EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** In situ and operando study of the electrospinning process coupled with a sol-gel reaction	**Experiment number**: MA-2423
Beamline: ID02	**Date of experiment**: from: 09/12/14 to: 12/12/2015	**Date of report**: 31/03/2015
Shifts: 6	**Local contact(s)**: Sylvain Prevost	*Received at ESRF:*

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1. Objectives

The experiments aim at understanding the formation of hybrid electrospun fibers when solutions containing both polymer and inorganic sol or nanoparticles are injected in an electric field. The main idea is to study how this electric field governs the organization of the hybrid interface and the nanostructure of the fibers during the solvents' evaporation. The expected results are fundamental for formulating the mechanism of formation of hybrid fibers according to both the processing parameters (electric field, injection rate) and the chemistry of the solution (concentration, polymer/inorganic ratio, aging time…). These sets of experiments are essential to design fibers with efficient functionalities. To our knowledge, the present study constitutes the first example ever reported of *in situ* electrospinning and SAXS/WAXS studies.

2. Results

Briefly, the setup that we designed for these experiments led to encouraging preliminary results. We demonstrated that ***it is possible to register simultaneously SAXS and WAXS spectra along the fiber*** up to 55 mm from the injection tip, indicating that the number of fibers encountering the beam at the timescale of the measurement allows getting a suitable signal to noise ratio, even in the unstable regime of the fiber.

Previous *ex situ* SAXS/WAXS studies on silica-PVDF-HFP electrospun membranes showed (i) at wide angle, the crystallisation of the polymer, and (ii) at small angle, the organization of the silica domains within the polymer and the correlation lengths due to the crystallites of the polymer. From *in situ* SAXS-WAXS experiments, we expect to follow the evolution of both signals at successive stages of formation of the fibers. Because, in an electrospinning experiment, a fresh solution is constantly ejected from the tip to form new fibers, recording SAXS-WAXS data along an horizontal line, at any time, starting from the top of the injection tip to the target, allows a step by step following of the process of formation of the fiber from the Taylor cone to the collection of solid fibers on the counter-electrode. Figure 1(a) illustrates the behaviour of the solution (i) when no voltage is applied and (ii) when electrospinning is in process. The origin of the x and y axes corresponds to the center of the top of the injection tip.

Figure 1(b) shows SAXS and WAXS spectra recorded along y = -0.4 mm for a typical formulation containing prehydrolyzed tetraethoxysilane, its sulfonated analog, the polymer PVDF-HFP and two more additives in dimethylformamide. The background has been subtracted. The signal of a drop of solution (reported in blue on Figure 1a-i) is also plotted in figure 1(b).

SAXS data show that the structuration of the silica domains within the polymer in a drop of solution (peak at 3.55 nm^{-1}) is different than the one (peak at 3.7 nm^{-1}) observed when the solution is electrospinned. But, the SAXS behavior at low q is identical along the fibers, i.e. various x (see Figure 1b). From x = 0.5 mm to x = 54.4 mm, the same upturn is mainly observed. This latter has also been observed for the membrane. The correlation length at 0.7 nm^{-1} due the intercrystallite distances varies with the distance. There is a competition between the decrease of the matter volume in the beam and an increase of the correlation. WAXS data showed amorphous contributions of the polymer phase in the drop. From the end of the drop, the crystalline peaks due to the semi-crystallinity of the polymer appear when the electrospinning process is activated. These correlation lengths are convolved with the amorphous contribution giving shoulders and peaks at 12.1, 24 and 26.7 nm^{-1}.

From these observations, we can postulate that, at the very early stage of the electrospinning process, both (i) a crystallization of the polymer and (ii) a correlation length between inorganic domains, similar to the one observed in the final membranes, are achieved. These results highlight the importance of the role played by the electrospinning parameters on the silica/polymer interface structuration.

3. Present drawbacks and next upgrades

In order to achieve a deeper understanding of the fibers formation, we need to obtain a better signal to noise ratio along the whole fibers path from the tip all the way to the target. We therefore want to suggest two main improvements to the present experimental set-up: the nature of the windows of the box and the type of target.

A plastic box cover has been designed (i) to maximize the signal/noise ratio working under He atmosphere, (ii) to allow incident/scattered X-rays in/out of the box using specifically designed windows and (iii) to avoid multiple target effect isolating the experiment from any close grounded metallic sources (like the nose of the source and the detector protective box itself). Initially the material selected for the windows (source and detector sides) was 25 µm thick Mylar, however it absorbed so powerfully the incident beam that we had to remove the windows. As a consequence, the measurements suffered from several drawbacks: (1) helium had to be flushed more intensively and the flow induced strong deviations of the path of the fibers which were very difficult to detect, not to mention the high He consumption; (2) the detector box and the source tended both to act as additional targets. We are now planning on designing 20 µm-thick optical quality mica windows: the quasi static helium flow will allow fibers to repetitively adopt a controlled horizontal path.

Besides, we previously used a nail as target in order to strongly focus the electric field and thereby spatially concentrate the fibers. This was very successful but did strongly limit the time of the measurements: after a few minutes only, a set of solid static fibers was formed and could get stuck between the injection tip and the nail. In order to continuously regenerate the fibers, we intend to use a small rotating coil as a target to continuously roll the fibers.

4. Perspectives

In situ experiment could also be extended to other multifunctional fibers systems, which use for example other sol-gel chemistries or crystalline preformed anisotropic inorganic nanoparticles and also polymers with different physical properties. It would be extremely interesting to study the nanostructuration of the hybrid interface during the fiber formation, when the polymer/inorganic affinity. The impact of processing parameters on the fiber formation will be explored as well.

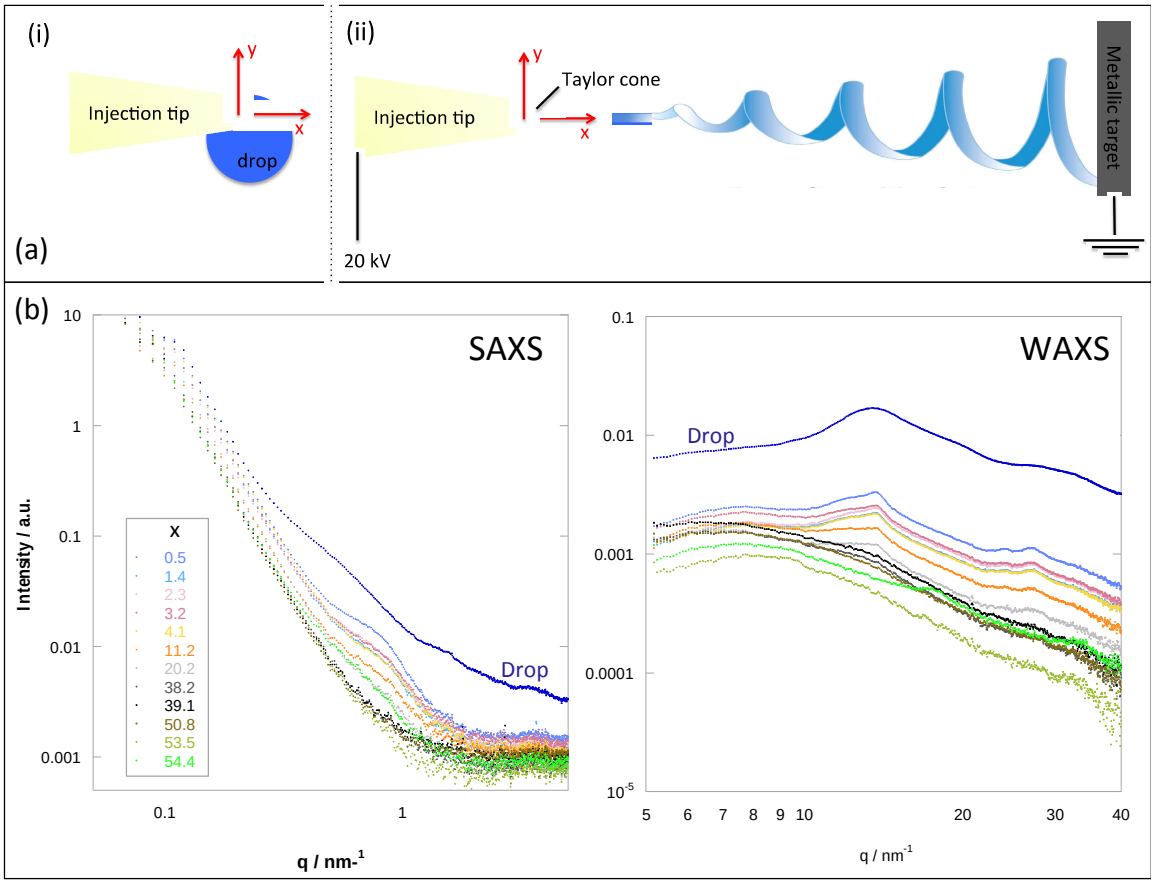

Figure 1. (a) Scheme of the fibers during the electrospinning process. (b) *In situ* SAXS/WAXS spectra of a silica/polymer fiber in formation recorded along y=-0.4 mm at different distance from the injection tip, x.