Experiment Proposal

Experiment number GP2024036

Principal investigator (*)	Dr Monica Tonelli, University of Florence, ITALY		
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Experiment title	Study of the alignment of halloysite nanotube in alginate wires		
MRF Instrument	**TEM High Resolution**	**Days requested:**	3
Access Route	Direct Access	**Previous GP Number:**	no
Science Areas	Chemistry, Materials	**DOI:**	-
Sponsored Grant	None	**Sponsor:**	-
Grant Title	-	**Grant Number:**	-
Start Date	-	**Finish Date:**	-
Similar Submission?	-		
Industrial Links	-		

Non-Technical Abstract

Halloysite nanotubes (HNTs) are naturally occurring biocompatible and economic aluminosilicate clays with a multi-walled tubular structure, which are promising candidates for the preparation of anisotropic biocomposites. In optimised conditions, HNTs can be homogeneously dispersed in alginate solutions, preventing the formation of aggregates. These dispersions can be injected in calcium chloride bath leading to the formation of a physically cross-linked wires of sub-millimetric diameter.

According to the preliminary tests, some optimised formulations showed a promising arrangement of the nanotubes at specific clays' concentration. In order to further demonstrate if we achieved an alignment of the nanotubes along the extrusion direction, TEM measurements would be fundamental. These experiments would allow for the direct visualisation of the inner sections of the wire composites, eventually highlighting the orientation of HNTs inside the matrices.

Publications -

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

Instruments		**Days Requested:**	
Access Route		**Previous RB Number:**	
Science Areas		**DOI:**	
Sponsored Grant		**Sponsor:**	
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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 **TEM High Resolution** **Days Requested:** 3

Special requirements:

SAMPLE

Material	wires made of alginate and halloysite nanotubes	wires made of alginate and halloysite nanotubes, with sodium hexametaphosphate	-
Formula	(C6H8O6)n + Al2Si2O5(OH)4*2H2O	(C6H8O6)n + Al2Si2O5(OH)4*2H2O + Na6(PO3)6	-
Forms	Solid	Solid	
Volume	cc	cc	
Weight	1 g	1 g	
Container or substrate	stub	stub	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

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

SAFETY

Prep lab needed	Yes	Yes	-
Sample Prep Hazards	no	no	-
Special equip. reqs	resin (if not epoxy resin) and ultramicrotomy for the preparation of the samples	resin (if not epoxy resin) and ultramicrotomy for the preparation of the samples	-
Sensitivity to air	No	No	-
Sensitivity to vapour	No	No	-
Experiment Hazards	no	no	-
Equipment Hazards	-	-	-
Biological hazards	no	no	-
Radioactive Hazards	no	no	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Removed By User	Removed By User	-

1. Background and Context

Designing biocomposite materials with unique architectures poses an intriguing challenge across various research domains. The combination of biopolymers and inorganic nanofillers is particularly stimulating, yielding materials with enhanced physico-chemical properties. With this aim, the combination of alginate (Alg), a polysaccharide able to chelate di- and trivalent cations (e.g., Ca^{2+}) resulting in physically cross-linked hydrogel, with specific additives like halloysite nanotubes (HNTs) can result in materials with improved functional 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 fields of applications. These Alg/HNTs biocomposites are promising candidates as anisotropic systems, with potential application as 4D printing systems, capable of shape-morphing in response to external stimuli.[1] Due to their elongated structure, HNTs can be oriented through the application of an external shear force, as the one applied by brushing,[2] to obtain anisotropic systems. The alignment of HNTs during the preparation of micro- and milli-metric wires, on the other hand, 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 dispersion, eventually using specific additives.[3,4] This study aims at developing biocomposite wires with oriented nanotubes composed of calcium cross-linked alginate and HNTs. 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 preparation, HNTs, and 3D printing of 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

This study focuses on the effects of different experimental parameters (HNTs concentration, dispersion method, shear force applied during the extrusion) on the global distribution, orientation, and alignment of the HNTs along the extrusion direction. In this view, High Resolution TEM ThermoFisher Talos F200X instrumentation available in the ISIS@MACH ITALIA infrastructure would be crucial, allowing for the direct visualisation of the inner section of dry wire.

These investigations could be also complemented with X-ray photoelectron spectroscopy, to gain information on the surface composition of some selected samples. These analyses could further provide quantitative information on the present elements, and on their chemical states, potentially allowing to unravel interactions between the nanotubes and the biopolymer.

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 (Figure 1A). First, some preliminary tests involved the study of the processing parameters, such as the flow rate and $CaCl_2$ concentration of the coagulation bath, to unravel the effect of these factors on the morphology and dimensions of the obtained samples. In parallel, to prepare stable clays' dispersions that could promote the orientation of the nanotubes upon injection, we investigated different concentration of HNTs, also exploring multiple methods of mixing, including magnetic stirring, sonication, and ultra-turrax dispersion, as well the incorporation of a dispersant (sodium hexametaphosphate, HMP). 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.

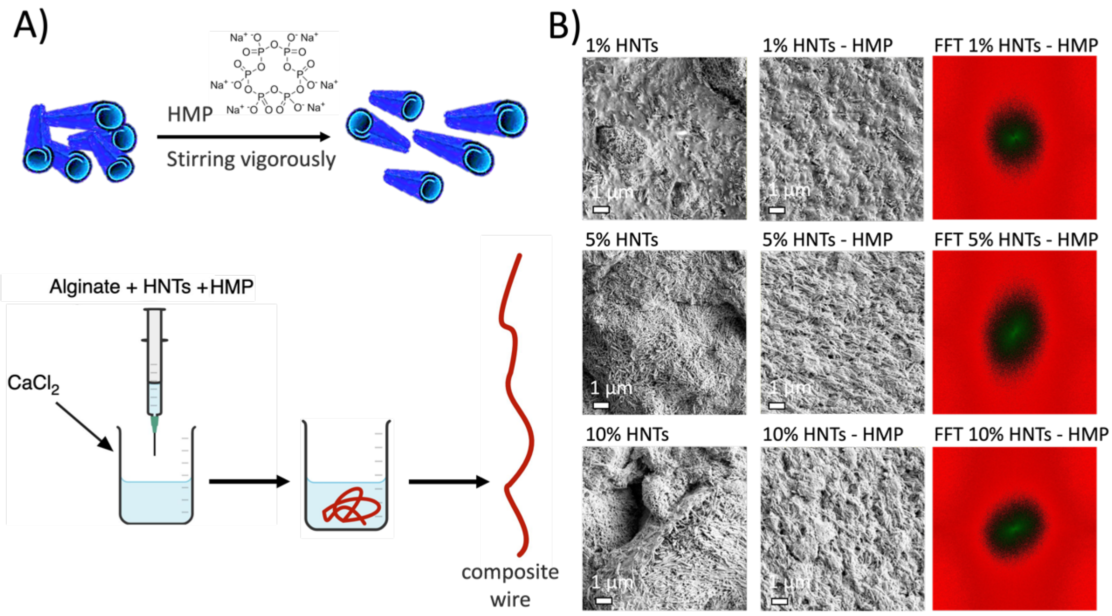

Fig 1. A) Schematic representation of the nanotubes' pretreatment and wires preparation, B) FE-SEM micrographs of the inner sections of alginate wires containing different concentration of HNTs, prepared without or with HMP dispersant. For the samples prepared in presence of HMP, the nanotubes alignment was also evaluated by means of Fast Fourier Transform.

According to the preliminary results, shown in Figure 1B, some optimized formulations display homogeneously dispersed HNTs, preventing the formation of aggregates and suggesting an alignment at specific clays' concentration.

4. Justification of experimental time requested

The opportunity to use the High Resolution TEM ThermoFisher Talos F200X instrumentation will provide paramount information about the inner structure of the composite fibres. These experiments will allow to unravel the arrangement of the nanotubes directly in the extruded biopolymer wire, and to correlate the formulations' compositions with the orientation of HNTs. We plan on investigating 4 different biocomposites, prepared in different conditions and thus potentially displaying different distributions and orientations of the nanotubes. The samples should be embedded in an epoxy resin, cut through the injection direction (*e.g.* using ultra microtomy) and then observed. Multiple areas will be investigated for each sample. To this purpose, a working time of 3 days is expected to be needed.

[1] Lai et al., *Materials & Design*, **2021**, 205, 109699.
[2] Zao et al., Small, **2019**,15, 1900357.
[3] Zhao et al., *J. Mater. Chem. B*, **2020**, 8, 838-851.
[4] Houta et al., *JCIS*, **2014**, 425, 67-74.