Research proposal

39th cycle PhD in Earth Science – Curriculum in Environment and Cultural Heritage

NEW NMR PROTOCOLS TO STUDY AND MONITOR THE DYNAMICS, INTERACTIONS AND CONSOLIDATION PROCESS OF CELLULOSIC MATERIAL

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INTRODUCTION AND STATE OF ART

When waterlogged wood is removed from its archaeological context, it seems to have preserved its appearance but in reality, it has undergone a severe chemical degradation, leading to a loss of strength and structural integrity (Broda & Hill, 2021). Moreover, the rapid evaporation of water causes further destruction resulting in shrinkage, cracking and deformation. In these conditions, wood requires an appropriate intervention with a substance that will strengthen its structure without evaporate and ruining its aesthetic (Kowalczuk J, 2019). In time, many kinds of consolidant have been tested and developed: alum, linseed oil, glycerol, sugars, organosilicon compounds and between them the most used especially for the treatment of large objects was polyethylene glycol (PEG). Early uses of PEG include the conservation treatment of the Swedish warship *Vasa* which started a year after its discovery (1961) without having been able to conduct appropriate studies on its compatibility with wood and its long-term stability over time.

It is now known that PEG makes wood more hygroscopic and sensitive to microbial and chemical degradation and that reacting with metal ions or sulfur compounds leads to the formation of formic, glycolic and oxalic acids causing a decrease in wood pH and determining conservative risks (Olek, Majka, Stempin, & Sinkora, 2016). Despite all the information gathered on the conservation status of PEG treated wood there is still little research on the dynamics of the polymer in solution and its molecular interaction with wood.

In the last decades, the studies on the drawbacks and the problems related to polyethylene glycol increased along with the necessity for a deeper awareness on the interaction between already tested products and wood. As alternative to PEG, sugar alcohol impregnation was suggested in the past by some authors in and in particular Morgós et al. found that an outstanding candidate could be lactitol with low molecular weight, high solubility, low hygroscopicity (Morgos, Imazu, & Ito, 2015). Lactitol is nowadays used in more than thirty museums and private conservation laboratories worldwide, but little is known on its dynamic behavior during consolidation process (Broda & Hill, 2021).

Among the cellulosic material of cultural heritage, paper-based works of art are considered important carrier of information about culture, science, politic and history and their safeguard is of common interest. The production process of paper changed during the centuries in response to market needs (Kolar, Strliˇc, Novak, & Pihlar, 1998), therefore the raw materials also changed. In addition to the production process, paper can undergo chemical treatments and beyond its pH, there are many other factors that influence paper durability, such as heat, humidity, oxygen, UV-visible light, pollution, lignin and degradation products (Stagno, et al., 2023). In time, the characterization of paper in terms of cellulose-water bicomponent material has been conducted (Paci, Federici, Capitani, Perenze, & Segre, 1995) and samples of old sheets of paper from different production areas have been compared with contemporary standards.

In the correct safeguard of Cultural Heritage, a multianalytical approach is desirable and the use of measurement techniques for non-invasive and non-destructive analysis should be encouraged. The use of Nuclear Magnetic Resonance (NMR) to study porous material of cultural heritage is a constantly evolving field whose potential has yet to be well developed (Longo, et al., 2023) but good results concerning its application on the study of soaked wood-consolidant system have already been obtained.

Relaxation NMR studies have proven to be extremely useful to provide information on aqueous solutions on a variety of time scales and solute concentrations allowing to identify the dynamics of different water distributions and helping to distinguish free from structured water in the presence of solutes. Clops and colleagues (Clop, Perillo, & Chattah, 2012) have used spin–lattice relaxation times measurements in aqueous solutions of polyethylene glycol (PEG 6000) to study the dynamical relation between the polymer and water molecules at different solute concentrations. Since T2 relaxation time can be used as an index of degradation occurring in cellulose based materials it is also possible to perform successfully 1H NMR relaxation studies on paper material (Castro, et al., 2011) as reported also by Mallamace and colleagues (Mallamace, Vasi, Missori, Mallamace, & Corsaro, 2018) who investigated the role of water and the hydration mechanism of cellulose fibrils in the degradation process of paper.

In the last five years, Magnetic Resonance Imaging (MRI) and NMR methods (1H NMR spectroscopy, relaxometry and self-diffusion) have shown promising perspectives to observe the drying stage of waterlogged archaeological wood conservation process with the use of different consolidant (Kowalczuk J, 2019) and on this trail a new research line has started at the NMR laboratory of the CNR ISC at the Department of Physics at Sapienza University of Rome where experiments aimed at studying time-dependent diffusion coefficient D(t) on different waterlogged wood species provide new and useful information about complex porous media, allowing the description of pore connectivity, fluid transport, the average-pore size and the anisotropic degree (Stagno, et al., 2021) that could be also applied for the study of preservative agents with the final purpose of translating the knowledge gained from high resolution investigations on consolidants and their interaction with water and wood, into a portable NMR instrument that can be used for in situ monitoring process.

It is also worth to note that portable NMR can be used for monitoring the degradation in cellulose based materials in a non-invasive way and has been recently applied in the NMR laboratory to monitor the UV artificial aging effect on paper (Stagno, et al., 2023) allowing the definition of a preliminary protocol to be further implemented with the purpose of comparing the degradation of paper realized with different production processes.

RESEARCH OBJECTIVES

General objective:
Definition of non-invasive protocols using portable NMR to monitor the conservation status of cellulosic material of cultural heritage interest.

Specific objectives:

1. Study of **water** and **consolidant dynamics** and their interaction at different concentration and pH conditions through spectroscopic studies, relaxation profiles and diffusion experiments.
2. Study of the **interaction** between **consolidant** solutions and **wooden** structure applying NMR relaxometry, diffusion and imaging (MRI).
3. Definition of a new protocol for the study of relaxation times and diffusion coefficient of treated wood through portable NMR.
4. Characterization of several types of paper, their aeging process and conservation treatments through non-invasive portable NMR.

IMPLICATIONS &/O APPLICATIONS

The definition of new portable NMR protocols could give valuable information in the study of cellulosic material of cultural heritage interest. In particular, on wood it could be useful to study the consolidation process, the state of conservation of already consolidated wood as well as monitoring the removal of previous treatment with in-situ measurement, while for paper could give information on cellulose degradation helping in the definition of the conservative status of aged paper.

WORK PLAN

Task 1: procure, creations and starting of high resolution NMR analysis on consolidant solutions – 3 months

The first step of this task will be dedicated to a punctual literary review not only on the two cited consolidant but also on finding new promising and biocompatible substances as an alternative to be tested. Subsequently one can proceed with the procurement of the materials (archaeological waterlogged wood and consolidants)

and the realization of the solutions at different concentration w/w also following literature procedures. Once the consolidating solutions have been implemented, NMR spectroscopy, relaxation and diffusion experiments for characterize their interaction with water and their behavior in different conditions (pH, concentration…) will be conducted.

Task 2: implementation and test of a protocol to realize diffusion experiment with portable NMR – 3 months

Inside waterlogged archaeological wood there is often a quantity of water which, depending on the degradation, can exceed 500%, thus exploiting the NMR diffusion studies it is possible to obtain essential information on the movement of this fluid within the porous medium. It is likewise possible to obtain information on the movement of preservative substances during the consolidation process. Considering the information that could be obtained during in situ campaign using sequences for the acquisition of the diffusion coefficient, during these months through an accurate literature review it is necessary to define an appropriate acquisition protocol thanks to which diffusion experiments with portable NMR could be realized.

Task 3: wood treatment and analysis/ paper relaxation experiments – 1 year and 4 months

Wood treatment requires successive steps of several months to allow water replacement with consolidant both in the case of polyethylene glycol and for sugar based substances. Before starting the treatment and after each step, high resolution NMR and MRI acquisitions will be conducted. Wood treatment with PEG at different molecular weight will be carried out at the NMR laboratory of the CNR ISC at the Department of Physics at Sapienza University of Rome where a collaboration had already started. At least 4 months of this task will be spent in Poland at the Faculty of Forestry and Wood Technology of Poznan University of Life Sciences with Dr. Magdalena Broda whose research focuses on the characterization and conservation of waterlogged archaeological wood developing new methods for historical wood conservation. During this period, lactitol treatment will be executed together with proton NMR spectroscopy, pulse gradient stimulated echo (PGSTE) NMR, MRI using multi slice multi echo (MSME) pulse sequence for image acquisition and single point imaging (SPI) pulse sequence to realize 1D profiles of the proton density. If possible, other consolidant will be tested in this phase. In collaboration with the Institute for the Conservation of Cultural Heritage at Shanghai University and the restoration laboratory of the Conservation Center of Shanghai Museum, experiments concerning the conservation degree of paper will be conducted through relaxation experiments (using portable NMR) within an exchange of PhD student for an indicative period of 1 to 3 months.

Task 4: data analysis and comparison of data from the different treatments – 4 months

The first part of this task should be carried out together with task 3 in fact, it is necessary to process MRI images after each step to understand what happens to wood microstructure once water starts to be replaced by consolidant substances. Even data form relaxation and diffusion acquisitions should be analyzed after any treatment, at the end of the consolidation process and after having analyzed all the data obtained, a comparison between the behavior of the two different consolidants dynamics and their interaction with wood microstructure must be done. All the results coming from the NMR and MRI acquisition will be brought together to define a protocol for low field NMR portable instrument.

Task 5: test a portable NMR protocol to study aged, consolidated wood – 5 months

According to the results obtained from the high field NMR monitoring of the consolidation process together with SEM observation on treated wood and FT-IR spectra of consolidant solutions a protocol for the study of already consolidated wood will be suggested to test if portable nuclear magnetic resonance can also give information on the conservation status of already displayed artefacts. In fact as happens for stone materials, portable NMR is a powerful tool to assess the presence of salt or humidity in the superficial layers of artefacts and in the case of consolidated archeological wood can be extremely helpful during diagnostic campaign to detect the residual presence of filling substances.

MILESTONES

- **Knowledge of the dynamical behavior of consolidant solutions -** from NMR spectroscopy, relaxation and diffusion experiments I expect to obtain information on the interaction between solute and solvent. (4-6 months)
- **Monitoring of consolidation process/ study of the interaction between wood and consolidants –** through high resolution NMR and MRI acquisitions I expect to observe the steps of consolidation process and to understand the interactions occurring between the porous matrix of wood and the filling substances highlighting differences between products also according to solute concentration/molecular weight. (18 months)
- **Definition of acquisition sequences for portable NMR analysis of already consolidated wood –** testing new protocols to obtain superficial information on treated wood to assess its conservation status. In this phase I will also evaluate the possibility of obtaining information from the removal process of consolidant from wooden matrix. (6-8 months)
- **Comparison of conservative status of paper realized with different production process –** as part of the collaboration with the Institute for the Conservation of Cultural Heritage of Shanghai, European and Chinese paper will be analyzed to highlight compositional differences and conservative status with portable NMR. (2-4 months)

DISSEMINATION PLAN & TRAINING ACTIVITIES

Dissemination will be articulated by presenting the research results in national and international conferences (i.e. Technart, MetroArcheo etc…) and by publishing scientific paper of the research in indexed journals (i.e. Journal of Cultural Heritage, Molecules, Cellulose etc…). On the I° year of work I expect to attend conferences, workshop and meetings as a listener and present preliminary results in poster session, during the II° year I will participate at national/international conferences presenting the results of my research as well as in the first part of the III° year. The last 6/7 months of the III° year will be dedicated to the thesis writing.

As for the training activities, I will attend the following institutional courses of the PhD school:

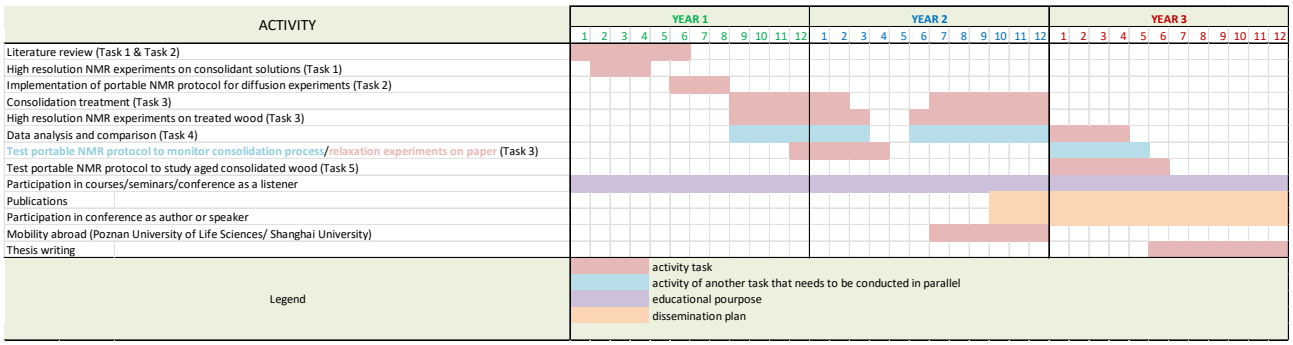
- Diagnostica applicata: progetto di valutazione e tutela di un bene culturale (Alessia Masi);
- Spettroscopie Raman e FTIR nei progetti di dottorato di Scienze della Terra (Laura Medeghini);
- Climate risk assessment for Cultural Heritage (Francesca Frasca);
- Suggerimenti su come scrivere un lavoro scientifico, preparare una presentazione e scrivere un progetto di ricerca (Cristiano Collettini, Marco Scuderi, Giovanni Andreozzi, Flavia Strani);
- Applicazioni al Microscopio elettronico a scansione (SEM) (Letizia di Bella);
- Postdoctoral Fellowships - Marie Skłodowska-Curie Actions. Starting Grant (Giuditta Carabella, Rosa Di Stefano).

I will also participate in summer schools and workshop on topics of interest.

MOBILITY DETAILS

During the II nd year of the PhD program a period of at least 4 months will be spent in Poland at the Faculty of Forestry and Wood Technology of Poznan University of Life Sciences with Dr. Magdalena Broda for the study of consolidant and treated wood. During the same year, as for the collaboration between the Institute for the Conservation of Cultural Heritage at Shanghai University (Prof. Jizhong Huan) and the NMR laboratory of the CNR ISC at the Department of Physics at Sapienza University of Rome a period between 1 and 3 months will be spent in Shanghai.

TIME SCHEDULE IN GRAPHIC FORM – GANTT CHART



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