Experiment Proposal

Experiment number GP2023028

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Experiment title	Study of the nanoscale structure of alginate fibers crosslinked with different cations by means of small angle X-Ray scattering

MRF Instrument	**SAXS Xenocs Xeuss**	**Days requested:** 1
Access Route	Direct Access	**Previous GP Number:** No
Science Areas	Chemistry, Materials	**DOI:**10.5286/ISIS.E.RB2220258
Sponsored Grant		**Sponsor:** -
Grant Title	None	**Grant Number:** -
Start Date	-	**Finish Date:** -
Similar	-	
Submission?	-	
Industrial Links	-	

Non-Technical Abstract: Alginate is a biocompatible and biodegradable anionic polysaccharide with promising application potential thanks to its reactivity and selectivity towards various metal cations. The interaction between alginate and metal cations involves both the hydroxyl and carboxylate groups on the polymer backbone and leads to the obtainment of crosslinked hydrogel structures with characteristic porosities and mechanical properties. We developed a protocol for the preparation of meter long alginate fibers, using an extrusion and crosslinking approach. The aim of the experiment is to characterize the organization of the polymer chains in the swollen crosslinked fibers by means of SAXS, to unravel the nature of both the diffusion process of the different ions within the hydrogel matrix and the crosslinking process, two aspects undoubtedly interconnected.

Publications:

ISIS neutron and muon source

Instruments Access	ZOOM
Route	Direct Access
Science Areas	Biology and Bio-materials, Chemistry, Medicine
Sponsored Grant	None
Grant Title	-
Start Date	-
Similar Submission?	
Industrial Links	

IM@IT E-platform: Yes - ISIS Facility

Days Requested: 3
Previous RB Number: 2220258
DOI:

Sponsor: –
Grant Number: –
Finish Date: –

Sample record sheet

Principal contact	Dr Rita Gelli, University of Florence & CSGI, ITALY		
MRF Instrument	**SAXS Xenocs Xeuss**	**Days Requested:** 1	
Special requirements:			

SAMPLE

Material	Alginate hydrogel crosslinked with Cu(II) ions	Alginate hydrogel crosslinked with Ca(II) ions	Alginate hydrogel crosslinked with Mn(II) ions
Formula	$(C_6H_8O_6)_n(Cu)_m$	$(C_6H_8O_6)_n(Ca)_m$	$(C_6H_8O_6)_n(Mn)_m$
Forms	Solid	Solid	Solid
Volume	0,1 cc	0,1 cc	0,1 cc
Weight	100 mg	100 mg	100 mg
Container or substrate	Sample holder for gels	Sample holder for gels	Sample holder for gels
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	Room temperature - K	Room temperature - K	Room temperature -
Pressure Range	Room pressure - mbar	Room pressure - mbar	Room pressure - mbar
Magnetic field range	No magnetic field - T	No magnetic field - T	No magnetic field -
Standard equipment	None	None	None
Special equipment	No special equipment	No special equipment	No special equipment

SAFETY

Prep lab needed	No	No	No
Sample Prep Hazards	No	No	No
Special equip. reqs	No special equipment required	No special equipment required	No special equipment required
Sensitivity to air	No	No	No
Sensitivity to vapour	No	No	No
Experiment Hazards	No	No	No
Equipment Hazards	-	-	-
Biological hazards	No	No	No
Radioactive Hazards	No	No	No
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Disposed of by instrument scientist	Disposed of by instrument scientist	Disposed of by instrument scientist

Science Case for ISIS@MACH ITALIA Experimental Proposal

Study of the nanoscale structure of alginate fibers crosslinked with different cations by means of small angle X-Ray scattering

1. Background and Context

Alginate is a biopolymer that has been attracting the interest of the scientific community due to its interesting features. In addition to its biocompatibility and biodegradability, the reactivity and selectivity towards various metal cations give alginate a high application potential compared to other polysaccharides. The interaction between alginate and metal cations involves both the hydroxyl and carboxylate groups on the polymer backbone and leads to the obtainment of crosslinked hydrogel structures with characteristic porosities and mechanical properties. With the aim of obtaining biopolymeric fabrics, we developed a protocol for the preparation of metal-alginate fibers, using an extrusion and crosslinking approach (also known as wet spinning). Filiform structures with lengths up to some meters can be easily produced thanks to the optimization of multiple parameters, namely the flow of extruded polymer and the concentration of both the polymeric and crosslinker solutions. The type of cation and the related complexation geometries allow one to obtain products suitable for several applications (wound healing, water purification, flame retardancy etc.). Furthermore, diffusion and crosslinking processes vary depending on the cation and strongly affect the structure of the fibers. It is therefore important to shed light on these phenomena, which are still not clarified, to design systems with finely tuned properties for multiple applications.

This project is part of Pietro Tordi's research activity as a Ph.D. student in co-tutorship between the University of Florence (Italy) and the University of Strasbourg (France), started on November 1st, 2022, and funded by the Italian Ministry of University and Research (MUR) for three years. The project aims to realize alginate-based composites for wound healing, water/air purification and pressure-based sensors. Part of the studies are currently being carried out at the *Institut de Science et d'Ingeniérie Supramoléculaires* (ISIS, University of Strasbourg), specifically in the Nanochemistry Lab of Professor Paolo Samorì. The Lab is an excellence in the preparation of 0D to 3D multicomponent nanostructures and networks for energy, sensing and optoelectronic applications. An accurate description of the self-assembly properties of alginate in the presence of cations will be useful for the preparation of 2D alginate-graphene pressure-sensitive devices.

2. Proposed experiment

The goal of the experiment is to study the structure of swollen alginate fibers crosslinked with various cations (Cu^{2+}, Ca^{2+}, Mn^{2+} and Ag^{+}) by means of Small Angle X-rays Scattering (SAXS). Structural organization of alginate chains depends on the characteristics of the cation (*e.g.,* charge, polarizability and preferential coordination geometry) and strongly influences the physico-chemical properties of the fibers. The fine structural characterization of the fibers is crucial to unravel the nature of both the diffusion process of the different ions within the hydrogel matrix and the crosslinking process. These two elements are undoubtedly interconnected and their knowledge will allow us to design materials with peculiar properties on different length scales. XEUSS Xenocs 3.0, due to its wide accessible wavevector (*q)* range, will be particularly useful to evaluate the order of the polymeric chains, in terms of both correlation lengths and fractal dimensions. Specifically, operating in both SAXS and USAXS configuration will allow us to unravel the organization of the polymer chains from a few nanometers to a few microns. The required scattering contrast is granted by the high amount of cationic species uniformly distributed within the polymeric matrix, as already demonstrated in some preliminary characterization. The obtained results will be complementary to SANS characterization of the swollen fibers that might be conducted at ISIS facility (proposal to be sent during the next round). Zoom instrument would be ideal to shed light on the organization of the polymer chains on the nanometer scale, taking advantage of contrast matching. Data will add value to the aforementioned USAXS and SAXS characterizations.

3. Summary of previous experimental proposals or characterisation

The fibers are prepared by extruding alginate solution in water (4% w/v) directly in the crosslinker aqueous solution by means of a 3D printer. The solutions can be either $CuCl_2$, $CaCl_2$, $MnCl_2$ or $AgNO_3$ 0.5 M, and according to the cation used the aspect and consistency of the fibers is remarkably different (see Figure 1A). The freeze-dried fibers, imaged by means of scanning electron microscopy (SEM), show a different structure at the micro-scale (see Figure 1B). Energy dispersive X-Ray spectroscopy (EDX) analysis coupled with SEM demonstrated that the fibers contain a significant amount of cation with respect to the polymer component (for instance, in Alginate-Cu the weight % of C is 46% and Cu 16%, while in Alginate-Ag the weight % of C is 29% and Ag 49%). This would reasonably guarantee a good contrast of the samples during SAXS experiments. Figure 1C displays FT-IR spectra of the alginate fibers crosslinked with Ag and Cu: the observed shift of the asymmetric stretching vibration band of the carboxylate group reveals a different complexation geometry between the two cations (pseudo-bridging unidentate for Ag and bidentate bridging coordination mode for Cu). All those data suggest that according to the cation used for the crosslinking process, modifications of the alginate structure on different length scales occur.

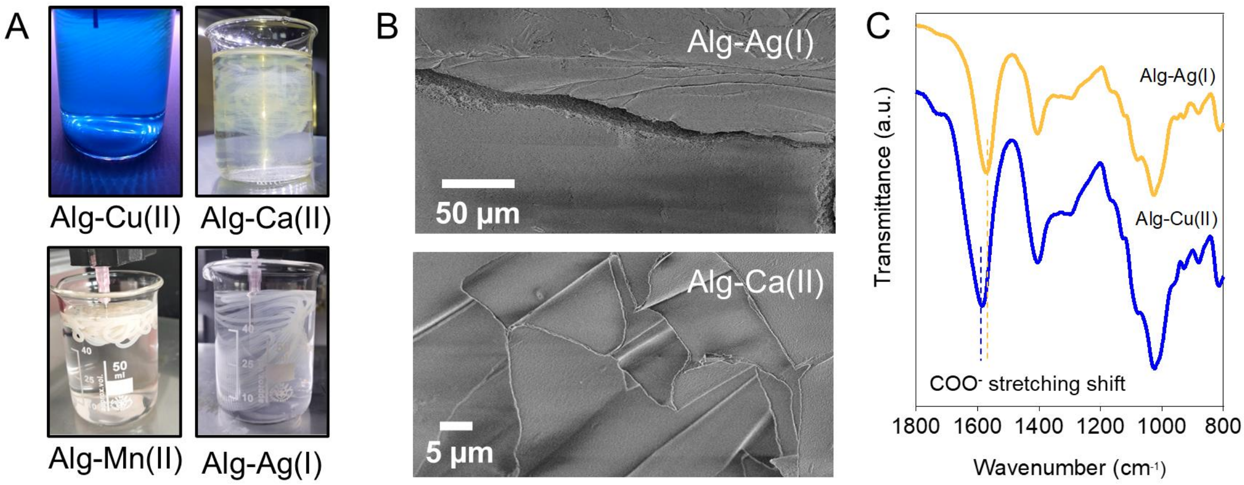

Figure 1. A) Photos of the extrusion process of the different alginate fibers; B) SEM images of the freeze-dried fibers crosslinked with Ag(I) and Ca(II); C) FT-IR spectra of Alg-Ag(I) and Alg-Cu(II).

4. Justification of experimental proposals request

XEUSS Xenocs 3.0 was selected for this experiment as it allows for the access to a wide wavevector (q) range. Specifically we are interested in operating in USAXS and SAXS configurations, therefore investigating the q range between 0.0002 Å^{-1} and 0.6 Å^{-1} approximately. The gel holder of XEUSS 3.0 is suitable for our analysis since, besides the possibility to work with swollen samples, its relatively high capacity does not force us to strongly alter the swollen polymeric fibers during sample preparation. Furthermore, the software XSACT from Xenocs is particularly user friendly and enables a fine data reduction before fitting. The number of samples to analyze would be four (swollen alginate fibers crosslinked with Cu^{2+}, Ca^{2+}, Mn^{2+} and Ag^{+}), in addition to a cell containing water for background subtraction and one containing un-crosslinked sodium alginate solution as a reference. Silver behenate (AgBeh) and Glassy carbon (GC) standards would be analyzed as reference, one time for each chosen sample-detector distance. To carry out the complete analysis, in both the USAXS and the SAXS configurations, a total of 1 day of operation is requested.