Experimental report

11/03/2020

Proposal: 5-26-218 **Council:** 10/2018

Title: Analysis of the wide-angle neutronscattering of non-graphitic carbon testing of an advanced evaluation approach

Research area: Materials

This proposal is a resubmission of 5-26-217

Main proposer: Bernd SMARSLY

Experimental team: Felix BADACZEWSKI
Torben PFAFF
Oliver OSSWALD

Local contacts: Henry FISCHER

Samples: Empty Sample Container
Carbon - Mesophase Pitch HT@1200 Â°C
Carbon - Coal Tar Pitch, HT@1800 Â°C
Carbon - Phenol Resin, HT@1800 Â°C
Carbon - Coal Tar Pitch, HT @1200 Â°C
Carbon - Phenol resin, HT@2850 Â°C
Carbon - Phenol resin, HT@2100 Â°C
Carbon - Mesophase Pitch HT@1800 Â°C
Carbon - Mesophase Pitch HT@2100 Â°C

Instrument	Requested days	Allocated days	From	To
D4	3	2	29/08/2019	31/08/2019

Abstract:

Non-graphitic carbons (NGCs) represent an important class of materials for several applications in research and industry. A quantitative description of the sp2-polyaromatic microstructure, showing substantial disorder compared to graphite, is desirable for linking material properties to the microstructure and tuning production processes accordingly. Ruland and Smarsly introduced a novel approach for the evaluation of wide-angle X-ray scattering (WAXS) data of non-graphitic carbons (NGCs), providing meaningful structural parameters describing size and disorder of the graphene stacks. Here we apply for beam time at the D4 instrument to acquire WANS data of six NGC samples D4 to further verify this algorithm and compare the structural parameters with those obtained from fitting WAXS data. Compared to WAXS and WANS experiments at the FIREPOD and E2 instruments at BER II, HZB (Berlin), WANS experiments at D4 allow for significantly larger values of the modulus of the scattering vector s (= Q / 2 Pi) due to the significant smaller neutron wavelength and thus will help to establish the WAXS evaluation as a routine method. In addition, a PDF analysis is to be performed.

"Analysis of the wide-angle neutronscattering of non-graphitic carbon testing of an advanced evaluation approach"

Proposal-Number:	5-26-218
Date:	29/08/2019 – 31/08/2019
Instrument:	D4
Experimental team:	Bernd Smarsly (JLU Giessen, main proposer), Felix Badazcewski (JLU Giessen), Oliver Osswald (JLU Giessen), Torben Pfaff (JLU Giessen)
Local contact:	Henry Fischer

Aim of the experiment

Non-graphitic carbons (NGCs) represent an important class of materials for several applications in research and industry. A quantitative description of the sp^2-polyaromatic microstructure, showing substantial disorder compared to graphite, is desirable for linking material properties to the microstructure and tuning production processes accordingly. Ruland and Smarsly introduced a novel approach for the evaluation of wide-angle X-ray scattering (WAXS) data of non-graphitic carbons (NGCs), providing meaningful structural parameters describing size and disorder of the graphene stacks. By applying for beamtime at the D4 instrument to acquire WANS data of several NGC samples, this algorithm can be further verified and the resulting structural parameters can be compared to the structural parameters with those obtained from fitting WAXS data. Compared to laboratory WAXS and WANS experiments at the FIREPOD and E2 instruments at BER II, HZB (Berlin), WANS experiments at D4 allow for significantly larger values of the modulus of the scattering vector $s = \frac{Q}{2 \cdot \pi}$ due to the significant smaller neutron wavelength and thus will help to establish the WAXS evaluation as a routine method, provided the results of the WANS and WAXS data agree. In addition, a PDF analysis is to be performed to get some information about the long range order.

Experimental details

For our studies we used different NGCs made from different precursors and heat treated at different temperatures regarding from 1000 °C to 3000 °C. The precursors were mesophase pitches (MP), low softening point pitches (LSPP/WP) and novolac/resole resins (H/N). The following samples were measured:

- H1000, H1200, H1500, H1800, H2100, H2300, H2800, H3000
- N1800
- WP1200, WP1800, WP2500, WP2800, WP3000
- MP2100, MP1500, MP1800, MP2100

The samples were loaded in a approx. 6mm diameter cylindrical vanadium cell at ambient conditions. Three identical cells were used to collect the data as efficiently as possible. The by a monochromator generated wavelength was about 0.5 Å (refined $\lambda = 0.4975$ Å), generating a neutron flux about $5.0 \cdot 10^7$ cm^{-2} s^{-1} and a quite high $Q_{max} = 23.6$ Å^{-1}. ($Q_{min} = 0.32$ Å^{-1}) with a resolution about $\Delta Q_{min} = 0.03$ Å^{-1}. The data collecting time for all samples was approx. 100 min.

The measurements were performed at room temperature and in vacuum with $p < 10^{-3}$ mbar. Measurements also performed of the empty cells and the background. Then the data was regrouped after performing some stability tests and corrected from background and inelastic contributions. All collected data were treated using the D4CREG routines with a therein integrated correct program.

Results

Assuming that a higher temperature leads to a higher order both in the graphene layers and between the layer stacking, the Bragg reflections from samples with higher treatment temperature should be sharper. As shown in fig. 1 H1000 shows very low and broad reflexes while H3000 has sharper and narrower reflexes. In addition, it can be seen that H1000 contains a high proportion of hydrogen, so that the scattering curve decreases with larger Q. The PDF analysis shows for all samples an ordered hexagonal structure. The next neighbours in a single layer with a C-C bond length of 1.42 Å are placed at 2.46 Å and 2.84 Å as shown in fig. 1. This means, that all reflexes between this range are defects in a nearly perfect hexagonal layer structure. Looking at the temperature series of the "H"-samples, it becomes clear, that samples heat treated at temperatures are showing a larger long-distance order than samples heat treated at lower temperatures. Even the defects in small distances are reduced, which corresponds to the expectation for this type of samples.

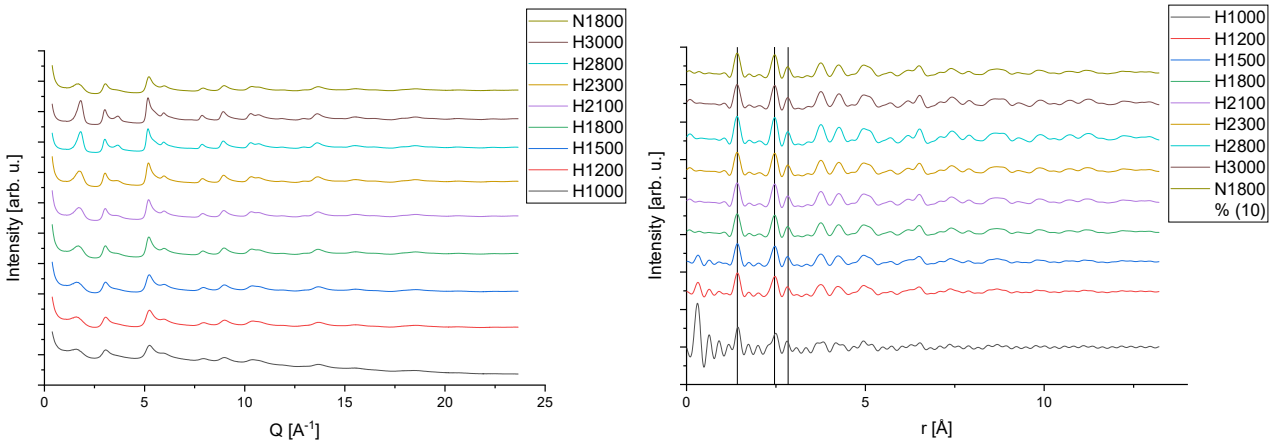

Figure 1: Scattering and PDF of phenol resins heated to different temperatures.

The scattering data of the mesophase pitch is shown in fig. 2. These samples generally have a higher ordered microstructure, which leads to even sharper and narrower. Also, all reflexes become much more sharper and narrower with increasing heat treatment temperatures of the samples. It is even possible to recognise reflexes in the higher Q range. That suggests a generally higher order both in the layers itself and also between the layers. This is also displayed by the PDF analysis: at higher distances up to the whole measured range still much or less sharp reflexes are visible. This is a very good indicator for having a very high and regularly order also at higher distances. The high amount of the reflexes could come from the fact that the layers are shifted and twisted against each other. In addition to this, the influence of the heating temperature become very clearly: The higher the

heating temperature, the higher the order of the carbons and the higher and sharper the reflexes become.

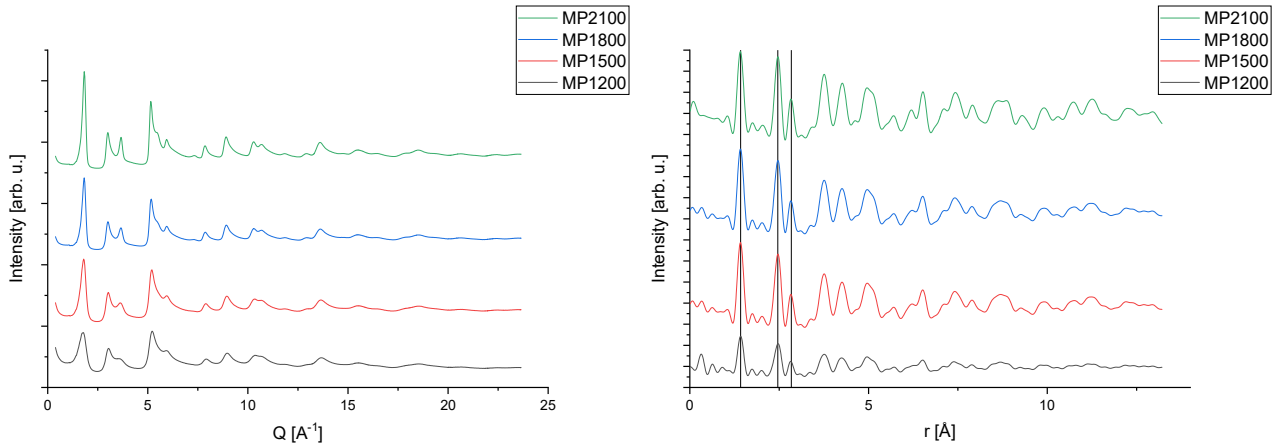

Figure 2: Scattering and PDF of mesophase pitch heated to different temperatures.

The low softening point pitches are showing even sharper and narrower reflexes both at low and at high *Q*-values. This suggests that these samples have an even higher order, especially at a greater distance, which is consistent with previous assumptions. This samples have an even higher order compared to mesophase pitches at all heating temperatures, which becomes clearly through the very sharp reflexes up to a Q = 10 Å^{-1}. However, since the higher order reflections (at first glance) are not higher or sharper, this could be an indication that the order within the stacks is like the MP samples. This information, which comes from the scatter pattern, is also comparable to the PDF analysis, which has already been shown for the other examples.

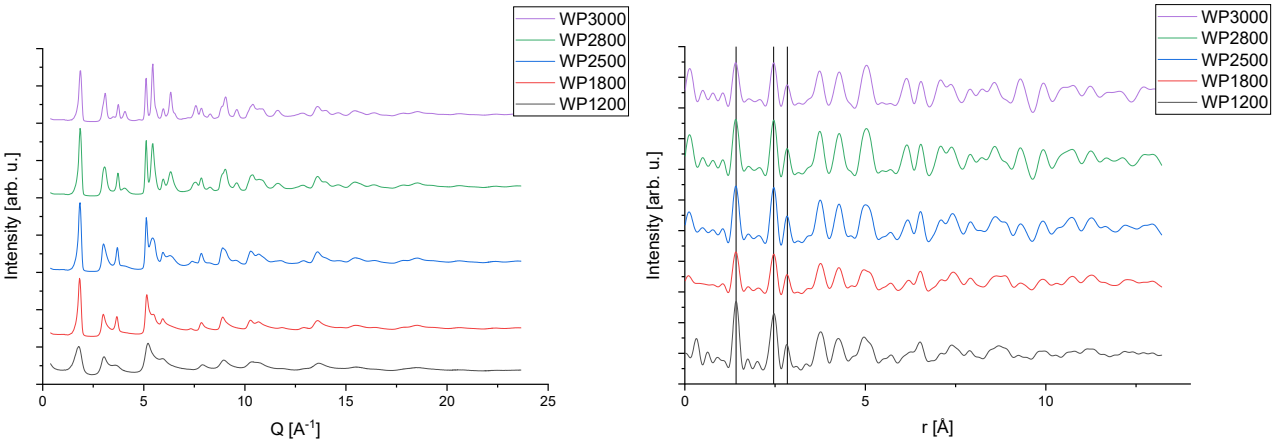

Figure 3: Scattering and PDF of low softening point pitch heated to different temperatures.

Further and more detailed evaluations are currently being carried out.