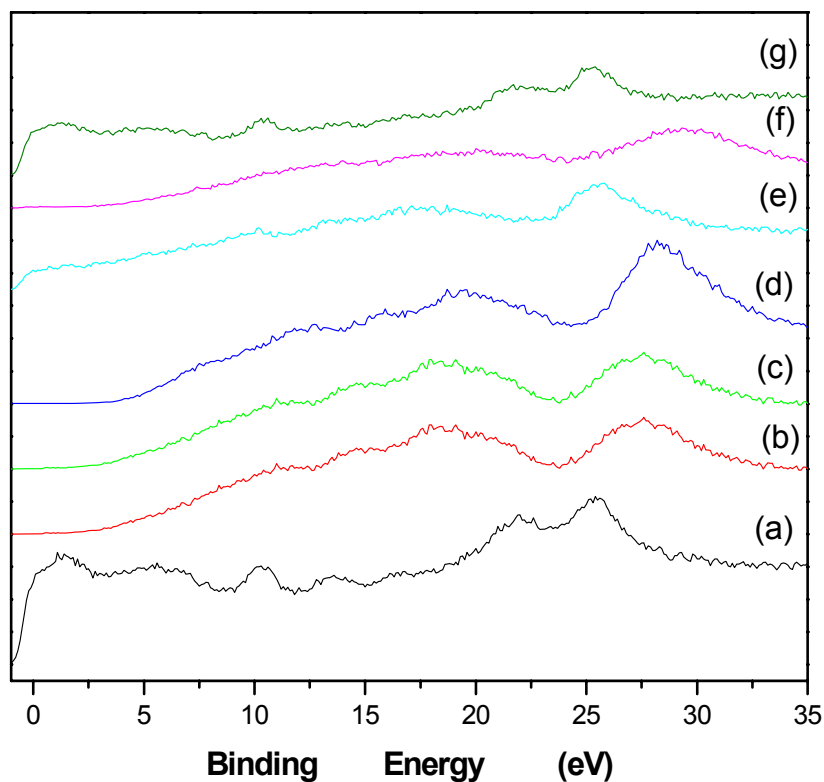


Figure 5. Valence band spectra showing separation between O2s (at higher binding energy) and C2s peaks for samples of mesophase pitch-derived tapes following exposure to oxygen for various temperatures and times (a) green tape (untreated), (b) treated in O₂ for 5hrs at 160°C, (c) treated in O₂ for 25hrs at 160°C, (d) treated in O₂ for 5hrs at 240°C, (e) treated in O₂ for 25hrs at 240°C & (f) treated in O₂ for 5hrs at 300°C.

Conclusions

X-ray photoelectron spectroscopy has proven to be a valuable technique for the characterisation of oxidatively stabilised mesophase pitch-based tapes. It offers a detailed insight into the functional groups present on the surface of the tapes resulting from various oxidation conditions. One major advantage of this technique is that it offers information which may help in optimising pitch-based tapes and fibres, either to tailor their mechanical properties, such as strength and ductility, or to adapt their surface functionality in order to allow them to display the desired chemical interactions between themselves or with other materials. Finally, the technique also yields information which can be used to optimise stabilisation conditions such as temperature and duration.

Acknowledgement

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