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Tailoring Crystallinity and Mechanical Properties of Poly (Lactic Acid) (PLA): Insights into D-Unit Inclusion and Plasticizer Addition

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Poly (lactic acid) (PLA), a biobased and biodegradable polymer derived from renewable resources, offers great potential for sustainable applications, however its performance is highly dependent on its enantiomeric composition, crystalline content and use of additives. A better understanding of the influence of these factors provides new opportunities to tailor the PLA thermal, structural and mechanical properties. The incorporation of D-lactic acid units in semi-crystalline PLA was found to reduce crystallinity, increase the mobile amorphous fraction (MAF), and slightly decrease the rigid amorphous one (RAF). XRD and FT-IR analyses proved the inclusion of D-units in the crystal lattice, facilitated by CH_3···O=C interactions, which cause a contraction of the interplanar distances and a reduction in crystal cell volume [1]. The role of green plasticizers, as acetyl triethyl citrate (ATEC) and acetyl tributyl citrate (ATBC), was also explored. During crystallization, these plasticizers were found to accumulate preferentially in the MAF, while the RAF retained limited concentrations. Thermal characterization revealed that plasticized PLA exhibits reduced glass transition and cold crystallization temperatures.
The PLA mechanical properties, including the elastic modulus of crystalline and amorphous fractions, were accurately predicted by using a three-phase model, emphasizing the role of the amorphous/crystal interphase in stress transfer [2].

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Pushing the limits of the Microwave-assisted Chemical Vapor Infiltration technology for the production of large SiC_f/SiC samples with different geometries

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Silicon Carbide fiber-reinforced Silicon Carbide Ceramic Matrix Composites (SiC_f/SiC CMCs) are promising candidates for several high-temperature applications in strategic industrial sectors as energy and aerospace. However, due to their high production costs (up to thousands of €/kg), new and more efficient processing technologies are actively investigated to develop simpler, more economic and efficient approaches for a rapid densification of these materials.

The use of a Microwave-assisted heating in Chemical Vapor Infiltration (MW-CVI) processes is attractive due to the peculiar volumetric heating mechanism which releases energy selectively in the sample thanks to its dielectric absorption. The resulting inverse temperature profile allows for an inside-out SiC matrix densification pattern, avoiding the premature surface pore occlusion due to crusting, and reducing the total processing times of about one order of magnitude (~ 100 h vs 1000 h) [1-2].

In this contribution an innovative MW-CVI pilot plant for processing of large SiC_f/SiC CMCs with different geometries, developed and upgraded during two EU projects, will be presented. The practical implementation and validation of the proposed technique will be illustrated on samples of industrial relevance, emphasizing the material tailored densification and the optimization of both the energy and chemical process efficiencies [3].

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Highly-ordered nanoparticles assembly in superstructures through slow destabilization

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Recent advances in colloidal synthesis have revolutionized the nanoparticle's (NPs) manufacturing, showing immense potential in technology. Quantum dots (QDs) and lead halide perovskite (LHP) nanocrystals have particularly intriguing electronic properties and emission features, highly requested for optoelectronic and quantum information applications.[1] For successful device integration, controllable microscale structures, such as supercrystals (SCs), can be fabricated while preserving NP properties.[2] SCs are large self-assembly of NPs into highly-ordered crystalline geometries, resembling the role of atoms in crystals growth,[3] with ligand-ligand interactions dictating the final structure.[4] Anticipated benefits of SCs include novel collective electronic properties arising from dipole-dipole or electronic coupling interactions.[5-7] Despite substantial efforts, achieving precise control over SC structures, viable for technological applications, remains a challenge, due to local inhomogeneity, poor reproducibility, brittleness, and weak coupling among NPs. Here, the slow destabilization method is investigated as preparative protocol for the direct growth of both CdSe QDs and $CsPbCl_xBr_{3-x}$ LHP nanocubes in solid-state crystalline superstructures. To more closely packing the assembled NPs, He plasma treatments are also performed. The prepared superstructures are investigated by confocal microscopy, SEM, XRD, and time resolved PL techniques. The results show the effectiveness of the assembly procedure and the optical and structural properties of the microstructures.

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Advanced Electrodes for Next-Generation Renewable Energy Applications

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The development of advanced electrodes for use in various energy applications, such as Dye-Sensitized Solar Cells (DSSCs), flexible solar cells, and hydrogen production, is a critical area of research aimed at enhancing energy efficiency and sustainability. This work focuses on the fabrication of electrodes that optimize the performance of DSSCs, which are known for their potential in low-cost and high-efficiency solar energy conversion. The electrodes are designed to meet the specific requirements of flexible solar cells, which are gaining interest for their light weight and versatility in integration with a variety of surfaces. Additionally, the electrode materials are tailored for use in hydrogen production, an essential process for the development of renewable energy solutions. The study explores the materials, fabrication techniques, and performance characteristics of these electrodes, highlighting their potential for advancing renewable energy technologies and contributing to the transition toward sustainable energy systems.

Real-Time Ab Initio Simulations: Probing Electron Dynamics in Solar Cells and Sensor Materials

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Engineering material response is critical for both green energy and smart material development. This talk demonstrates how surface modifications of TiO_2 and graphene can significantly alter their conductivity, enabling their use in integrated applications such as Dye-Sensitized Solar Cells (DSSC) and ammonia sensors. Using real-time ab initio simulations under diverse boundary conditions, we explore the response of these materials to electromagnetic stimuli, providing critical insights for device optimization.

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Cutin as potential innovative biobased additive on biodegradable/biobased polymers

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Using green and innovative materials is a critical approach to addressing environmental challenges and improving industrial processes by designing innovative products from renewable resources and agrifood wastes. Tomato processing industry is one of the most important sectors in the Italian productive scenario. Italian tomato production reached about 6.1 million tons in 2022 (39.8% of total European production) [1]. The total waste amounts to approximately 5-13% by weight of global tomato production also considering the waste from defective tomatoes discarded during processing. Currently, tomato waste is used as animal feed and/or fertilizers or disposes in landfill [2]. For these reasons, innovative valorization strategies of tomato waste are currently among the top environmental targets, and alternative uses need to be proposed. Cutin is one of the main components of the cuticular membrane of the tomato peels. Cutin is essentially a hydrophobic bio-polyester made up of esterified hydroxylated and epoxy hydroxylated C16-C18 fatty acids which exhibits excellent barrier properties [3]. Despite its ubiquity in terrestrial plants, cutin is traditionally underutilized as a raw material due to its insolubility [4]. This work assesses innovative strategies for the exploitation of cutin in new biodegradable materials [5].

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Biohydrogen production from photosynthetic microorganisms

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Hydrogen is considered the most promising green fuel among clean and renewable energy sources due to its high conversion efficiency, great energy potential, and sustainability. The production of biological H_2 represents the most sustainable approach, and within this category, the use of photosynthetic microorganisms is considered the greenest [1]. Photosynthetic bacteria can produce biohydrogen by utilizing organic acids as carbon and energy sources. Additionally, biodegradable industrial byproducts rich in carbohydrates, such as brewery and coffee wastes, can be used as secondary feedstocks for bacterial growth and, eventually, hydrogen production.
The photosynthetic bacterium *Rhodobacter sphaeroides* was chosen for its remarkable metabolic versatility and its ability to export electrons through the extracellular electron transfer mechanism. Its growth and the photoinduced electron transfer process (both anodic and cathodic) can be suitable tuned to enhance biohydrogen production. The encapsulation of *R. sphaeroides* with polydopamine [2, 3] was explored as a strategy to improve electron transfer efficiency and stability in biophotoanodes. This bio-inspired conductive polymer acts as a mediator, facilitating the interaction between bacterial cells and the electrode surface while preserving cellular viability and activity. Furthermore, the use of waste-based substrates represents an innovative approach to combining industrial waste valorization with the generation of clean and sustainable energy.

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Stone wastes valorization by melt blending with biodegradable polymers

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An important scientific interest is devoted to the recovery and recycling of stone sludges from mining activities and processing plants. In this framework, the STONE subproject (SusTainable ecOdesign reusiNg quarrying wastE) in the frame of PNRR Project PE_00000004 MADE IN ITALY CIRCOLARE E SOSTENIBILE aims to promote the sustainable use of stone sludge from local quarrying and manufacturing activities coming from 3 national geoclusters: Sicily, with the «Pietra Lavica dell'Etna» (Lava Stone, LS) and the «Perlato di Sicilia» (Marble Sicily, MS), Puglia, with the «Pietra di Apricena» (Marble Puglia, MP) and Tuscany with the «Marmo di Carrara» (Marble Tuscany, MT). The four different marble powders were characterized thermally and morphologically and used as fillers for the preparation of biodegradable matrix composites in batch mixers [1] by IPCF. Poly(Lactic Acid) (PLA) and polybutylene adipate-*co*-terephthalate (PBAT) are chosen as polymer matrices due to their biodegradability, availability on the market the former and its elasticity the latter. The tunability of the composition is demonstrated in both cases and the composites are completely characterized [2]. Small 3D printed manufacts from composite powders are shown [3, 4].

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BIOSMARTFERT: Advancing Sustainable Biofertilizers through Smart Release Technology

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In the framework of the circular economy, the **BIOSMARTFERT** project aims to develop a new generation of **sustainable biofertilizers**, known as **SMART Release Fertilizers (SRF)**, derived from biowaste digestate. The production process begins with the **anaerobic biorefinery treatment** of agri-food waste, including dark fermentation in continuously stirred tank reactors to generate digestate and volatile fatty acids (VFA). These VFAs serve as precursors for **polyhydroxyalkanoates (PHA) biosynthesis** by photosynthetic microorganisms [1]. The extracted PHAs are characterized and then processed into **hydrogels and pellets** that encapsulate granulated digestate, enabling a **controlled and efficient nutrient release [2]**. SRF formulations will be tested on agronomic plants in mesocosms; **NMR spectroscopy will be employed to monitor the release of** nutrients from SRF. The SRF production is then evaluated through **life cycle assessment (LCA) and economic analyses**. **IPCF is involved in the investigation and set-up of** environmentally friendly, low impact or water-based extraction and purification methods to replace conventional toxic solvents like chloroform ($CHCl_3$), aligning with green chemistry principles [3]. NMR will allow linking PHA properties to composition, aiding extraction, formulation and release evaluation. BIOSMARTFERT represents a breakthrough in biofertilization, offering a **smart, sustainable, and eco-friendly** alternative for modern agriculture.
Other partners of the projects are: CNR-IRET, Università di Pisa, Università degli Studi della Campania "Luigi Vanvitelli".

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Towards compact and portable Raman Optical Tweezers setups for the detection and chemical analysis of micro and nanoplastics

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Every year, 11 million tons of plastics enter our ocean and estimates suggest that 92% of all the plastic objects on the ocean surface are microplastics. Our understanding of the fate and distribution of micro- and nano- plastics in the marine environment is limited by the intrinsic difficulties of the techniques currently used for the detection, quantification, and chemical identification of small particles (usually greater than 20 μm) in liquid. We use optical tweezers, a powerful tool for the contactless manipulation of micro-objects by light, combined with Raman spectroscopy to investigate single micro and nano plastics made of different materials and shapes overcoming the capacities of standard Raman spectroscopy in liquid, intrinsically limited to ensemble measurements. Here we report on the development and first applications of a portable Raman tweezers system integrated with a microfluidic system for the investigation of microplastics dispersed in water. This system enables us to count and characterize microplastics in water directly after collection, as well as in their collection areas such as seas, rivers and lakes. By conducting analyses immediately after collection, we mitigate potential issues arising from sample aging, such as sedimentation or bacterial growth.

Implementation of microfluidic platform to portable Raman tweezers: application to microplastics detection.

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The presentation will describe an implementation of microfluidic platform with portable Raman tweezers. The setup has been used to identify microplastic pollutants in environmental samples, such as trapping and analyzing microplastics in digested mussels, digested zebrafish, and detection of degraded expanded polystyrene. The setup conjugated with the microfluidic platform allows us to detect sub-20 µm plastics particles in real-world samples under controlled conditions, increasing of the volume limit of the analyzed sample. This work is part of Nanosoftlab's ongoing research and development [1-3].

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Road traffic noise new challenges for data gathering

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Road traffic noise estimates are crucial for limiting health effects due to noise in cities. In IPCF studies are carried on within PRIN 2022 OUTFIT, Bilateral project CNR – RA and GIOVANISI INTREPID. Besides the new CNOSSOS-EU modeling method has increased accuracy on emission database of vehicles, input data are difficult to gather on large scale. Crowd-sourced data are a valuable resource since travel times can provide dynamic information to model road traffic. In fact, any traffic model needs a local input regardless of the approach used. These data potentially can drive traffic policy and decisions to decrease noise or air pollution and improve citizens' health in cities. Since crowdsourced data are limited available, not always free, and needs to be tuned to the context, studies also explores data gathering with AI cameras and compared results with other more costly input data collection methods. Studies have shown the usability of crowdsourced data to estimate noise with sufficient accuracy compared to other methods, but only for limited roads and periods which are over a threshold of traffic, essentially on main roads. Together with other tools like ITS, cameras for traffic recognition through machine learning, crowdsourced can enable dynamic decisions for health.

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Environmental acoustic research and Sound Event Classification using Transfer Learning

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The presentation will explore the on-going activities on environmental acoustic, with particular focus on supporting to long-term noise monitoring, which are essential to ensure compliance with regulations. In fact, this process requires the removal of spurious sounds unrelated to the target or to the typical soundscape of the area where the source under investigation is located. Traditionally, such tasks relied on manual labelling by operators, but recent advancements in data analysis highlight that the moment has come to automate the process with advanced tools like machine learning. Pre-trained models, widely available in the literature, are trained on extensive datasets covering numerous classes and serve as a foundation for developing specialized machine learning models fine-tuned for specific tasks or classes subsets. This study presents a Transfer Learning approach to leverage the knowledge of the Contrastive Language-Audio Pretraining (CLAP) model for a classification task focused on a subset of its original classes. Although the CLAP model has demonstrated adaptability across a broad range of classes with good results, the findings of this study suggest that the application of Transfer Learning can enhance accuracy for the selected subset of environmental sound classes.

Preparation and characterization of antioxidant and electroconductive PLGA/gelatin-based films for biomaterial applications

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Biodegradable polymeric films with antioxidant and electroconductive properties are being investigated for different applications in biomaterials, particularly in tissue engineering, as oxidative stress and impaired electrical conductivity are key challenges in the design of functional scaffolds for electrically active tissues like cardiac and neural tissues.

This study focuses on the preparation and characterization of PLGA/gelatin-based films incorporating different antioxidant and potentially conductive molecules to evaluate their physicochemical properties and functional performance.

Films were prepared via spin-coating and controlled solvent evaporation and analyzed through Fourier-transform infrared spectroscopy (FTIR) for chemical composition, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for thermal properties, and tensile testing for mechanical behavior.

Antioxidant activity was assessed using the DPPH assay, while impedance spectroscopy was used to evaluate conductivity.

Degradation and release studies were conducted to determine stability and bioactive compound availability over time.

These results will be used for the selection of the most suitable molecules for future biological evaluations and potential applications in tissue engineering.

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Synthetic and Physiological Nanovectors: Designing the Future of Diagnosis and Therapy

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Smart nanocarriers for diagnostic and therapeutic applications offer promising advancements in medical practice. Tailored artificial nanocarriers can be synthesized using organic and/or inorganic components for clinical purposes. Commonly explored nanovectors include lipid-based, polymeric, and mesoporous silica-based nanostructures, which effectively encapsulate and deliver therapeutic or diagnostic agents to targeted sites. Additionally, inorganic nanostructures, such as those composed of metals, semiconductors, carbon, or oxides, can be incorporated into these carriers, forming hybrid nanoplatforms with enhanced targeting, drug delivery, photoactivity, and magnetic properties, expanding their clinical utility[1-6]. Moreover, naturally occurring extracellular vesicles (EVs) can be isolated and loaded with bioactive compounds, representing next-generation drug delivery systems due to their high biocompatibility, biorecognition, stability, and target specificity[7-10].

Based on these foundations, we developed a comprehensive platform of multifunctional nanovectors, subjected them to physicochemical and biological characterization. The results demonstrate the successful creation of these nanoplatforms, positioning them as promising candidates for inflammatory disease applications.

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Investigating Cosmic Dust Analogues with Acoustic Raman Tweezers

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Meteorites and cosmic dust hold crucial information about the origin and evolution of the Solar System (Jacket et al., 2024). Identifying their composition and assessing the presence of organic matter on their surfaces, while minimizing alteration or contamination, is essential for planetary science.

In this work, we explore the application of **Acoustic Raman Tweezers (Ferretti et al., 2024)** to study materials that mimic meteorite composition, including phyllosilicate dust and other minerals such as magnesium sulfate, artificially doped with organic molecules in the laboratory.

Acoustic Raman Tweezers provide a powerful, contamination-free approach for trapping and analyzing small particles. This technique combines **Acoustic Levitation (AL)** for contactless manipulation of grains (ranging from 10 µm to 1 mm in size) with **Raman Spectroscopy** for molecular identification. The levitator used in this study is a **TinyLev device** (Marzo et al., 2017), which consists of two opposing spherical-cap arrays of ultrasonic transducers. Within this system, an acoustic standing wave creates multiple trapping sites along the device's symmetry axis, positioning particles at the nodes of this wave. The traps can be displaced collectively by adjusting the phase delay between the ultrasonic transducer arrays, allowing controlled manipulation of the levitated samples.

This approach offers a promising pathway for the non-invasive study of extraterrestrial materials, preserving their pristine properties while enabling precise spectroscopic analysis.

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Application of Fast Differential Scanning Calorimetry in the study of Soft Condensed Matter

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DSC has always been an invaluable tool for studying the thermodynamics of materials thanks to its reliability and versatility. Recently, with the improvements made in the field of chip-based calorimetry, Fast DSC (FDSC) has emerged as a new type of calorimetry [1], opening new perspectives in the field of thermal analysis. Indeed, the reduction in mass by three orders of magnitude gives access to scan rates of up to 40,000 K/s, allowing faster kinetics (down to ms) to be monitored and reorganization processes to be better suppressed. Traditionally, FDSC has been applied to ideal samples such as polymers or metallic glasses. However, thanks to recent improvements in data analysis methods, small organic molecules can also be studied [2].

We here propose two case studies of FDSC applied to molecular compounds of pharmaceutical interest. In the first case, Indoprofen, a highly crystallisable drug is studied, demonstrating how the high scanning rates now available allow the study of crystallisation kinetics that would otherwise be inaccessible. The second application is on PLX4720, a drug used in the treatment of melanoma, to demonstrate how the same phenomenon, crystallisation, can be suppressed or induced using the same high scanning rates.

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Antimicrobial Screening of the Engineered Nanocomposites and Nanosystems

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In recent years, bacterial drug resistance has sharply increased, posing serious risks to human health and the environment[1]. Traditional disinfectants face limitations that promote the development of resistant pathogens[2], motivating the search for alternative solutions. Nanomaterials have emerged as promising alternatives[3], due to their exceptional antimicrobial properties[4].

At IPCF-CNR in Bari, in collaboration with the Chemistry Department (Bari' University), advanced nanostructured materials and innovative strategies are under continuous investigation to combat pathogens. This study reports on the antimicrobial activity of various nanostructures and nanocomposites, including mesoporous TiO_2–AgNPs, AgNPs encapsulated within or anchored to mesoporous silica nanoparticles, carboxylated nanographene oxide–AgNWs, histidine-reduced graphene oxide–AgNPs, and TiO_2-based coatings, synthesized by using state-of-the-art colloidal chemistry techniques, to elucidate different pathogen inhibition mechanisms, such as metal cation release, catalytic, and photocatalytic activities.

Results showed that Ag-based nanostructures enhance antimicrobial activity at low doses by stabilizing AgNPs with mesoporous silica, while engineered TiO_2-based nanostructures inhibit pathogen growth by generating reactive oxygen species via photocatalysis. Two graphene-based nanocomposites demonstrated effective antimicrobial action through different via: photocatalytic mechanism and ions release.

The study evaluates the antimicrobial effectiveness of nanocomposites under light and dark conditions, analysing different doses and exposure times for optimizing their efficacy.

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Microwave-assisted processing of materials at IPCF Pisa

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Microwaves are well-established as heating mechanisms in many chemical processes, thanks to their peculiar advantages such as selective energy release, volumetric heating, and fast temperature dynamics [1].

In IPCF Pisa, there is a decennial experience in Microwave-assisted Chemical Vapor Infiltration (MW-CVI) of SiC-based, Ceramic Matrix Composites (CMCs) preforms using a pilot-scale reactor [2], and in their dielectric characterization at high temperatures [3].

In processing CMCs, relevant interest has recently been raised in the microwave joining of different components. This technique exploits the localized heating of the joint area made possible by electromagnetic waves. The first experimental results on the joining of SiC_f/SiC tubes will be illustrated.

A second branch of activity involves developing a lab-scale reactor for processing and characterizing small samples. This reactor is currently employed for the microwave-assisted sintering of biocompatible ceramics [4] and for investigating microwave-activated catalytic ceramics [5]. Some preliminary results of these activities, aiming to highlight the potential of the employed technique, will be briefly illustrated.

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Microwave dielectric characterization at high temperature

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Characterization of dielectric properties of materials in the range of microwave radiation is essential for processing them using the energy provided by microwaves. In particular, the microwave heating has been proven to be effective to bring about either physical or chemical processes that provide materials with desired properties.

In this contribution two techniques are described for the measurement of the complex permittivity of materials at microwaves and various temperatures. Both methods are based on a resonant cavity, whose resonance frequency ν and quality factor Q are modified by the sample. The dielectric properties are obtained from the variation of ν and Q.

In the first method, the sample is heated in a conventional oven before entering the microwave cavity for the measurement [1, 2]. This method is very accurate but relatively slow, being constrained by the thermalisation of the sample.

The measurement method is fundamentally non-perturbative and the data analysis consists in a rigorous numerical modeling of the cavity. This is required since the changes in the dielectric response of the material during the heating process can be large and the permittivity imaginary part can induce a great rearrangement of the electric field.

The second method differs from the first one only in the heating of the sample that is based on the microwaves. It enables much faster measurements, at a cost of a lower accuracy and control of the process. The second method is currently under development. Its benefits and drawbacks are discussed.

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Development of a resonant microwave cavity for the evaluation of dielectric properties of apatite ceramics

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Controlled carbonate substitution in hydroxyapatite (HA) ceramics is a relevant approach to generate biodegradable bone substitutes. Their biodegradation, ruled by the precise location and proportion of carbonates, grain size and porosity [1], is difficult to manage with conventional sintering. Allowing fast heating, microwave (MW) sintering could provide a solution to obtain CHA with biologically relevant physico-chemical properties. While MW sintering of stoichiometric HA is well documented [2], its carbonation under CO_2 to produce CHA remains to be investigated [3]. The efficiency of MW heating depends on the dielectric properties of the material. Understanding its evolution can provide solutions to avoid thermal gradients and overheating.

This contribution aims to study the changes in dielectric properties of HA during MW reactive sintering according to composition and densification evolutions. To this aim, a dedicated measurement setup was developed, which can characterize the dielectric response of the sample during the sintering process. It includes a MW cavity resonating at 2.45 GHz, a tunable MW source, a high-resolution thermal camera, and routines to automate the acquisition of the resonance curves. An *a posteriori* rigorous data analysis is applied to obtain the dielectric data. First results showed a significative impact of OH-sites chemistry evolution on dielectric properties, implying important consequences on the thermal behavior of HA during reactive sintering. Also, an important increase of the dielectric losses occurs at the densification's onset temperature.

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Contribution of the Amorphous/Filler Interphase to Properties of Poly(lactic acid)-based Nanocomposites

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Bio-based and biodegradable polymers, sustainable alternatives to traditional petroleum-based polymers, are interesting materials because able to positively contribute to the current environmental concerns in terms of the plastic pollution and greenhouse gas emissions. In this regard, poly (lactide) (PLA) has been and is widely used due to its biodegradability, biocompatibility and quite low cost.

To improve its mechanical and barrier properties, various modification techniques have been utilized, as for example incorporation of nano-sized fillers to produce nanocomposites. Owing to their nanoscale dimensions, the polymer/nanofiller interphase represents a significant volume fraction even at low filler concentrations [1].

In this regard, the major challenges to develop PLA-based nanocomposites for advanced technological applications is the capacity to understand the structure and properties of the interphase between the polymer and nanofiller.

The present study contributes to a better knowledge and understanding of the role that the nano-sized interphases (at the amorphous/crystal and at the amorphous/filler boundaries) can have on the mechanical and barrier properties of PLA nanocomposites.

Various nanofillers have been used for the preparation of PLA nanocomposites by extrusion. Thermal, mechanical, viscoelastic, barrier properties have been evaluated. The aim of the study has been to identify how the various macroscopic properties are differently influenced by different nanofillers.

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Amorphous/Crystal and Amorphous/Filler Interphase in Poly(butylene furandicarboxylate)-based Nanocomposites

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Bio-based and biodegradable polymers, which are sustainable alternatives to traditional petroleum-based polymers, are interesting materials because able to positively contribute to the current environmental concerns in terms of the plastic pollution and greenhouse gas emissions.

Furandicarboxylate-based polyesters have emerged as new interesting bio-based polymers, alternative to terephthalate-based polyesters. All the furandicarboxylate-based polyesters exhibit better mechanical, thermal, and gas barrier properties with respect to the homologous terephthalic-based polyesters [1] Biodegradation of this family of polyesters can be improved by introducing aliphatic units in the chain. But this chemical modification worsens the mechanical and barrier properties of the material [2]. A technique useful to counterbalance the negative effects of the aliphatic sequences on the mechanical and barrier properties is the incorporation of nano-sized fillers to obtain nanocomposites.

This study has been focused on the preparation of bio-based and biodegradable nanocomposites of poly(butylene furandicarboxylate) (PBF) and PBF-based copolymers to produce materials with good mechanical, barrier and biodegradation properties.

The aim of the present study has been to investigate the role that the nano-sized interphases, at the amorphous/crystal and at the amorphous/filler boundaries, have on the mechanical and barrier properties of nanocomposites of PBF and PBF-based copolymers.

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Local dielectric spectroscopy as a scanning probe method for nanoscale crystallinity mapping in semicrystalline polymers and polymeric nanocomposites

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Determining crystal size, typology, and distribution in the amorphous matrix in semicrystalline polymers becomes challenging when the crystal size is reduced to the nanometric scale. Spatially resolved diffraction techniques, like electron diffraction in transmission electron microscopy, demand high crystalline order, often absent in polymers, where crystalline structures can be somewhat disordered. Furthermore, functional properties of crystals in contrast to those of the surrounding amorphous material can be of interest, for instance, the dielectric constant and the role in establishing Maxwell-Wagner-Sillars or interfacial polarization that is at the base of nanodielectrics [1]. Another relevant issue is how the properties of the polymer are perturbed at the interface with inclusions in nanocomposites. Measurement methods to access directly to these properties are scanning probes with sensitivity to electrical properties. Local Dielectric Spectroscopy (LDS) [2] allows obtaining local dielectric spectra with a few nanometers spatial resolution [3], with a frequency range of up to 8 decades [4], not far from that of Broadband Dielectric Spectroscopy (BDS). In this work, applied LDS to semicrystalline polymers like poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and its nanocomposite with BaTiO3 nanoparticles (NPs) [5]. By exploring the dependence on temperature and position of spectral features [6] related to the amorphous or the crystalline state, that can be derived from studies of the bulk, discrimination of different phases can be possible.

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CircularEconomyCable PROJECT - Sviluppo e prototipazione di innovativi cavi elettrici e per telecomunicazioni ad elevata circolarità, tracciabilità e visibilità, per consentire la piena attuazione dei principi del circular economy e della transizione digitale nei settori del trasporto energia e della connettività dati

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The CircularEconomyCable project involves the design, development and prototyping of innovative cables for energy transport and telecommunications. The cables produced will integrate innovative compositions characterized by levels of environmental sustainability superior to the current state and innovative functions such as high visibility by the addition of specific additives with properties of high reflectance, fluorescence and phosphorescence, thus increasing the speed and efficiency of the laying, maintenance and verification procedures, minimizing the possibility of collision or involuntary contact, indelible marking with anti-counterfeiting characteristics.

The PolyGreenLab research group of the IPCF is involved in all objectives of the project starting with the analysis of the state of the art, and then in design and preparation on a laboratory scale and their characterization of new polymer formulations with low environmental impact [1]. These materials aim the replacement of those currently used by the lead company with improved characteristics of high visibility by the selection and addition of selected additives [2]. It supports also the other process steps for industrial scale-up. IPCF coordinates also research activities carried out by data modeling and machine learning, also through innovative methods based on the so-called Topological Data Analysis (TDA) carried out by ISTI-CNR. IPCF is also focused on training activities and dissemination and exploitation of the knowledge deriving from the research results by organization and participation to both scientific and public engagement events.

Partner Leader: Tratos Cavi S.p.A

Other partners: LASI S.r.l., OPUS AUTOMAZIONE S.p.A., KODE S.r.l., SPIN-PET S.r.l.

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ATTITUDE PROJECT - vAlorization of wasTe products for the fabrication of sustainable paTient-personalIzed paTches targeting different phases of the woUnD hEaling cascade

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ATTITUDE project engineers 3D printed patches targeting specific phases of Chronic skin wounds (CSW) recovery process (persistent inflammation/bacterial contamination and wound closure/normal healing) according to a patient-personalized approach in terms of geometrical features, payload type/content, and cell source to overcome drawbacks of available therapeutic approaches.

ATTITUDE develops 3D in vitro bioengineered wound models for a more reliable and sustainable testing of newly developed therapeutic approaches in a more realistic scenario and according to the 3R principle, by combining sustainable and eco-friendly materials, therapeutic agents and fabrication approaches, releasing a new way of thinking and approaching CSW management.

In this frame, the PolyGreenLab research group of the IPCF with the support of the its associated researchers from Biomedical Engineer Lab of Politecnico of Torino, is directly involved in the coordination of the project, due to the large experience collected in the field [1-3] and in all the research activities from the analysis of the state of the art on new bioink formulations, to the set-up of low impact extraction of **natural polymers from renewable**, design of drug-loaded patch, development of in vitro bioengineered wound model and support the validation of the approach.

Other partners: IFC CNR di Pisa.

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Process controlled nanostructure and superhydrophobicity of thin film prepared ablating titanium in mixed Ar/N_2 atmosphere

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Thin films were synthesized using pulsed laser ablation of a titanium target in a controlled atmosphere of argon (Ar) and nitrogen (N_2). By varying the Ar/N_2 ratio at constant total pressure of 40 Pa, we explored the effect of the gas composition on the surface morphology and superhydrophobic properties of the films. In films deposited in pure gas (Ar or N_2) arrays of nearly spherical nanoparticles grow, whereas in films grown in mixed Ar/N_2 atmospheres complex cauliflower-like structures develop. These morphological differences, influenced by the Ar/N_2 ratio, resulted in varying sizes and densities of the surface features, with contact angles exceeding 150°, corresponding to superhydrophobic behavior. Numerical analyses, including Fourier transform and multifractal analysis, confirmed the presence of dual-scale hierarchical structures responsible for the superhydrophobicity. Our results demonstrate that by adjusting the Ar/N_2 ratio it is possible to tune the surface properties of thin films, offering potential applications in coatings and sensors requiring specific wetting characteristics.

Optical forces in front of Epsilon-near-zero (ENZ) metasurfaces

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Optical tweezers [1] can be used to measure very tiny forces, in the order of few tens of fN, with a sensitivity one order of magnitude lower [2]. A micro- or nano-sized trapped particle can be used as a probe of the interaction forces in front of surfaces, obtaining an all-optical scanning-force microscope [3]. Recently, it has been demonstrated [4] that in front of Epsilon-Near-Zero (ENZ) metasurfaces a repulsive force is expected on a point dipole. Thus, a theoretical and experimental study of the interaction forces between larger particles and ENZ metasurfaces is interesting. Here we review the results [5] obtained by means of different theoretical approaches, looking at the general features of the repulsive-attractive optomechanics of a range of complex particles (dielectric, core-shell, plasmonic ellipsoids), with size ranging from the nano to the microscale. Also, we show the experimental results obtained by using photonic force microscopy to measure forces in front of dielectric, plasmonic and metamaterial surfaces. As a probe we use a dielectric bead in liquid environment, trapped by a tightly focused near IR laser beam. The axial position of the trapped particle is perturbed by a second pulsed laser in the visible. We observe that the optomechanics of the particle depends on the type of surface in front of which it is trapped. Moreover, in front of ENZ surface a dependence on the wavelength of the probing beam is observed. The possible origin of these behavior is also discussed.

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Boosting Raman and Photoluminescence by plasmon-enhanced spectroscopies: ultrasensitive detection and characterization of biomolecules and 2D materials

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Surface- and tip- enhanced Raman spectroscopies (SERS and TERS) are advanced techniques for ultrasensitive detection and characterization of molecules and nanomaterials. Here it will be shown how to exploit optical forces to push gold nanorods and to control their aggregation into SERS-active clusters enabling biomolecular detection at trace level in liquid environment [1]. Within the activities of PRIN2022 SEMPER project, we explored the possibility to use new dye molecules as Raman or Photoluminescence (PL) reporter for a more efficient in-liquid specific SERS detection of microRNA. This takes advantage of the dye integration into properly designed DNA strands, which specifically bind to the target biomolecule.

Finally, the potentialities of TERS spectroscopy will be shown. Thanks to the combination of scanning probe microscopy with plasmonic nanotips, this technique enables a simultaneous morphological and spectral nano-characterization of thin molecular films and nanomaterials [2,3]. Within the activities of PRIN2022 FLASH-2D project, we have monitored at the nanoscale the Raman/PL response of transition metal dichalcogenides 2D materials (2D TMD), like few layered MoS_2 flakes, while interacting with plasmonic periodic substrates. This spectral analysis can provide new insight to the electronic band structure of these hybrid systems, fostering the optimization and miniaturization of optoelectronic devices.

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Ag Nanoparticles decorated Reduced Graphene Oxide based hybrid nanocomposites for antimicrobial textile coatings

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In response to the demand for effective pathogenic bacteria control and the limitations of traditional treatments, the advancement of antimicrobial materials has become imperative. Ag nanoparticles (NPs) are among the most widely used solutions for tackling this issue due to their broad biocide effect, but their strong tendency to aggregate and oxidase, leads to a deterioration of their antibacterial activity [1]. Reduced Graphene Oxide (RGO) has been found an ideal scaffold for stabilizing Ag NPs and their biocidal effect. In this work, a novel, *in situ*, colloidal approach was used for synthesizing a new colloidal hybrid nanocomposite formed of RGO functionalized with histidine (His), and decorated with citrate coated Ag NPs, starting from $AgNO_3$ in presence of trisodium citrate and sodium borohydride. The role of the synthetic parameters on the morphology of the Ag NPs and on their coating density onto His-RGO has been investigated to elucidate the mechanism of NPs formation. Ag NPs, 24± 4 nm in size, were found to form on His-RGO anchoring by coordination to the $-COO^-$ and -N- groups of His [2], and the interplay between trisodium citrate and borohydride concentration, along with the pH, were found to define sheets coating density and NPs morphology. The quantitative standard ISO 20743:2021 protocol was used to assess the hybrid nanocomposite as an antimicrobial coating against E. coli upon transfer on cotton, against coatings based on His-RGO and Ag NPs. The nanocomposite showed a superior and longer-term biocidal effect with respect to pristine Ag NPs based coatings.

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Sustainable and flexible SERS Sensors for non-invasive Cultural Heritage analysis: achievements and perspectives

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As part of the SAMOTHRACE project, a sustainable approach for the development of flexible Surface-Enhanced Raman Spectroscopy (SERS) sensors has been designed for non-invasive identification of pigments, dyes, and alteration products in cultural heritage. The SERS devices are based on cellulose substrates derived from biomass waste, coated with nanostructured Ag films via Pulsed Laser Deposition (PLD). Alternative solutions employing Ag colloid nanoparticles are also under investigation. The prototypes of sensors demonstrated high sensitivity, achieving a detection limit of 10^{-10}M for Rhodamine 6G and 10^{-7}M for violacein, a natural bacterial pigment used as an alternative sustainable probe molecule, under identical conditions. Their performance was validated through extensive laboratory testing using mock-up samples simulating real-world applications on different substrates such as wood, canvas, and plaster. The system, integrated with portable and benchtop Raman spectrometers, enables in situ analysis while ensuring eco-sustainability using renewable materials and green manufacturing processes. Currently, we are expanding the application to real artifacts collecting data from Museum artifacts, to assess the full potential of these sensors. This research represents a significant step towards the development of sustainable, portable, and non-invasive analytical tools for cultural heritage diagnostics.

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Enhancing Solar Cell Efficiency through Nanotechnology: Integrating Quantum Dots and Gold Nanoparticles

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Engineered quantum solar cells, incorporating both traditional quantum dots (QDs) and carbon quantum dots (CQDs), have been developed with an emphasis on enhancing light absorption and improving charge carrier separation. These advancements explore innovative concepts like multiple exciton generation to further boost device efficiency. An optimization study was conducted on dye-sensitized solar cells (DSSCs) using both synthetic and natural dyes. This process involved the integration of gold nanoparticles into a TiO_2 semiconductor and fine-tuning the TiO_2 particle sizes in the scattering layer. By incorporating gold nanoparticles into the mesoporous TiO_2 layer and adding a scattering layer, we were able to enhance the power conversion efficiency (PCE) [1-4]. The results from these experiments showed promising improvements in light absorption and charge transfer efficiency—critical factors for optimizing solar cell performance. These findings mark a significant step forward in photovoltaic technologies and open up new possibilities for the widespread use of QDs in energy harvesting applications.

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B-ME: Biobased Materials for Energy

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The rapid growth of electrochemical energy storage devices, such as batteries and supercapacitors, demands more sustainable solutions to reduce reliance on critical raw materials. Conventional metal-foil current collectors, typically aluminum and copper, contribute significantly to the environmental and economic impact of these devices. [1] Various alternative materials and structures have been extensively explored to improve the electrochemical stability and performance of these components, with the goal of achieving higher energy densities, extended lifespan, and enhanced sustainability throughout the device's lifecycle. [2,3]

In this work, we present a novel metal-free, bio-based polymer-carbon composite current collector developed within the B-ME project. This flexible, large-area film is composed of emerging polyesters, such as polyhydroxyalkanoates (PHA), combined with conductive carbon fillers like graphite and carbon fibers. The composite films was tested as current collectors in aqueous supercapacitor devices, demonstrating excellent electrochemical stability in challenging low-resistance and high-corrosion water-based electrolytes. Our results show high device durability, with over 95% capacity retention after 10,000 cycles.

These findings validate the feasibility of bio-based current collectors as a scalable and cost-effective alternative for sustainable energy storage, supporting the industrial adoption of aqueous electrolytes and fostering greener energy solutions. Based on these results, we are now establishing a spin-off company to further develop this technology, accelerating its transition from research to real-world applications.

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Advancements in instrumental development, modeling and environmental applications within the SAMOTHRACE project.

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The SAMOTHRACE project (www.samothrace.eu) is the Sicilian "ecosystem for innovation" funded by the EU and MUR within the NextGenEU – PNRR framework. Research is developed around the common themes of micro and nano technologies, micro- and nanophotonics, nano-materials, systems and devices, and directed towards six main areas: energy, health, intelligent mobility, environment, cultural heritage and smart agriculture. IPCF carries out research in the Environment Pillar, with the goal of developing advanced spectroscopic technologies, nano-materials and models for pollutants detection in air and water. This contribution summarizes the major advancements of the project in the fields of Raman Acoustic/Optical tweezers instrumental development and applications for microplastics detection, ab-initio modeling of water under intense electric fields, electromagnetic modeling of optical trapping forces, 2D nanomaterials for pollutants sensors [1-7].

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Agri-food wastes as new resource: Kiwi Peels as adsorbent material for water remediation

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In recent years, population growth has caused the increase in supply demands, like water and food [1]. That represents the source of the different global issues, particularly the management of water resources, including pollution, treatment, and protection concerns, and handling of agri-food wastes end-life [2]. In contrast with linear economy approach, which enhances these problems, by following the principles of Circular Economy, the same agri-food wastes can represent a solution for water treatment [3,4]. In this context, the use of Kiwi Peels, an agri-food waste, was proposed as an adsorbent material to remove various Concern Emerging Contaminants and textile dyes from water. The adsorbent substrate was characterized by adopting FTIR-ATR, TG and SEM analyses, before and after its use, proposing it as a recyclable material. UV-VIS spectroscopy analyses were performed for the purpose. Ciprofloxacin and Direct Blue 78 were selected model contaminants to infer information about the behaviour of Kiwi Peels during water treatments; so, the role of several parameters affecting the process was assessed. The study encompassed thermodynamics, adsorption isotherms, and kinetics.
To extend the lifetime of Kiwi Peels, desorption experiments were carried out by using hot water or salt solutions. 10 cycles of adsorption/desorption were studied, evidencing the recycling of both pollutants and Kiwi Peels. Moreover, the solid-state pollutant photodegradation was proposed as a possible alternative for the adsorbent regeneration.

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Towards a bio-mimetic sunlight pumped laser based on photosynthetic antenna complexes

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Addressing escalating energy demands in space and on Earth necessitates innovative, self-sustaining technologies. APACE proposes a bio-inspired sunlight-pumped laser leveraging photosynthetic complexes for efficient solar energy conversion. This system utilizes *R. sphaeroides* bacteria, extracting chromatophore units containing LH1 and LH2 complexes. The reaction center is passivated and functionalized with engineered molecules, creating a supramolecular gain medium within an optical cavity.

This design exploits the near-unity efficiency of bacterial photosynthetic antennas, enabling laser operation under unconcentrated sunlight, achieving a two-order-of-magnitude efficiency enhancement over conventional methods. The core strategy involves attaching lasing units (engineered molecules or doped nanocrystals) to these antennas, optimizing solar energy funneling.

APACE aims to establish a scalable solar harvesting technology, potentially fabricated in situ on space stations. The generated energy can support in-situ resource utilization, such as hydrogen production, and facilitate wireless power transmission via infrared laser beams to satellites or Earth. This bio-inspired approach offers a promising pathway towards sustainable energy solutions for space exploration and terrestrial applications.

ECOSEA PROJECT Integrative solutions for aquaculture and ecosystem health

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The project ECOSEA aims to act on a broad spectrum, to introduce, in the emerging and continuously growing sector of aquaculture, innovative technologies both for marine monitoring and for ordinary and extraordinary interventions in the fencing and containment networks used in the sector.

After participating in the Marta Project [1], CNR-IPCF team entered a new project partnership, funded by Regione Toscana [2], which focuses on solutions for the marine environment.

The project will be divided into three specific and parallel aspects: development of BIO-CABLE TIES for aquaculture applications, development of a sensor for water monitoring in aquaculture and research and development of an innovative multifunctional buoy for water monitoring (JOLLY SMART BUOY).

The CNR-IPCF team of Pisa involved in the project has gained experience over the years in sectors, usefully for the project objectives, of development of polymeric materials and bioplastics and in the study of their behavior in marine environment [3].

In ECOSEA, CNR-IPCF team will contribute to all phases of the development of Bio-CABLE TIES: from the development of formulations, creation of lab-scale and industrial scale prototypes, materials characterization, prototypes testing for the evaluation of degradation times and durability at sea.

Partnership: RES MARINA, CNR-IPCF, BAMAPLAST, DMG ENGINEERING S.R.L.

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Characterization of derivatized biopolymers *via* solution NMR spectroscopy

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Thiolated Hyaluronic Acid (HA-SH) and Gelatin Methacryloyl (GelMA) can be used as starting materials for the fabrication of crosslinked hydrogels. To this purpose, Hyaluronic acid (HA) was derivatized with thiol groups [1-3], whereas Gelatin was covalently modified with methacrylic anhydride (MA) [4].
Nuclear Magnetic Resonance (NMR) spectroscopy was used for the characterization of HA-SH and GelMA, together with their precursors HA and Gelatin [3-5]. The spectroscopic analysis focused on the confirmation of the derivatization processes, the determination of the degree of substitution (DS for HA-SH and DM for GelMA), and the characterization of the derivatized biopolymers.

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Interdisciplinary advances in biomaterials for nanomedicine and tissue engineering

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The most promising research strategies in medical science today are nanomedicine and tissue engineering. Our recent research consists in the study of advanced technologies for the development of cardiac tissue-engineered constructs and nanomaterials for drug delivery. Innovative nanomaterials were prepared using various methods such as oil in water emulsion, precipitation polymerization and microfluidics. Nanoparticles produced using emulsion technique enabled prolonged release of a very sensitive drug. Molecularly imprinted nanoparticles, with recognition sites towards a specific cardiac enzyme and a membrane receptor, were obtained providing a versatile tool for myocardial infarction and cancer treatment. Moreover, the application of microfluidic approach allowed the production of monodisperse nanoparticles enabling significant improvements in drug delivery systems. In this work particular attention is given on the effects of the sterilization method (Ethylene Oxide) on drug-functionalized patch performance. Morphology, physico-chemical and mechanical properties were evaluated using SEM, FT-IR Chemical Imaging, HPLC, DMA and INSTRON. Overall, the analyses evidenced that the sterilization did not affect significantly the mechanical properties, the surface microstructure of the scaffolds or degradation and release kinetics. Finally, the implementation of the patch with an inner layer showed higher mechanical properties, longer degradation and release kinetics, and confirmed the physical-chemical properties of the scaffold.

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GOrGONA: new Strategies in the Global Optimization of NanoAlloys

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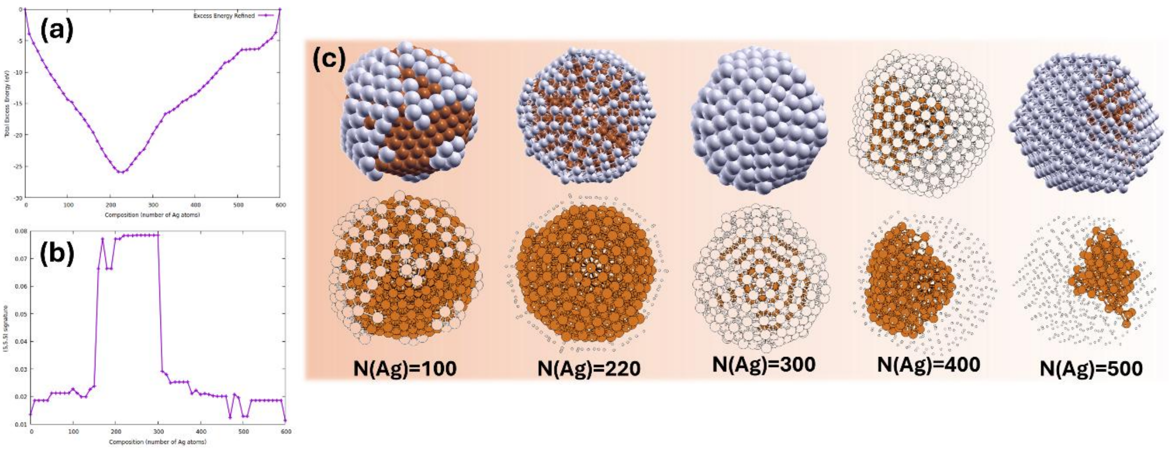
Given the experimental difficulties in achieving a high-level atomistic characterization on alloyed nanoparticles, computational modeling can play a key role in elucidating structures and structure/properties relationships, in view of potential applications in many technological fields, like catalysis, sensing, optics, etc. At this purpose, we will present a free-source code, GOrGONA (Grouping Ordering for Global Optimization in Nano Alloys) based on global optimization statistical algorithms to efficiently single out low-energy structures of metallic nanoclusters made of two different elements (nanoalloys). The complexity of the problem stems from the need to explore simultaneously both the phase space of structural configurations and that of chemical ordering patterns, combining exhaustiveness and speed. A recent method [1] has demonstrated how "Grouping" methods can significantly improve the identification of chemical ordering patterns, maintaining a high level of exhaustiveness. Within this framework, we will show how GOrGONA can exploit an intertwined approach by implementing the Grouping method within an efficient engine for the Global Optimization of NanoAlloys previously developed at the Genoa University [2]. This project is part of the "National Center in High-Performance Computing, Big Data and Quantum Computing (CN-HPC)" of the Italian PNRR.



(a) convex hull and (b) (5,5,5) signature of the lowest-energy structures characterizing the AgCu alloy at size 600; (c) some characteristic low-energy structures covering the full compositional range of the alloy.

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Formation of Sulfur Dioxide in Exoplanets' Atmospheres Investigated by Quantum Chemistry

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The chemical composition of exoplanet atmospheres represents one of the most intriguing aspects in astrochemistry. In a recent study, we have proposed, by using quantum-chemical calculations a reaction scheme leading from •PO radical to phosphine (PH_3) at conditions of Venus' atmosphere (Mráziková et al., 2024). Another controversial issue concerns the presence of sulfur dioxide (SO_2) in the atmospheres of some exoplanets. In fact, SO_2 has recently been detected in the atmosphere of the exoplanet WASP-39b, exhibiting an external atmospheric temperature of ~1100 K. A reaction scheme starting with hydrogen sulfide (H_2S) and leading to SO_2 has been suggested based on 1D photochemical models that tightly rely on reaction rates published either in chemical databases or in the literature (Tsai et al., 2023). The scheme includes a source of •H and •OH radicals, hydrogen abstraction from H_2S and •SH by •H radicals, and subsequent oxidation of atomic :S and :SO diradicals by •OH radicals. Simultaneously, results from 1D photochemical models reported in (Tsai et al., 2023) indicate that the formation of SO_2 is likely unfavorable for temperatures below ~1000 K. However, SO_2 has been detected also on exoplanets WASP-107b (Dyrek et al., 2024) and GJ3470b (Beatty et al., 2024) with atmospheric temperatures of ~740 K and ~600 K, respectively. Herein, by elevating the quantum chemistry methodology employed in (Mráziková et al., 2024) we investigate reaction mechanisms and thermodynamics of the scheme suggested in (Tsai et al., 2023) leading from H_2S to SO_2 at 1100 K and 600 K. Our results suggest that the reaction scheme is thermodynamically similarly favorable at both temperatures.

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