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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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:** New hybrid nanocomposite materials from high pressure polymerization of small unsaturated hydrocarbons in graphene oxide and related systems	**Experiment number**: CH-4542
Beamline: ID27	**Date of experiment**: from: 11/02/2016 to: 14/02/2016	**Date of report**: 09/09/2016
Shifts: 9	**Local contact(s)**: Andrew Cairns, Mohamed Mezouar	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Graphene Oxide (GO) is a non-stoichiometric layered material obtained by the oxidation of graphite under strong acidic conditions. Due to the presence of O-containing functional groups, the C layers of graphite become puckered and the distance between them increases from the typical 3.3 Å value up to 12 Å, according to the hydration of the material [1]. Recently pressure has been demonstrated to be able of inducing the insertion of small molecular systems between the GO layers up to observe an auxetic effect in the case of water and ammonia [2,3], and, in combination with temperature and photo-excitation, of activating chemical reactivity of GO with N-bearing moieties having different chemical properties such Ar, N_2 and NH_3 [CH-4116], thus opening new perspectives for the synthesis and functionalization of advanced 2D carbon based materials [4].

Following these results and according to our experience in the pressure and photo-induced polymerization of simple unsaturated hydrocarbons [5], in this proposal we used pressure and temperature for synthesizing a new nanocomposite layered material made of GO and polyethylene.

Before arriving to ESRF, we performed FTIR experiments at LENS on pure Ethylene to explore the HP-HT phase diagram of ethylene, traced the polymerization boundary with respect to the stability region of ethylene and found the optimal polymerization conditions, in terms of quantitative transformation and reaction kinetics (paper submitted), to be reproduced at ESRF-ID27 during the beam time.

Two samples of GO/Ethylene were previously cryo-loaded in our DACs and spectroscopically characterized by FTIR and Raman spectroscopy at LENS before arriving to ESRF. The polymerization process was then induced by high T and followed by X-ray diffraction experiments performed at ESRF-ID27, through the monitoring of the interlayer d(001)-spacing of GO. High temperature was generated by resistive heating of the DAC, hosted inside a water-cooled vacuum chamber, and measured by means of thermocouples. The pressure was measured by the ruby fluorescence method. XRD patterns were acquired before, during and after the occurrence of the reaction and several mappings of the sample with 5 μm spatial resolution were performed to gain insight about the heterogeneity of the sample at different constant P-T values. We successfully performed two experiments in different thermodynamic conditions as a function of pressure and temperature, respectively.

In the first one, the pressure was rapidly increased at room temperature from 1.2 GPa, where Ethylene is in the liquid phase, up to 6.4 GPa, where Ethylene polymerizes from the crystalline phase I (monoclinic $P2_1/n$) [4]. In the second one we gently increased the pressure at room temperature up to 1.7 GPa, then rapidly increased the temperature up to 440 K, to activate and follow the polymerization in the liquid phase of Ethylene.

The XRD mapping of the samples, acquired in different P-T conditions, indicate a distribution of interlayer d-spacing values across both samples. In particular, in some areas of the samples the peak profile of the d(001) reflection reveals the presence of more than one component, which can be related to different GO environments. Whereas the lowest limit value of the distribution coincides with the interlayer d-spacing of empty GO, the higher values correspond to a lattice expansion of GO with increasing degree of filling, indirectly confirming the insertion of Ethylene and the occurrence of the polymerization. Under certain experimental conditions a very remarkable increase of interlayer d-spacing is achieved.

These conclusions are confirmed and supported by the spectroscopic Raman analysis performed at LENS, revealing the presence of confined polyethylene chains, which have characteristic band shapes compared to crystalline polyethylene (paper under preparation).

As emerged also for the case of GO in the presence of other small molecule [2], the relative amount of Ethylene compared to GO is a critical parameter to be taken into account in order to observe an auxetic behaviour of the material.

A microscopic analysis of the reaction products recovered at ambient conditions is currently under progress, to morphologically characterize the nanocomposite materials synthesized by the high pressure polymerization of Ethylene between the GO layers.

References

[1] D. R. Dreyer et al., Harnessing the chemistry of graphene oxide, Chem. Soc. Rev. 2014, 43, 5288.

[2] A. V. Talyzin et al., Colossal Pressure-Induced Lattice Expansion of Graphite Oxide in the Presence of Water, Angew. Chem., Int. Ed. 2008, 47, 8268; Pressure-Induced Insertion of Liquid Alcohols into Graphite Oxide Structure, J. Am. Soc., 2009, 131, 18445; Pressure-Induced Insertion of Liquid Acetone into the Graphite Oxide Structure, J. Phys. Chem. C, 2010, 114, 7004.

[3] M. Ceppatelli et al., Lattice expansion of graphite oxide by pressure induced insertion of liquid ammonia, Carbon 2015, 93, 484.

[4] M. Ceppatelli et al., High-Pressure Chemistry of Graphene Oxide in the Presence of Ar, N_2, and NH_3, J. Phys. Chem. C 2016, 120, 5174.

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