

CHEMICAL TRANSFORMATIONS RESULTING FROM PYROLYSIS AND CARBON DIOXIDE ACTIVATION OF KEVLAR

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Introduction

Activated carbon fibres are usually prepared from low crystallinity precursors such as poly[acrylonitrile], viscose rayon and coal tar pitch. Carbonization and activation of polymers with more ordered crystalline structures, such as poly(aramids), has been shown to lead to adsorbents with specific properties and relatively narrow pore size distributions in the micropore size range (4-12Å) [1][2][3]. However, whilst pore sizes and their distribution are significant factors in determining non-specific adsorption, by dispersion interaction, the chemistry of external surfaces and pore walls can play a significant role in the adsorption of polar species. Carbonized chars and active carbons derived from polymers such as Kevlar and Nomex are interesting in that they are likely to contain molecular dispersions of both oxygen and nitrogen. These materials offer a source of pure carbons with which to develop techniques for probing heterogeneous sites within carbon structures.

In this paper we report results from a study to identify the concentrations and chemistries of oxygen and nitrogen functionalities produced when Kevlar (poly[*p*-phenyleneterephthalamide] flock is carbonized in argon and then subjected to varying levels of CO₂ activation.

Experimental

Samples of Kevlar flock (DuPont) were carbonized in a horizontal tube furnace, at a linear heating rate of 4 K.min⁻¹ in an argon flow of 80 cc. min⁻¹ to 1173 or 1123 K. Chars were then activated in various CO₂ flow rates at 1023 K or 1073 K to burn off up to 73 wt. %. Characterisation of porosity by analysis of CO₂ adsorption data using the D-R approach has been discussed elsewhere [3].

Morphological characterisation was carried out using scanning electron microscopy SEM (Cambridge Stereoscan 360). Surface chemistry was studied by X-ray photoelectron spectroscopy (XPS) with a VG Escalab Mk1 using Al K α radiation at 200 W). Surface compositions were calculated from C1s, O1s and N1s peak areas of broad scan spectra (5 scans, 0.3 eV step 50 ms dwell time) after subtraction of Shirley background. High resolution scans of 1s lines were accumulations of 200 scans at a pass energy of 25 eV with 0.05 eV step size and 50 ms dwell time. Peak envelopes were fitted with a mixed Lorentzian-Gaussian algorithm

Results and Discussion

Kevlar precursor - XPS indicates the surface composition of the Kevlar to be C-80.3, O-0.3, N-9.4 at % which is close to the theoretical one.

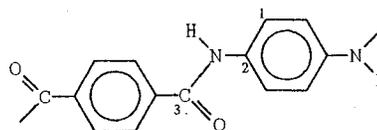


Figure 1. Kevlar structure

The C1s envelope consists of a main peak at a binding energy of 284.6 eV, which is attributable to the -C-C- bonding in the polymer aromatic rings (carbon¹ in Figure 1). The line shift which corresponds to the C²-N functionality (+0.8 eV) is unresolved, and therefore contributes to the broadness of this peak. A lower intensity peak, at a shift of 3.2 eV to the higher binding energy side of the main peak, which corresponds to the amide carbon N-C³=O is partially resolved and a broad, low intensity, peak, at a shift of 5.8 eV is attributable to shake-up satellite due to the sp² hybridised carbons of the

aromatic ring. The N1s spectrum shows only one peak, corresponding to the amide N and the O1s envelope similarly contains a single amide oxygen line.

Chars - The corresponding data from the char show that the surface oxygen and nitrogen levels are decreased to 4.1 and 4.7 at % respectively and the 1s envelopes contain significantly more structure. The C1s envelope now shows pronounced structure to the higher binding energy side but, no unique solution could be found to the curve fit and we therefore base our chemical discussions on the O1s and N1s data for which a first order fit was obtained relatively easily and for which satisfactory C1s fits could also be obtained.

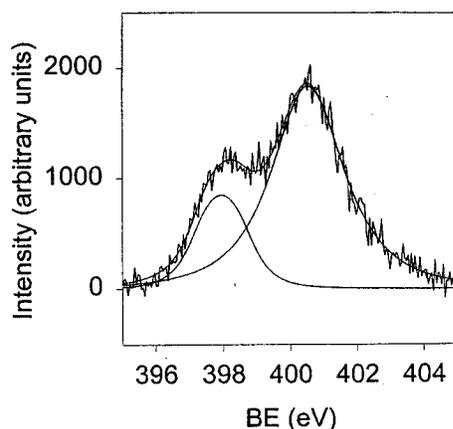


Figure 2. N1s XPS peak envelope from Kevlar 850°C char

The N1s envelopes are all broadly similar in that they now contain signals from at least two groups of chemical species which give rise to partially resolved peaks at 398.0 eV and 400.7 eV. These have been reported before for N containing carbons, the lower energy peak has been attributed to nitriles or aromatic species whilst the higher energy peak has been assigned variously to amines, lactams, amides and aromatic groups. In terms of thermal stability, the explanation of both peaks by the presence of N substituted into the aromatic carbon network is attractive. The lower BE peak has been reported before as corresponding to pyridinic (acridine) N whereas the higher BE peak is thought to be due to N substituted into 6 - membered rings of the type described by Pels *et al.* [4].

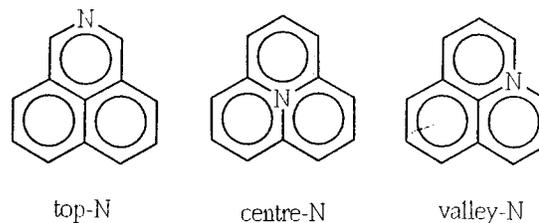


Figure 3. N aromatic structures (from ref. [4]).

The O1s peaks contain peaks at 530.9 eV (C=O), 533.4 eV (C-O) and a component at 536.2 eV which may be due to adsorbed water/CO₂.

Activated carbons - The N1s spectra from these materials are very similar to those from the char which implies that the N chemistry formed at that stage is stable under the activation conditions used subsequently.

The O1s spectra show the same 3 components as the char but the relative intensities of the C=O and C-O peaks vary across the activation series

Conclusions

XPS indicates a decrease in surface nitrogen and oxygen species in the Kevlar char in relation to the polymer precursor. N1s data can be explained in terms of aromatic nitrogen species formed at the char stage. These appear stable under the activation conditions used so far in this work. Surface oxygen species appear to be C-O and C=O with the relative proportions changing according to sample history. The data also indicate the presence of some adsorbed H₂O/CO₂.

References

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