EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Stress-induced changes in porous texture of carbon fibres and activated carbon fibres evaluated by in-situ micro-small angle X-ray scattering	**Experiment number**: ME-366
Beamline: ID13	**Date of experiment**: from: 12-nov-03 to: 15-nov-03	**Date of report**: 23rd Aug 2004
Shifts: 9	**Local contact(s)**: Dr. Manfred BURGHAMMER	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Diego Cazorla-Amorós [a]

Dr. Dolores Lozano-Castelló [a]

Mr. Juan Antonio Maciá-Agulló [a]

Prof. Dr. Martin Mueller [b]

[a] Departamento de Química Inorgánica; Universidad de Alicante; E-03080, Alicante, SPAIN

[b] Institut fuer Exp. Und Angewandte Physik; Universitaet Kiel; D-24118 Kiel, GERMANY

Report:

1. INTRODUCTION.

Small angle X-ray scattering (SAXS) technique offers some advantages for the characterization of the porosity in activated carbons, such as it is sensitive to both closed and open porosity. Another important advantage is that SAXS intensity profiles are sensitive to shape and orientation of the scattering objects so that additional information can be obtained on anisotropic features in oriented samples such as fibres. In the first series of experiments carried out at ID13 (ESRF), the suitability of μSAXS technique (SAXS with a beam of micrometer size) to characterize single activated carbon fibres was demonstrated [1,2]. The isotropic distribution of porosity along the fibre axis in activated carbon fibres prepared from different precursors and using different "physical" activating agents (CO_2 and steam) was shown. In addition, scattering measurements across the fibre diameter were also obtained, which allowed us to analyze the porosity development inside the carbon fibres.

In the second series of experiments carried out at ID13 (ESRF), the study has been extended to anisotropic PAN-based carbon fibres (CF) and chemically activated carbon fibres to deepen into the development of porosity. Additionally, simultaneous tensile stress and microbeam small angle X-ray scattering (μSAXS) measurements were performed for the first time on single activated carbon fibres. Two types of carbon fibres (pitch and PAN based CF) were used for the preparation of activated carbon fibres (ACF) using chemical (KOH and NaOH) and physical (CO_2 and steam) activation methods. The changes in the porosity and microstructure of the materials during the application of the stress were analysed. In addition, information on the chemical activation process from the point of view of the porosity development was deduced from the two dimensional scattering patterns.

The results corresponding to the experiments carried out at ID13 by our research group (experiments number: ME-93 and ME-366) were presented as an invited talk (Keynote "Pergamon Award") at the "Carbon 2004" (an international conference on Carbon at Brown University, 11-16 July 2004, Providence, Rhode Island, USA).

2. EXPERIMENTAL.

The carbon materials used in these experiments are two carbon fibres (used as precursors for the preparation of activated carbon fibres (ACF)) and three ACF. The two different precursors employed in the preparation of ACF were: commercial petroleum pitch-based carbon fibres (CF, Kureha Chemical Industry) and commercial high performance PAN-based carbon fibres (Hx, Hexcel). Two ACF (CFK33 and HxK25) were prepared by chemical activation with KOH of both precursors, petroleum pitch- and PAN-based carbon fibres, respectively. In addition to the aforementioned samples, commercial ACF (A15, Osaka Gas) were also studied. The beam size for this series of experiments was 0.5 μm and the distance of the area detector (MAR-CCD) to the samples was 190 mm.

3. RESULTS AND DISCUSSION.

3.1. Characterization of chemically ACF by mSAXS.

Figure 1 contains the two-dimensional scattering patterns corresponding to the isotropic pitch-based CF before and after chemical activation with KOH. As expected, the development of porosity during a chemical activation process produces an increase in the scattering. It should be remarked that, similarly to the physical activation, the development of porosity in chemical activation is isotropic, i.e. the porosity development does not present any preferential orientation along the fibre axis.

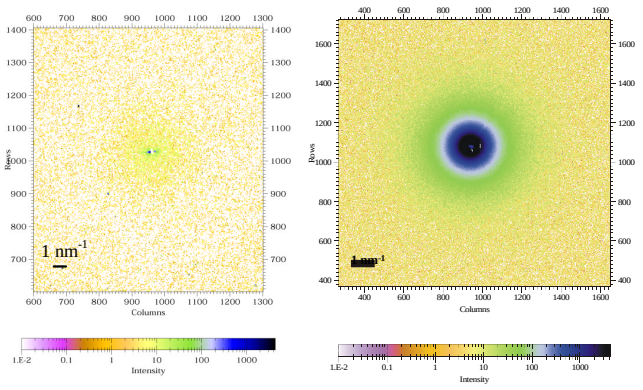
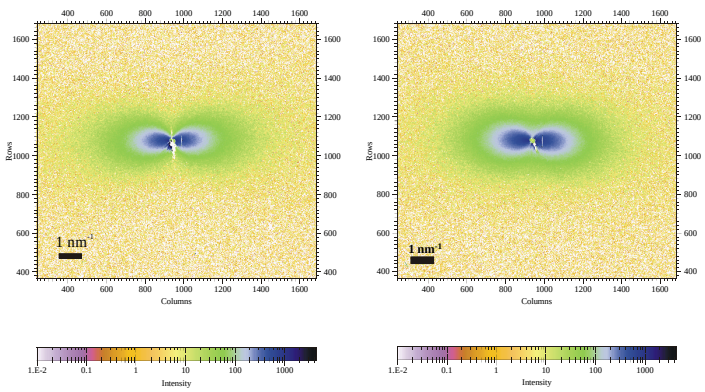


Figure 1. Two-dimensional scattering patterns of the petroleum pitch fibre (CF)(left) and the same fibre after activation by KOH (CFK33) (right).



Figurs 2. Two-dimensional scattering patterns of the PAN-based carbon fibres (Hx) (left) and the same fibre after activation by KOH (HxK25)(right).

Figure 2 includes the scattering patterns corresponding to the PAN-based CF fibre before and after KOH activation. In these figures very different features to those observed in Figures 1 can be observed:

(i) PAN-based CF presents microvoids oriented along the fibre axis, which results in a higher scattering intensity in the horizontal direction ("fan-shaped" scattering) [3,4].

(ii) the porosity development by chemical activation of PAN-based CF (Table 1) essentially focuses along the fibre axis, resulting in an anisotropic development of porosity.

The results obtained with this type of materials show the usefulness of this technique to characterise the development of porosity with single fibres, being specially useful to detect porosity orientation. The comparison of both 2D scattering patterns in Figure 2, show that the "fan-shaped" is more defined in the raw PAN-based CF (Hx) than in the activated carbon fibre (HxK25), which indicates the existence of a higher misorientation of the pores in the activated fibre. In order to quantify more precisely the misorientation of the pores, the angular intensity distribution was calculated at different values of constant scattering vector (q). The width of angular intensity distribution multiplied by q was plotted versus q. The slope of this plot corresponds to the angular width (z), which is only related to the misorientation of the pores. The values of the angular width for the raw PAN fibre (Hx) and the activated fibre (HxK25) were z=57.6 and z =61.8degrees, respectively, which confirms that during activation, misorientation of the pores in the PAN fibre increases.

As a conclusion from the results presented above, it can be said that depending on the precursor, the chemical activation process produces isotropic or anisotropic development of porosity. These results also show the usefulness of μSAXS to detect porosity orientation on a single fibre.

3.2. Simultaneous tensile strength and mSAXS measurements.

Simultaneous tensile stregnth and SAXS experiments were carried out by measuring the scattering pattern at the centre of the fibres while applying a given stretching rate. The ESRF/ID13 stretching device was used for the experiments. This type of experiments have been done for the first time with activated carbon fibres, what emphasizes the novelty of this study. The main objective of these measurements is to analize the changes in the porosity and microstructure of the materials during the application of the stress, to deepen into the knowledge of the porous texture of the ACF.

It should be mentioned, that μSAXS measurements carried out across the fibre diameter at different loads demonstrated that the fibre diameter remains constant by stretching the fibre. This agrees with the small negative strain that should occur along the fibre diameter as estimated from the Poisson coefficient. For a Poisson coefficient of 0.25, a strain of about 0.06 μm should occur. Additionally, the μSAXS measurements showed the reversibility of the deformation (i.e., pure elastic deformation).

From the results obtained in these experiments it was seen that the two-dimensional scattering patterns change upon the increase in load. To analyze these changes in more detail, the two-dimensional scattering patterns were integrated to obtain the intensity versus scattering vector (*q*). Integration was done in two different intervals: (i) integration between angles 155º and 205º (horizontal direction) and, (ii) integration between angles 65º and 115º (vertical component). The main changes in the scattering curves occur in the q region where the shoulder due to the scattering from the high micropore concentration, appears. Figure 3 presents the integrated curves in this q region, for the horizontal (left) and vertical component (right). To make the plot clearer only three curves are included (measurements number 1, 5 and 7). Figure 3, on the left, shows that during stretching the horizontal component is not affected; therefore, pores oriented vertically are not changed. However, the curves corresponding to the vertical component (Figure 3 right) shift to lower *q* values, thus indicating that stretching produces a modification of microporosity oriented perpendicular to the axis fibre (vertical component of scattering), which becomes wider due to the stretching. Calculations of the Guinier radius done for the pores oriented perpendicular to the axis fibre, indicate that there is an increase of 0.3 Å from the starting pore size to the pore size corresponding to the fibre under the maximum load.

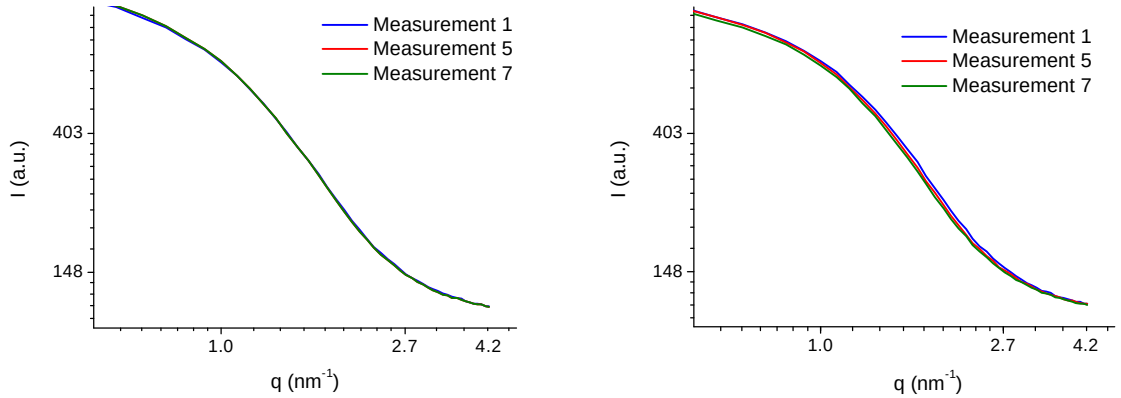


Figure 3. Integrated curve for the horizontal component (left) and the vertical component (rigth).

4. CONCLUSIONS.

Information on the chemical activation process from the point of view of the porosity development was deduced for two different carbon fibres: PAN and petroleum pitch-based carbon fibres develop anisotropic and isotropic porosity, respectively, after KOH activation. Simultaneous tensile stress and μSAXS experiments were performed for the first time on single activated carbon fibres. The results obtained for a physically ACF show different behaviour of the horizontal and vertical scattering component. The results demonstrate that the porosity perpendicular to the axis fibre becomes wider during stretching.

5. REFERENCES.

[1] Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amoros D, Linares-Solano A. Müller M, Riekel C. Carbon 2001;40: 2727-2735.
[2] Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amoros D, Linares-Solano A. Müller M, Riekel C. Studies in Surface Science and Catalysis. Characterisation of Porous Solids VI, 2002, 51-58.
[3] Perret R, Ruland W. Single. Journal of Applied Crystallography 1969;2:209-218
[4] Perret R, Ruland W. Journal of Applied Crystallography 1970;3:525-532.