Experiment Proposal

Experiment number GP2024035

Principal investigator (*)	Dr Monica Tonelli, University of Florence, ITALY		
Co-investigator	Miss Giulia Mugnaini, University of Florence, ITALY		
Co-investigator			
Co-investigator			
Co-investigator			
Co-investigator			
Co-investigator			
Co-investigator			
Co-investigator			
Experiment title	Investigation of alginate composites containing clay nanotubes		
MRF Instrument	**ESCALB QXi**	**Days requested:**	3
Access Route	Direct Access	**Previous GP Number:**	-
Science Areas	Chemistry, Materials	**DOI:**	-
Sponsored Grant	None	**Sponsor:**	-
Grant Title	-	**Grant Number:**	-
Start Date	-	**Finish Date:**	-
Similar Submission?	-		
Industrial Links	-		

Non-Technical Abstract

The aim of this work is the development of biocomposite wires made of calcium cross-linked alginate and halloysite nanotubes (HNTs). The combination of this polysaccharide with inorganic nano fillers results in a material with enhanced physico-chemical properties, attractive across various fields of research. To prevent the aggregation of the nanotubes and obtain homogenous composites, HNTs were dispersed in presence of sodium hexametaphosphate. According to the preliminary results, some optimised formulations allowed to homogeneously disperse the HNTs, prevented the formation of aggregates, and in turns promoted the alignment of the nanoclays in specific conditions upon extrusion of the formulations. XPS analyses will provide paramount information about the interactions between the components of the composite, unravelling the environment configuration and chemical state of some selected atoms.

Publications -

ISIS neutron and muon source — **E-platform:** No

Instruments	**Days Requested:**
Access Route	**Previous RB Number:**
Science Areas	**DOI:**
Sponsored Grant	**Sponsor:**
Grant Title	**Grant Number:**
Start Date	**Finish Date:**
Similar Submission?	
Industrial Links	

ISIS@MACH ITALIA

ISIS Neutron and Muon Source

Science and Technology Facilities Council

Sample record sheet

Principal contact	Dr Monica Tonelli, University of Florence, ITALY
MRF Instrument	**ESCALB QXi** — **Days Requested:** 3
Special requirements:	

SAMPLE

Material	Alginate	Halloysite nanotubes	sodium hexametaphosphate
Formula	$(C_6H_8O_6)_n$	$Al_2Si_2O_5(OH)_4 * 2H_2O$	$Na_6(PO_3)_6$
Forms	Solid	Solid	Solid
Volume	cc	cc	cc
Weight	3 g	3 g	3 g
Container or substrate	glass vial	glass vial	glass vial
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	room temperature - K	room temperature - K	room temperature - K
Pressure Range	atmospheric pressure - mbar	atmospheric pressure - mbar	atmospheric pressure - mbar
Magnetic field range	none - T	none - T	none - T
Standard equipment	None	None	None
Special equipment	none	none	none

SAFETY

Prep lab needed	No	No	No
Sample Prep Hazards	no	no	no
Special equip. reqs	no	no	no
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 by IS	Disposed by IS	Disposed by IS

1. Background and Context

The development of biocomposite materials with fine-tuned architectures is an attractive challenge across various research fields. The combination of biopolymers and inorganic nanofillers is particularly stimulating, yielding materials with enhanced physico-chemical properties. Nowadays, numerous studies are focused on the use of alginate (Alg), a polysaccharide derived from marine brown algae able to chelate di- and trivalent cations (e.g., Ca^{2+}) resulting in physically cross-linked hydrogel. Alg can be also enriched with various additives, either to reinforce it or to include specific functionalities. In this perspective the use of halloysite nanotubes (HNTs) can result in materials with interesting physico-chemical properties. HNTs are naturally occurring biocompatible and economic aluminosilicate clays with a multi-walled tubular structure, able to entrap and gradually release various active molecules, already proven to be effective in different research areas. Alg/HNTs biocomposites are promising candidates as innovative multi-functional systems. In particular, due to their elongated structure, HNTs can be oriented through the application of an external shear force, as the one applied by brushing,[1] or during the injection procedure. Nonetheless, the alignment of HNTs during the preparation of micro- and milli-metric wires, is not straightforward, also due to the tendency of these nanotubes to form aggregates. To this purpose, a pre-treatment can be beneficial to select high aspect ratio nanotubes, separate the aggregates, and improve the stability of the dispersions, eventually using specific additives.[2,3]

This study aims at developing biocomposite wires with oriented nanotubes composed of calcium cross-linked alginate and HNTs, with or without sodium hexametaphosphate as deflocculant. This research involves the work of a PostDoc and a researcher. The team contributes to the development of such systems with their complementary experiences on biopolymers, wires extrusion, HNTs, and composites. Overall, the research is supported by a fellowship, and by The National Recovery and Resilience Plan of Italy "3A-Italy Circular and Sustainable Made in Italy" (PNRR, 3A-ITALY - B83C22004890007)

2. Proposed experiment

In order to investigate the effect of the dispersant on the interaction between the nanotubes and Alg fibres, the binding energy of some selected elements could be determined with X-ray photoelectron spectroscopy (XPS). This technique could be employed both on HNTs as powders (before and after the pretreatment involving the use of HMP, as shown in Figure 1A), and on the dry composites (Alg/HNT and Alg/HNT-HMP). To this purpose, ESCALAB QXi instrument available in the ISIS@MACH ITALIA infrastructure could be crucial, allowing to gain information on the present elements and on their chemical states.

These investigations could be also complemented with TEM experiments, to confirm if the selected process parameters induced an alignment of the HNTs along the flow direction.

3. Summary of previous experimental proposals or characterisation

We investigated various wires composed of calcium cross-linked Alg and HNTs, prepared by injecting the Alg/HNTs dispersions in a $CaCl_2$ water solution using an Hyrel 3D printer. In order to prepare stable clays' dispersions that could promote the orientation of the nanotubes upon injection, we investigated different concentration of HNTs, and we explored multiple methods of mixing, including magnetic stirring, sonication, and ultra-turrax dispersion, as well the incorporation of sodium hexametaphosphate (HMP) as dispersant (see Figure 1A). The dispersions were evaluated by means of sedimentation tests, granulometry and ζ-potential measurements, and then used to prepare the wires. Some selected dry Alg/HNTs wires were preliminarily characterized by means of SEM, both looking at the external surfaces and at the inner sections, after cutting these extruded fibres toward the extrusion direction (see Figure 1B).

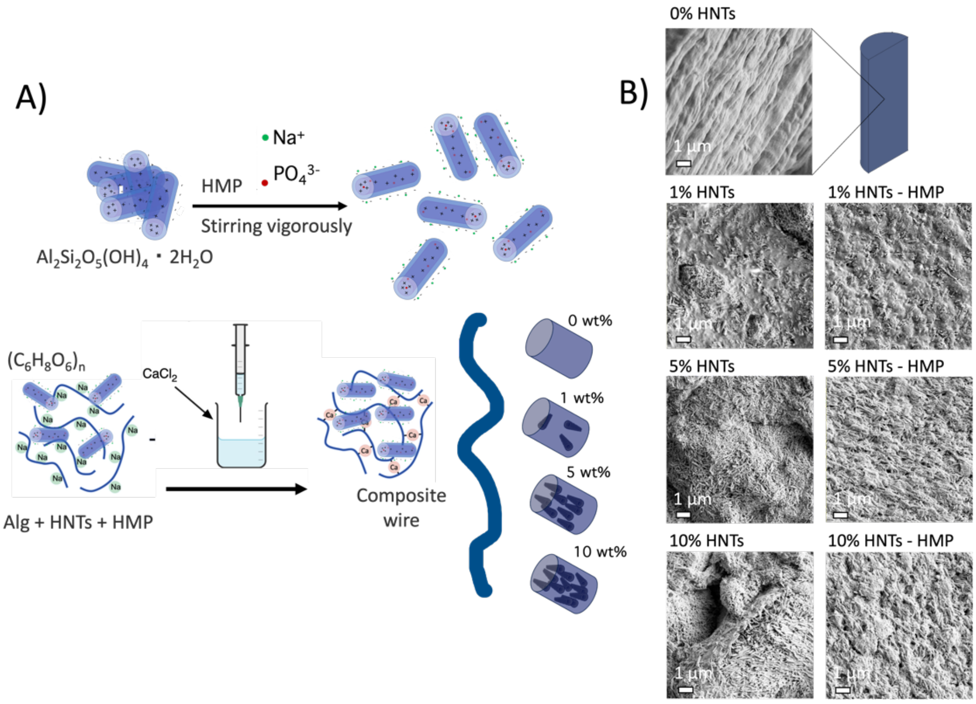

Fig 1. A) Schematic representation of the nanotubes' pretreatment and wires preparation, B) FE-SEM micrographs of the inner sections of alginate wires containing different concentration of HNTs, prepared without or with HMP dispersant.

According to the preliminary results, some optimized formulations allowed to homogeneously disperse the HNTs, preventing the formation of aggregates, and in turns promoting the alignment of the nanoclays in specific conditions.

4. Justification of experimental time requested

The opportunity to use the ESCALAB QXi instrumentation will provide paramount information about the interactions between the components of the composite. The photoemission experiments will allow to unravel the environment configuration and chemical state of selected elements, arising to the nanotubes (*i.e.* O, Al, Si and C), that could be used to evidence interactions with the other components.[4] We plan on investigating 6 different samples: pristine HNTs powder, pristine Alg powder, pristine HMP powder, HNTs/HMP powder, Alg/HNTs composite, Alg/HNTs-HMP composite. To this purpose, a working time of 3 days is expected to be needed.

[1] Zao et al., Small, **2019**,15, 1900357.
[2] Zhao et al., *J. Mater. Chem. B*, **2020**, 8, 838-851.
[3] Houta et al., *JCIS*, **2014**, 425, 67-74.
[4] Kubala-Kukuś et al., *Radiation Physics and Chemistry,* **2020**, 175, 108149.