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

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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:**	**Experiment number**: SC 4420
Beamline:	**Date of experiment**: from: 26 ago 2016 to: 29 ago 2016	**Date of report**: 11/01/2018
Shifts:	**Local contact(s)**: Daniel Hermida (email: hermidam@esrf.fr)	*Received at ESRF:*

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Report:

Summary:

The aim of this proposal was to investigate by Grazing incidence X-ray Scattering at Small (GISAXS) angles the inner structure of a series of multilayer thin films of polysaccharides, chitosan (CHI) and alginate (ALG), with embedded iron oxide magnetic nanoparticles (NPs) prepared on spray assisted layer-by-layer (LbL) technique. These hybrid films are able to heat in response to an alternating magnetic field and this response seems to be dependent on the inner architecture of the film, that is, number of NPs layers and distance between them. Likewise, nanomechanical properties are also dependent on the preparation conditions. We expected to elucidate the distribution of NPs layers inside the polymer films.

Scientific background:

In polymer LbL films containing inorganic nanoparticles, the distribution of NPs and structuration of NPs layers inside films influence the final properties of the resulting hybrid materials. A varying architecture in multilayer films fabricated from polymers and magnetic NPs have revealed different magnetic properties depending on the distance between NPs layers[1]. In this case, a linear growing of the thickness of the polymer films is well established which implies the absence of interpenetration between polymer layers. In contrast, LbL films obtained from polysaccharides, are expected to yield greater interlayer diffusion and disorder, due to increased polydispersity and a reduced degree of polymer–polymer ion-pairing within a multilayer[2]. In this context, the distribution of NPs within polysaccharidic films could vary from films with well separated monolayers to films with dispersed NPs all over the thickness. To the best of our knowledge, such study involving LbL hybrid polysaccharidic films has not

been previously reported. GISAXS would allow to determine structural information on the arrangement of polymer and nanoparticles in the direction perpendicular to the free surface, as previously reported for polymer thin films[3].

Experimental:

GISAXS measurements were carried on (Alg/Chi)n films and (Alg/Chi)n(NPs/Chi)m films prepared by spray and dipping LbL on BM26 beamline of the European Synchrotron Radiation Facility (ESRF) sited in Grenoble (France). A standard GISAXS configuration was used[3]. A longitudinal beamstop was used located in the position of the intermodular gap of the Pilatus detector. An X-ray wavelength of $\lambda = 0.103$ nm, was used in our experiments. The scattered intensity was recorded by a two-dimensional (2D) detector (Pilatus 1M) with a camera of 981x1043 pixels (size of the pixel 172x172 μm^2) and a sample-to-detector distance of 6.87 m to data acquisition. An incidence angle of the beam of $\alpha_i = 0.4º$ was chosen, which is larger than the reflection angle for the polymer materials. Thus, full penetration in the sample is ensured. The treatment of the GISAXS images was performed using the software FIT2D.

Results and Discussion:

1.1. Materials preparation

Chitosan (Chi) (Aldrich ,448869, lot SLBG1673V) and Sodium alginate (Alg) (Sigma-Aldrich,A2158, lot 090M0092V) were used to prepare based ferrofluid containing iron oxide nanoparticles (NPs) with a magnetite concentration of 8.0 mg/mL and an average size of 8 nm. Two LbL protocols, spray and dipping, were used to prepare films on silicon wafers (20 × 40 mm, Siegert) previously cleaned with piranha solution (3:1 H2SO4/H2O2) for 10 min and rinsed extensively with distilled water. As the silicon substrate is negatively charged, a first layer from 1 mg/mL solution of Poly(ethylenimine) (PEI) (Aldrich,M_w=f 25000) was deposited providing a positively charged homogenous substrate. In the case of films built up through spray assisted LbL, the substrate was inclined 45° with respect to the vertical to allow the drainage of the solution during the spraying process. Nanocomposite Alg/Chi films were obtained by spraying a bilayer of alginate and chitosan followed by a bilayer of the ferrofluid containing the iron oxide NPs and a chitosan layer. Fixed alginate and chitosan solutions with concentrations of 2.5 mg/mL and 1.0 mg/mL, respectively were used and each layer was sprayed for 5 s. Alg solution was sprayed onto the substrate for 5 s. After a waiting time of 15 s, Chi solution was sprayed for 5 s. After an additional waiting time of 15 s, the cycle was repeated until obtaining the desired number of layers. Sample was denoted as $(Alg/Chi)_n$ where n stands for the number of bilayers (n = 5). Two series of nanocomposite films were obtained by applying 1.5 and 3 cycles and samples were denoted as $(Alg/Chi)_n/(NPs/Chi)_m$ where n stands for the number of Alg/Chi bilayers (n = 2 and 3) and m stands for the number of NPs/Chi bilayers (m = 1 and 3). Additionally, an Alg/Chi film without nanoparticles was prepared. Additionally, nanocomposite Alg/Chi films were obtained by a sequential dipping of the substrate either in alginate (2.5 mg/mL) or in the ferrofluid (8.0 mg/mL) and chitosan solutions (1.0 mg/mL). First, the substrate was immersed in Alg solution for 5 min and then in a buffer pH 3 solution for 2 min. This was followed by the immersion in Chi solution for 5 min and then in a buffer pH 5 for 2 min. After that, the sample was immersed in the ferrofluid solution for 5 min and then in distilled water for 2 min. Finally, this was followed by the immersion in Chi solution for 5 min and then in buffer pH 5 for 2 min. The cycle was repeated until obtaining the desired number of layers. Sample was denoted as (Alg/Chi)n/(NPs/Chi)m where n stands for the number of Alg/Chi bilayers (n = 2) and m stands for the number of NPs/Chi bilayers (m = 1).

1.2 GISAXS experiments

Figure 1 shows the GISAXS patterns at an incident angle of 0.4º of two films prepared by dipping LbL, a $(Alg/Chi)_5$ film (Figure 1a) and the nanocomposite $(Alg/Chi)_2/(NPs/Chi)_1$ (Figure 1c) with one layer of nanoparticles respectively.

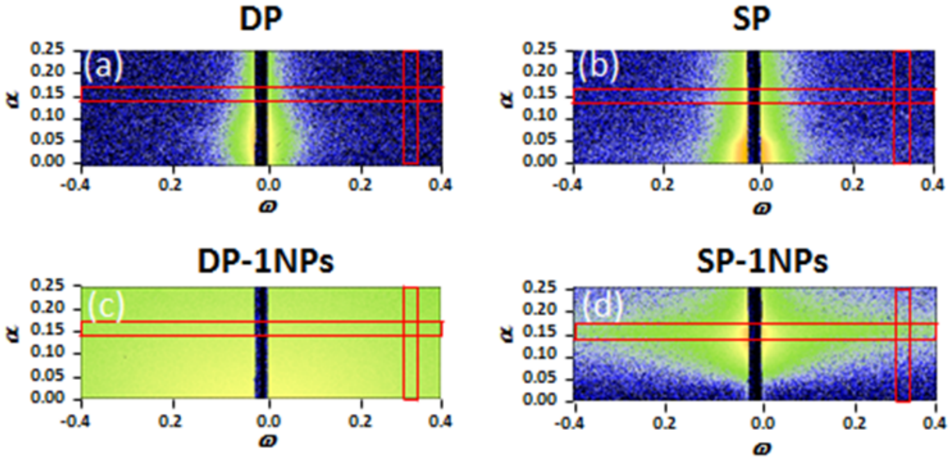

Figure 1. GISAXS patterns at α_i = 0.4º of films : (a) $(Alg/Chi)_5$ prepared by dipping (DP) and (b) spray $(Alg/Chi)_5$ (SP) and with a layer of nanoparticles prepared by (c) dipping $(Alg/Chi)_2/(NPs/Chi)_1$ (DP-1NPs) and (d) spray $(Alg/Chi)_2/(NPs/Chi)_1$ (SP-1NPs) .

The scattering intensity of these films prepared by dipping is the characteristic one of samples with a rough surface which typically scatters the incident beam in a continuous of exit angles provoking a continuous scattering rather than in a Yoneda peak corresponding to the critical angle of the material. Figure 1 also shows the GISAXS patterns at an incident angle of 0.4º of different films prepared by spray LbL including a film $(Alg/Chi)_5$ (Figure 1b) and a nanocomposite $(Alg/Chi)_2/(NPs/Chi)_1$ (Figure 1d). It is noteworthy that the scattering pattern corresponding to a $(Alg/Chi)_5$ film prepared by spray LbL (Fig.1b) is qualitatively similar to the one prepared by dipping LbL (Fig.1a). Thus, revealing that the inherent roughness of the films prepared by spray LbL, although being lower than that of the films prepared by dipping LbL is higher enough as to provoke a continuous scattering. With regards to films with one NPs layer prepared by spray LbL the scattering intensity concentrates in a particular region which is the characteristic one of the Yoneda peak. This suggests that the intercalated layer of nanoparticles exhibits a roughness which is low enough as to provoke scattering effects associated to its reflection angle. The reported GISAXS are being anaylized by using modeling although it can be anticipated that the inherent roughness[4] of the films prepared either by spray or dipping LbL is playing a significant role on the scattering features.

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