FIT4MEDROB

D8.1.1

RTA1 - New materials: methods and prototypes #1

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Editors/PIs: Giuseppe Mensitieri (UNINA), Tonia di Palma (CNR-STEMS)

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CO	Confidential, restricted under conditions set out in Partners Agreement	

History of Changes

VERSION	SUBMISSION DATE	CHANGES
1.0	30/11/2023	First version
2.0	20/09/2024	Executive summary modified following reviewers' suggestions.

TABLE OF CONTENTS

1 EXECUTIVE SUMMARY

Mission 3 is devoted to support **frontier research topics** pertaining to physical and computational aspects of robot *bodies*, robot intelligence, and interfaces with the patient. Seven research topics (RTa1…RTa4, RTb1..RTb3) are articulated in 19 sub-projects, running in parallel and covering complementary enabling technologies in the field of robotics and biorobotics.

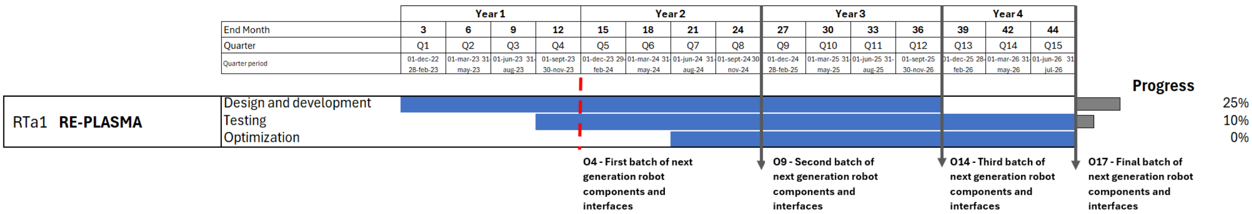
Research Topic a1 is dedicated to the development of new materials and protocols with the ultimate goal of gaining insights into possible applications of such technologies for robot prototypes. RTa1 involves two sub-projects addressing different aspects of prototype conceptualization and design. The **first sub-project**, **RE-PLASMA**, aims at the conceptualization and set up of novel mathematical models describing the mechanical behaviour of tunable elastic metamaterials synergistically coupled with unconventional fluids exhibiting specific visco-elastic tunable properties, which are intended as components or even whole soft or hard exoskeletons and prototypes. The issue of powering these active biomedical devices is also central to their applicability, by incorporating mandatory eco-sustainability needs. In fact, the **second sub-project**, **POLIECO-BAT**, aims at realizing safe and eco-sustainable batteries, focusing the research on the case study of innovative metal-air batteries to power disposable sensors of glucose in sweat.

As per the proposal, the expected impact of Mission 3 is a new wave of technologies (<u>proofs of concept or proofs of viability</u>) and of knowledge, at the basic or component level, to become <u>key enabling components</u> of future healthcare and personal care robots.

RE-PLASMA progress

The REPLASMA project timeline is outlined in the following Gantt chart.

- The **"Design and Development"** phase, which focuses on exploring unconventional materials and methodologies for robotic applications, has advanced by **25%** compared to the Gantt chart. Up to month 12, preliminary research has been conducted to identify effective structural configurations, and simplified digital models of prosthetic components have been created. Analysis of basic models and computational simulations of poro-viscoelastic structures have been started, and preliminary investigation on magneto-rheological fluid formulations are ongoing. For prosthetic design, initial digital representations have been generated, though further refinement is needed before more advanced modelling techniques can be applied.
- The **"Testing"** phase is currently at **10%**. Some early-stage evaluations have been conducted to understand the fundamental mechanical properties of selected materials. Additionally, basic tests on foamable and conductive polymeric materials have started, with initial extrusion trials providing insight into their structural characteristics.
- The **"Optimization"** phase has **not yet started**.

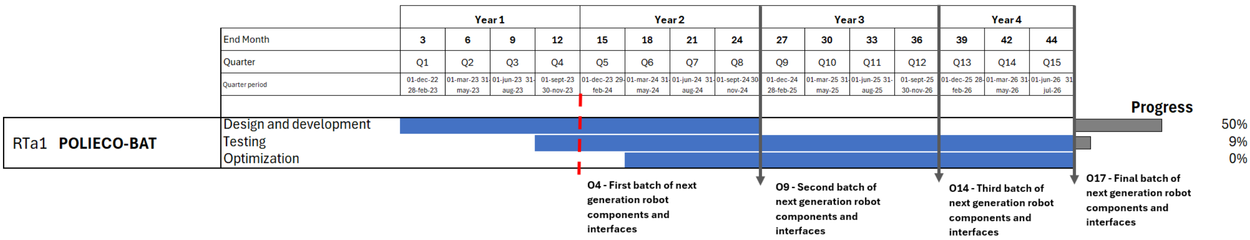


There are no deviations on the original plan and the research is progressing as originally foreseen.

POLIECO-BAT progress

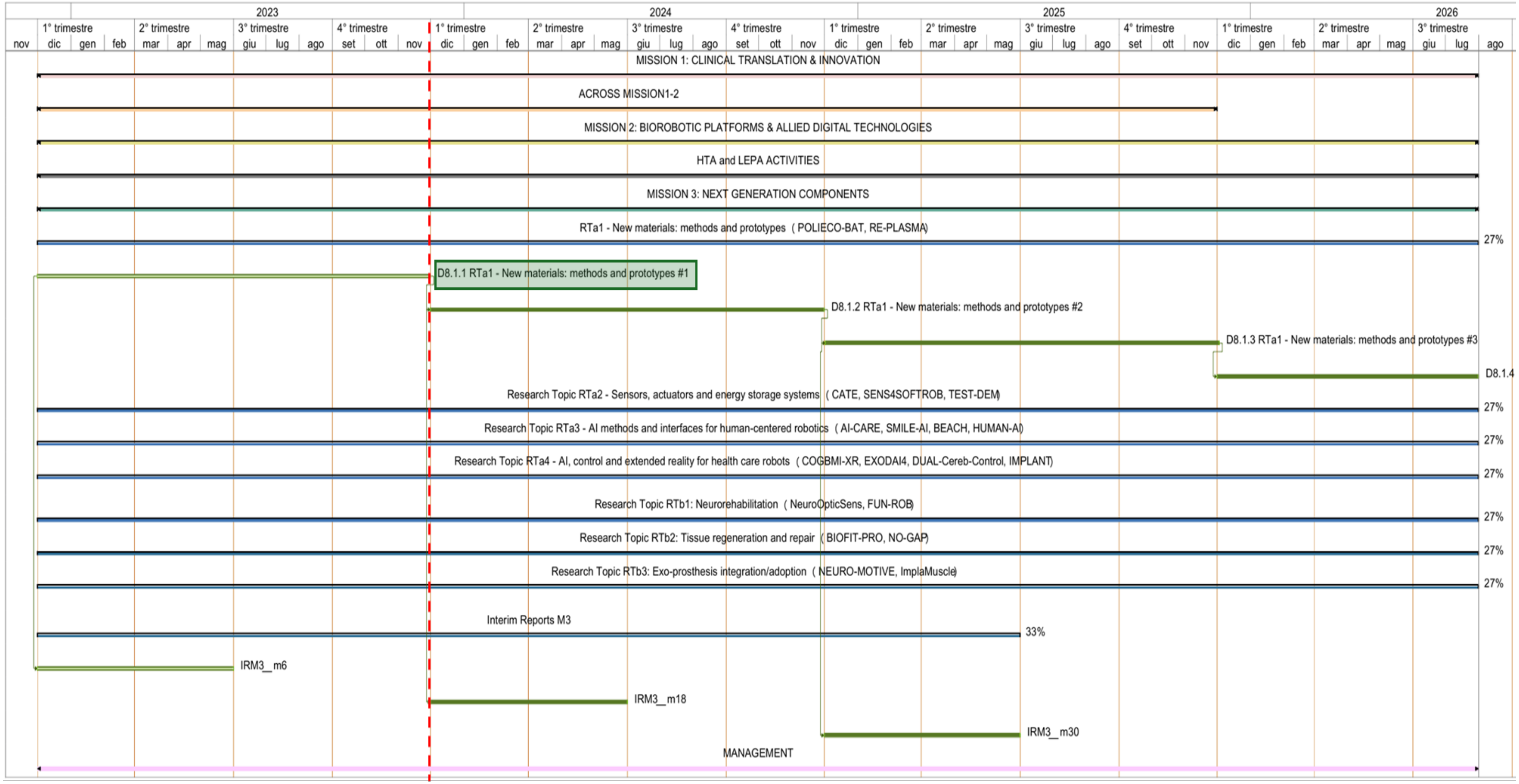
The expected progress of POLIECOBAT activities is reported in the GANTT diagram.

- **"Design and development"** refer to the development of new materials for sustainable electrochemical cells. Up to month 24 new electrolytes with ionic conductivity useful for practical application in Al-air cells have been developed. Also, biomass-derived cathodes with electrochemical performances superior to cathodes using platinum as electrocatalytic material have been prepared. Anodic efficiencies have been also measured. Thus, the M12 "design and development" reached the **50%**. Development of material with optimized electrochemical performances is expected in the next months.
- The **"Testing"** phase is almost **9%** and is related to the first preliminary measurements on the glucose sensors.
- The **"Optimization"** phase has **not yet started**.



There are no deviations on the original plan and the research is progressing as originally foreseen.

The progress and main results for each subproject is presented in detail in the following.


2023
2024
2025
2026
1° trimestre
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3° trimestre
4° trimestre
nov dic gen feb mar apr mag giu lug ago set ott nov
MISSION 1: CLINICAL TRANSLATION & INNOVATION
ACROSS MISSION1-2
MISSION 2: BIOROBOTIC PLATFORMS & ALLIED DIGITAL TECHNOLOGIES
HTA and LEPA ACTIVITIES
MISSION 3: NEXT GENERATION COMPONENTS
RTa1 - New materials: methods and prototypes (POLIECO-BAT, RE-PLASMA)
27%
D8.1.1 RTa1 - New materials: methods and prototypes #1
D8.1.2 RTa1 - New materials: methods and prototypes #2
D8.1.3 RTa1 - New materials: methods and prototypes #3
D8.1.4
Research Topic RTa2 - Sensors, actuators and energy storage systems (CATE, SENS4SOFTROB, TEST-DEM)
27%
Research Topic RTa3 - AI methods and interfaces for human-centered robotics (AI-CARE, SMILE-AI, BEACH, HUMAN-AI)
27%
Research Topic RTa4 - AI, control and extended reality for health care robots (COGBMI-XR, EXODAI4, DUAL-Cereb-Control, IMPLANT)
27%
Research Topic RTb1: Neurorehabilitation (NeuroOpticSens, FUN-ROB)
27%
Research Topic RTb2: Tissue regeneration and repair (BIOFIT-PRO, NO-GAP)
27%
Research Topic RTb3: Exo-prosthesis integration/adoption (NEURO-MOTIVE, ImplaMuscle)
27%
Interim Reports M3
33%
IRM3_m6
IRM3_m18
IRM3_m30
MANAGEMENT

1.1 RE-PLASMA: REPORT ON RESULTS

The first main objective of the RE-PLASMA sub-project is to take inspiration from the actual biomechanical behaviour of biological tissues with the aim of opening new ways of conceiving and designing soft and hard exoskeletons for human rehabilitation. In particular, the new concepts of materials to be developed for the Project will focus on the highly hierarchical and self-similar structures met in tissues and joints in the human body by taking advantage of the typical fluid-solid interactions occurring across scales in natural systems. To do this, a new class of materials will be designed and built up by combining solid poroelastic media and active fluids for obtaining structural elements with tailored unconventional mechanical properties. Experimental efforts will be coupled with advanced modelling strategies needed to address the complex resultant behavior of such structures. Novel theoretical approaches are thus required to predict and optimize the performance of these new structures, to finally translate them into possible patient-specific solutions for rehabilitation.

Sections 1.1.1.1 and 1.1.1.2 are respectively devoted to describe the theoretical tools for modelling the above mentioned solids and the criteria for selecting and designing active fluids for the Project purposes. In detail, Section 1.1.1.1 reports a brief introduction to the class of nonlocal continuum theories potentially helpful for the applications of interest. Furthermore, some inherent affinity of the nonlocal continua with typical structures involved in rehabilitation of the musculoskeletal system is highlighted. Also, the possibility of obtaining at the macroscopic scale a number of material behaviours, such as auxeticity, morpho-elasticity and instability, is mentioned with respect to energy-harvesting and displacement magnification mechanisms, ultimately leading to devices that may support the movement of weakened parts of the joints, relying on the healthy ones, minimizing the impact of rehabilitation solutions on patients' life quality. Section 1.1.1.2 is instead dedicated to analyse possible active fluids whose rheological properties can be controlled and modified via magnetic and electrical fields. In this way, new wearable exoskeleton technologies can be developed and optimized by using magnetorheological (MR) or electrorheological (ER) 'smart' fluids to be combined with poroelastic structures exhibiting non-conventional mechanical properties.

A second main objective is the exploitation of additive manufacturing technologies to allow the creation of complex shapes and to enhance the performance of critical components (see Section 1.1.1.2). To this aim, the first step was to perform a critical analysis of commercially available devices and related manufacturing processes. Benefiting from the information reported in the literature, the mechanical and functional requirements were properly identified to re-define design and manufacturing guidelines for next generation components of robotic devices. Accordingly, case studies were also preliminarily identified, spanning from orthoses, prostheses and implants to tissue engineering and regenerative medicine. In addition, further technical data and information related to the global 3D printed prosthetics market were suitably analysed.

Finally, a further objective is the development of soft active coatings for wearable robots to induce sensations signalling directly to the skin. The coatings will be based on the combination of photo-responsive compounds with polymer chemistry.

In summary, the goals to be reached after the first 12 months by the RE-PLASMA sub-project were:

a) the conceptualization and set up of models of behaviour of mechanically tuneable solid poroelastic materials and nonlocal micro-structures intended as possible components of hard exoskeletons.
b) the building up of virtual models to predict mechanical behaviours and to envisioning prototypes.
c) preliminary analyses and identification of unconventional fluids with tuneable rheological behaviour to be synergistically coupled to tuneable elastic (meta)materials.
d) additive foam manufacturing to obtain complex, polymer-based, foamed structures that cannot be obtained by conventional manufacturing procedures.
e) development of soft active coatings for wearable robots to induce sensations signalling directly to the skin; they will be based on the combination of photo-responsive compounds with polymer chemistry.

Taken all together, the key innovative contribution of the RE-PLASMA project is to develop a platform of new metamaterials and related theoretical and computational tools for designing enhanced physical properties and simulating complex mechanical behaviours needed for next-generation exoskeletons.

The approaches adopted are two-fold. On one side, are explored the opportunities offered by the development of an entirely new class of solid-fluid hybrid structures with tuneable properties, to be used for conceiving hard and soft adaptive exoskeleton components that cannot be realized with currently available material solutions. On the other side, the issue of improving performances of classical prostheses and devices, beyond the state-of-art, is addressed by exploiting advanced 3D manufacturing technologies and new design strategies.

1.1.1 PART 1 - REhabilitation bionics: a PLatform for Active Structures and Innovative Materials

1.1.1.1 Mechanically tunable visco-elastic (meta)materials

In the field of human rehabilitation, a growing body of recent scientific research has focused on the development of lightweight and high-performance materials and systems. These systems are characterized not only by reduced mass and improved mechanical resistance, but also by the embodiment of spatially graded mechanical properties. The ability to tailor stiffness and elasticity across space has been shown to significantly influence the effectiveness of rehabilitation protocols, thereby enhancing patient outcomes and adaptability of therapeutic devices.

Within this context, a key focus of the present subproject is the design of exoskeletons with tuneable elastic properties intended for rehabilitation purposes. *The envisioned system consists of a composite material in which a deformable solid matrix is permeated by a specialized fluid*. The interplay between the elastic skeleton and the internal fluid phase allows for active modulation of the overall mechanical response, potentially enabling customized stiffness profiles suited to individual patient needs or varying stages of recovery.

The biological systems targeted by these engineered devices are primarily human joints and connective tissues, as for example tendons. Tendons—especially in humans and other vertebrates—exhibit a complex hierarchical organization, composed of progressively larger fibre structures: from collagen fibrils, to fibres, to fascicles, and ultimately to macroscopic bundles. This multi-scale architecture allows tendons to transmit *forces across distant regions*, thus playing a crucial role in coordinated joint motion and mechanical feedback throughout the musculoskeletal system.

To replicate such behaviour in artificial systems, the elastic solid component of the proposed material – hosting the internal fluid that moves freely within a network of interconnected cavities – may necessitates from microstructural features capable of generating nonlocal interactions, wherein the mechanical state at a point depends on the behaviour over a finite surrounding region rather than purely local variables. The required techniques to model such a behaviour rely on advanced mathematical theories such as nonlocal field theory of elasticity.

Nonlocal continuum theories, particularly those developed since the 1970s by A. Eringen, provide a rigorous mathematical framework for modelling long-range interactions. A prominent example is peridynamic theory (PD) [1,2], which departs from classical local theories by representing continua as collections of particles linked by force-transmitting bonds over a finite range, referred to as the horizon (δ). These bonds can follow a variety of constitutive laws—including those that account for damage via irreversible bond breakage—making PD particularly suitable for applications involving fracture, delamination, and failure in complex materials. Notably, PD has been successfully applied to the modelling of delamination in thin composite laminates through dimensionally reduced formulations [1].

Beyond explicit architecture choices for the solid body, nonlocality may also emerge from the intrinsic physics of coupled systems. For instance, in porous media consisting of a deformable solid saturated by an active fluid, the governing balance equations can naturally give rise to higher-order gradient terms that may result from fluid flow dynamics, pressure gradients, or from microstructural features such as pore interconnectivity over long distances. Nonlocal fluid flows naturally arise in framework where the porosity is characterized by channels of different lengths. In such scenarios, nonlocal effects are not merely a modelling convenience, but an inherent consequence of the multi-physics nature of the system.

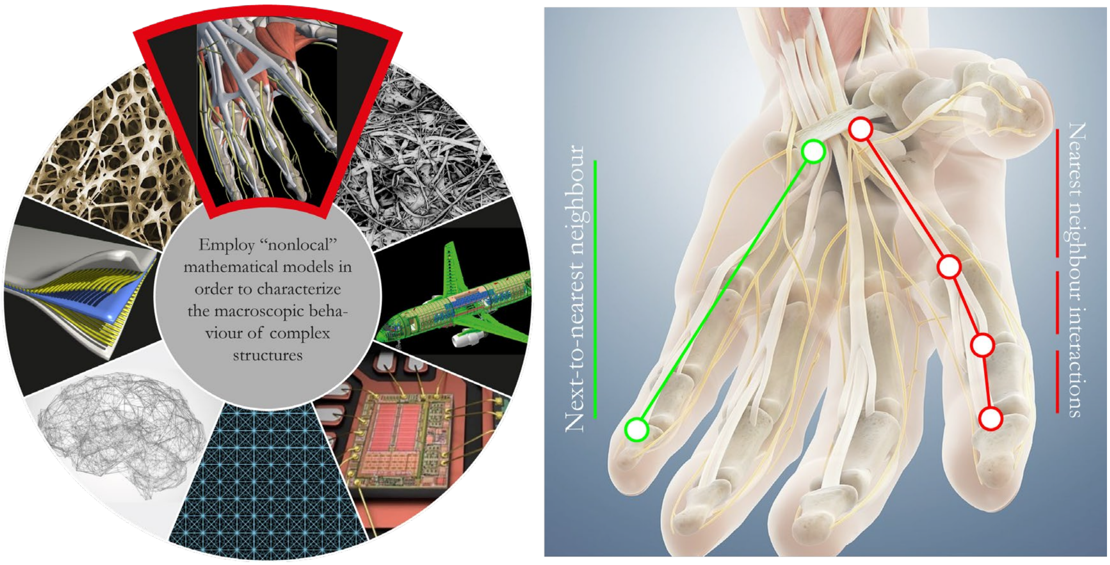


Fig. 1- Nonlocal models range of interests. On the left: the wide varieties of applications in which nonlocal theories of continuum mechanics are necessary for a correct overall characterization; these applications include, but are not limited to, highly heterogeneous materials such as composite laminates, bodies whose structure is composed of bundles of long fibres, such as paper, micro-electro-mechanical systems, MEMS for brevity, architectured materials, and biological structures. On the right: tendons in a human hand introduce interactions – highlighted in red and green – which happen at a finite distance between bones, joints and tissues – such as skin.

***'Design and Development' task:* Material model implementation**

The non-local theory of continuum mechanics becomes thus a reference framework to model the complex behaviour of biological systems characterised by architectural microconstituents or by interconnected porosities. The first case is dealt with by modelling the solid structure as nonlocal, while the latter by modelling the filtration process as one. This is achieved by tailoring the relative stiffness of the bonds of the PD model. By playing with the mechanical characteristics of these elements, several outstanding mechanical behaviour can be obtained, such as auxeticity, incompressibility, instability, and morpho-elasticity, all solidified concept in the field.

A paradigmatic application of the protocol

The long-range interactions of tendons and bones in the human hand naturally point to the possibility of modelling its overall behaviour, at the macroscale, as nonlocal, see **Figure 1**, on the right.

By embedding ad hoc conceived microstructure for the elastic component in a thin bio-compatible material layer we point at producing a soft glove with tuneable stiffness. Augmenting the microstructure with particular stiffnesses distribution and/or bond-to-bond constraints allows it to reproduce nonlocal mechanical behaviours also shown by some biological structures, useful for the goal of rehabilitation or movement support, like morphoelasticity and instability as displacement enhancers and auxeticity for directional stiffening.

The soft glove, thanks to its ad hoc microstructure (see **Figure 2**) is thus designed for favouring the movement of weakened part (for example a finger) of the hand through the amplification of the movement of the healthy region (for example the thumb).

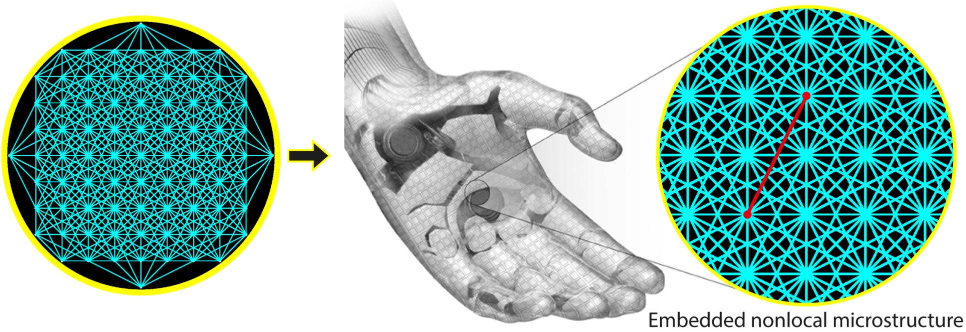


Fig. 2 - Soft glove for hand rehabilitation. By implementing non-conventional materials for the underlying microstructure of a soft glove with a nonlocal network, hand rehabilitation can be fostered in a passive way by training the weakened regions of the hand through the movement of the healthy parts.

1.1.1.2 Preliminary analyses and identification of unconventional fluids with tuneable viscoelastic behaviour

Wearable exoskeleton technology can be improved and optimized using magnetorheological (MR) or electrorheological (ER) 'smart' fluids when used in synergic combination with structures with non-conventional mechanical properties described above. The aim is that of exploiting these materials with tailorable rheological properties that can be widely modified and controlled, ranging from Newtonian fluid to solid-like behaviour, by means of modulation of externally imposed fields (see **Figure 3**). ER and MR fluids are stimuli-responsive smart dispersions with yield stress, viscosity and shear modulus, that are reversible and controllable in a continuous manner with the usage of an externally applied electric field (E) or magnetic field (H), respectively [3].

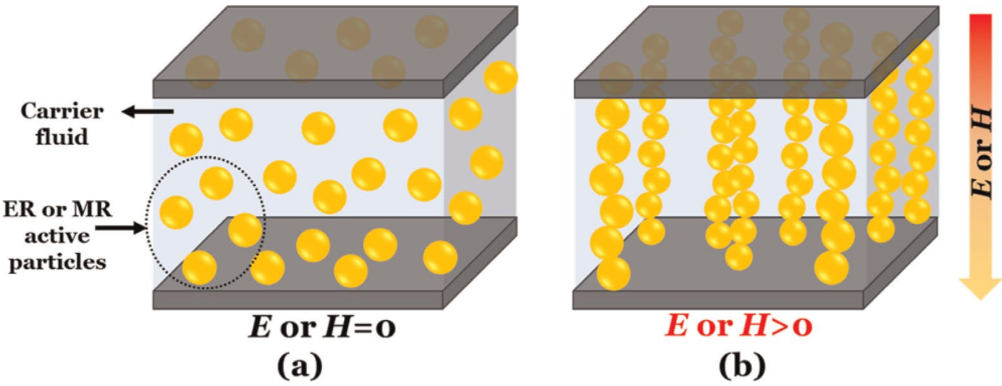


Fig. 3 - Schematic representation of the microstructure of ER or MR fluids under off-state. (a) and on-state (b) of E or H.(from ref. [3])

The ER fluids are commonly composed of polarizable/semiconducting micron/nanosized particles as a dispersed phase, in an insulating dispersing medium with low volatility and high chemical/thermal stability, whereas their magnetic counterpart, the MR fluids generally consist of highly magnetizable micron-sized dispersed particles in a no magnetizable carrier fluid such as mineral oil, silicone oil, polyesters, polyethers, synthetic hydrocarbons, or water. These smart fluids transform reversibly and rapidly from a liquid-like state to a solid-like state within a millisecond with the aid of an E or a H. These fluids, based on their properties, can be used in several applications where the active control of vibrations or the transmission of torque are required.

When an E is applied to an ER fluid, the particles randomly dispersed within the fluid form a dipole moment in view of the different dielectric constant of the dispersant and of the dispersed particles. Therefore, an attraction builds up between these particles attract along the field between the parallel electrodes promoting the formation of chain and/or columnar-like structures along the field direction. A similar process occurs in the case of MR fluids exposed to a magnetic field: dispersed particles are magnetized and oriented along the direction of the field generating anisotropic aggregates.

For both types of smart fluids, the field induces a structuration in the fluid that resists the flow of the carrier fluid, resulting in an enhanced apparent viscosity and viscoelasticity of the fluid.

In the following we focus on the types of fluids we consider the most attractive for the applications of interest.

ER smart fluids

Early electrorheological (ER) fluids used water-activated particles such as starch, silica gel, and zeolite [4], but suffered from high leakage currents, corrosion, and limited temperature range. Anhydrous inorganic particles with high dielectric constants (e.g., rutile, perovskite) [5] improved performance but caused sedimentation and abrasiveness. Nanoparticles mitigated dispersion issues [6] but required high concentrations, increasing off-field viscosity. Organic polymer particles, especially polyelectrolytes like poly(lithium methacrylate) and ion-exchange resins [7–9], showed promise but relied on water for ion mobility, causing thermal/electrical issues. Bayer developed anhydrous PEO-salt systems [9], yet moisture sensitivity persisted. Recently, hydrophobic poly(ionic liquid)s (PILs) [10, 11] demonstrated strong, stable ER effects without water.

MR smart fluids

Magnetorheological (MR) fluids are suspensions of magnetic particles in a nonmagnetic carrier liquid whose rheological properties change under a magnetic field. Upon application of magnetic field, the particles align themselves in the direction of magnetic field to form chains, which represents the change in the rheological properties such as viscosity and yield stress characterizing the so-called MR effect. These properties mainly depend on magnetic field strength and particle volume. Carbonyl iron (CI) is commonly used due to its high magnetic permeability, soft magnetic characteristics, high magnetization value, low remanent magnetization, and common. The mixture of micro- and nano-sized particles are called bidisperse MR fluids. Adding nanoparticles, such as maghemite (γ-Fe_2O_3), enhances redispersion and chain formation, improving stability [12,13]. Variants like magnetorheological elastomers and use of ionic liquids are also under investigation [14].

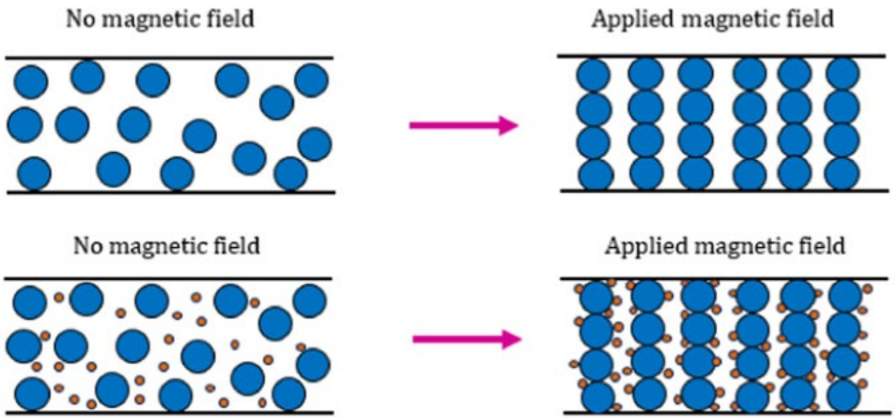


Fig. 4 - Schematic image of MR effect of γ-Fe2O3 nanoparticles added to the CI particles. from ref [12]

Magnetorheological Fluids Based on (magnetic) Ionic Liquids

Magnetic ionic liquids (ILs) are a class of ionic liquids with intrinsic paramagnetism due to transition metals, lanthanides, or actinides integrated into their cationic or anionic structures. This incorporation leads to magnetic, optical, catalytic, and photophysical properties. ILs typically consist of quaternary organic cations and small inorganic anions, offering low volatility, non-flammability, high stability, and tunable structures. Magnetic ILs, as single-component systems, align their spins under magnetic fields, altering system behavior. Alternatively, magnetic nanoparticles dispersed in room-temperature ILs form magnetically responsive fluids. ILs stabilize these nanoparticles, enhancing colloidal stability and reducing sedimentation, making them promising carriers for magnetorheological fluids [15].

1.1.2 PART 2 - Integrated DEsign Methods and MAnufacturing for next Generation Components of Robotic devices in Medicine

1.1.2.1 Additive foam manufacturing

STATE OF THE ART AND PRELIMINARY TECHNICAL CONSIDERATIONS

Additive manufacturing technologies are revolutionizing industrial production by enabling the creation of complex shapes and improving component performance across fields like aerospace, automotive, and biomedical applications [16-29]. However, achieving desired functional properties often requires optimizing process parameters, microstructure, and mechanical properties. Studies have explored various lattice structures and analyzed commercially available devices to redefine design guidelines for future robotic components [30-48], including prosthetics and tissue engineering [49].

EXPLORING DESIGN STRATEGIES FOR ADDITIVE MANUFACTURING OF ADVANCED DEVICES

The aim of this research step was to provide further insight into the design of advanced and lightweight additive manufactured devices as well as of innovative/integrated technological solutions in the field of medical robotics.

Different strategies of design for additive manufacturing were defined, explored, and implemented, to create next-generation robotic device parts ranging from orthoses and implants to tools for tissue engineering and regenerative medicine. The explored strategies led to several design alternatives in the form of 3D solid, cellular, lattice, functionally graded or solid-lattice hybrid structures.

An integrated approach using a two-step optimization process classical and lattice topology optimization was proposed. The design process began with a conceptual sketch and concluded with a manufacturing drawing, navigating trade-offs such as aesthetics versus functionality and cost versus manufacturability. Simulation-driven strategies guided the conceptual phase, promoting innovative solutions over the simple validation of existing designs [16, 17]. Specifically, in the current research an optimization-driven design process was considered for the development of metal and polymer-based parts and components using different additive manufacturing technologies (e.g., selective laser melting, fused deposition modeling, integrated/combined technological approaches). A special focus was given to draw direction and fabrication constraints, pattern repetition and grouping, combination of multiple manufacturing constraints.

The topological optimization problems were solved using a density method (i.e., solid isotropic material with penalization SIMP), where the density of an element is usually correlated to its stiffness according to the following equation:

$$\mathbf{K}(\rho)= \rho^{p}\,\mathbf{K_0}$$

where K(ρ) and K0 represent the penalized stiffness matrix of an element and the real stiffness matrix of an element; ρ is the (relative) density and p represents the penalization factor. [16, 17]

Different design solutions for prosthetic devices were preliminarily obtained using several values of the penalty factor (p), thus allowing to explore high, medium, and low values of porosity. High-density regions were preserved, low-density ones removed, and intermediate-density ones transformed into lattice structures. Generative design using level set methods complemented this, enabling complex geometries without fixed boundaries. It supported multiple material options and offered time-efficient, creative solutions.

In this research step, as results of generative design, several design alternatives were obtained satisfying the input data and objectives in different ways. The employed algorithms also considered the manufacturing limitations; accordingly, some of the obtained results did not need further redesign.

As an example, **Figure 5** and **Figure 6** are related to the methodologies and results obtained in this research step according to a specific case study (i.e., a prosthetic arm). The chosen objective of the case study was to minimize mass and the minimum value of the safety factor was properly defined. Different metals and alloys (e.g., Ti6Al4V, AlSi10Mg …) as well as polymer-based materials (e.g., PLA, PCL, PC/ABS, PEI, PEEK, Carbon Fiber PEEK …) were chosen. Furthermore, two options were also considered in terms of manufacturing: unrestricted method and additive manufacturing.

If compared to topology optimization, generative design involved a different approach from the beginning. **Figure 5** reports the workflow adopted for the selected case study.

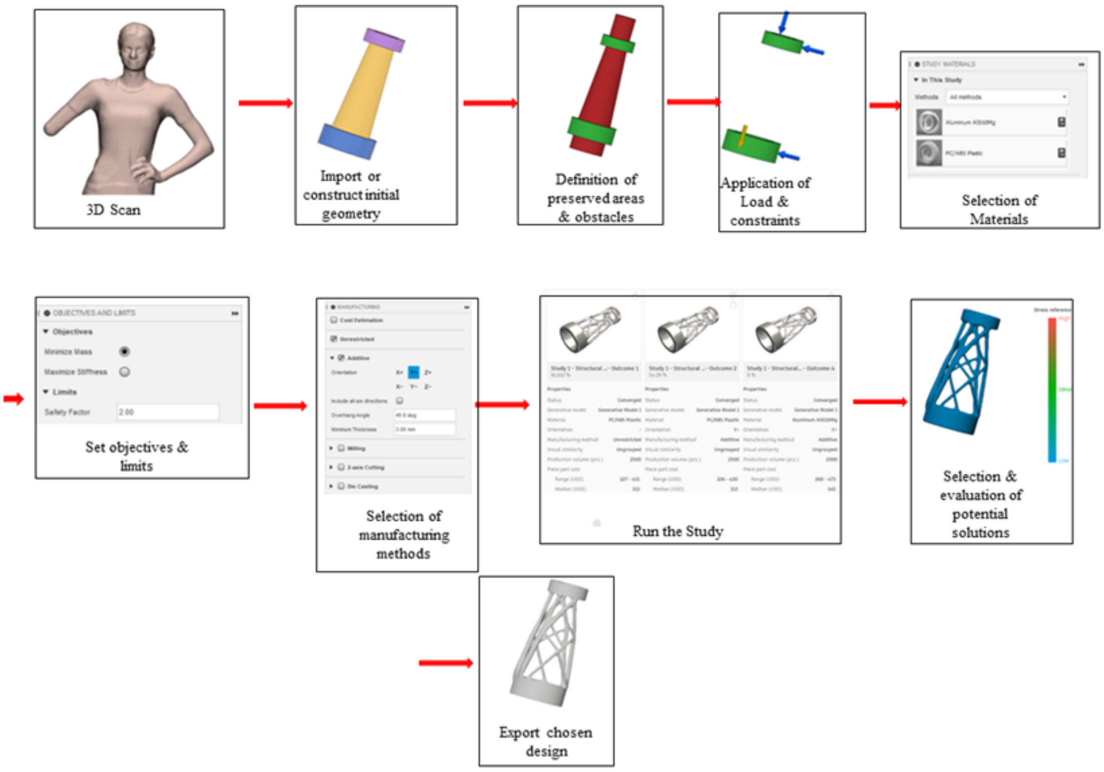


Fig. 5 - Generative design: workflow adopted in a case study.

Starting from the solid model of the prosthetic device, **Figure 6** reports some of the generated lightweight alternatives providing a suitable combination of geometry and manufacturing option (additive manufacturing).

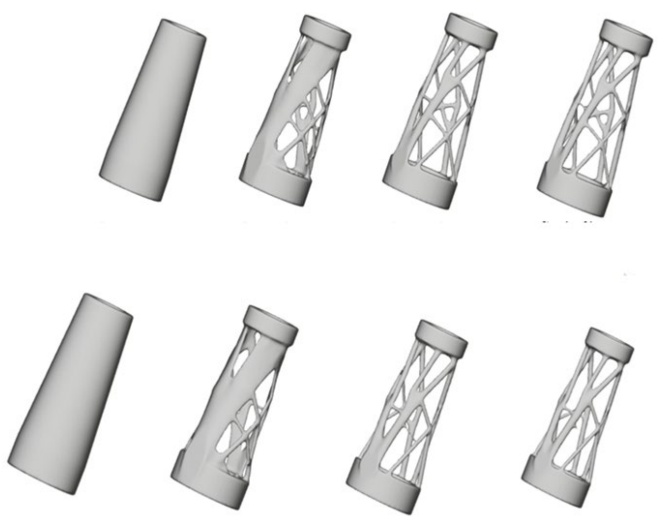


Fig. 6 - Generative design: examples of some of the generated results – additive manufacturing, orientation Y+ - using polymer-based materials (top) or metals (bottom).

The results summarized in the current section, as well as the related technical considerations, are not limited to the reported example(s) and may be seen as a route to develop several components of robotic devices for different medical applications, benefiting from the explored and integrated design principles.

ADDITIVE FOAM MANUFACTURING

Polymer cellular materials are used in several applications and technological fields (e.g., biomedical, engineering, aerospace, nautical, sport and leisure), due to their unique properties arising from pore morphology (size, orientation, density) [50]. As a matter of fact, Nature has often chosen optimized cellular structures to shape life on our planet. The pores' characteristic size, shape, and organization are important factors in determining these materials' structure–property relationship. Natural cellular materials, such as echinoid and beeswax honeycombs [52, 53], are usually complex foamed structures, designed to carry out a specific task or optimize a specific property.

Additive Manufacturing (AM) enhances component design through tools like generative design and lattices, achieving high strength-to-density ratios, though design complexity increases [54]. Recently, foam AM (FAM) that has been developed by Tammaro et al. [55], enables precise, cost-effective foam production via pre-treated filaments with physical blowing agents (PBAs).

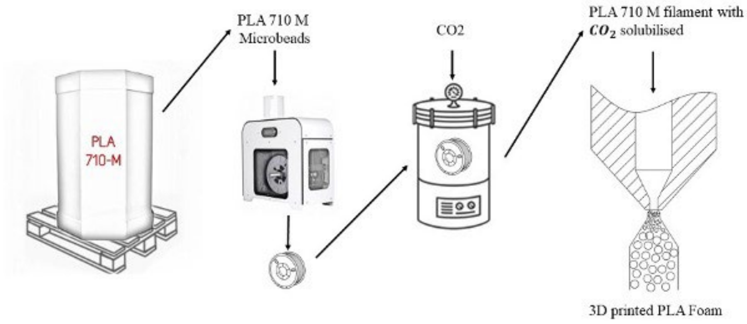


Fig. 7 - Schematic representation of the steps in a FAM process

During fused filament deposition (FFD), the physical blowing agent (PBA) expands, forming bubbles in the polymer. Unlike chemical blowing agents (CBA), PBAs foam most thermoplastics without altering their chemistry, benefiting recyclability. Nofar et al. [56] reviewed key FAM parameters affecting foam properties. The process includes solubilisation, where PBA is infused into the filament in an autoclave, and extrusion through a heated nozzle [57]. During the extrusion phase, the polymer experiences a rapid pressure drop and a temperature rise from the inside to the outside of the nozzle. Due to this effect, the PBA expands and causes the polymer foaming. The rapid temperature rise, and expansion allow the foamed polymer to crystallize.

The amount of PBA in the polymer is controlled by pressure (Pa): higher Pa increases solubilized PBA. Absorption (ta) and desorption (td) times affect its distribution: longer ta enhances core foaming, while longer td reduces surface bubbles. In extrusion, the filament moves through a cooled (cold end) and heated (hot end) zone. As is represented in **Figure 8** the extruder consists of two zones, a heated zone, referred to as the hot end, and a cooled area, referred to as the cold end.

Key parameters like extruder temperature (Te), speed (Se), and nozzle diameter (Nd) shape foam morphology [58–61], influencing pressure, viscosity, and PBA expansion at the nozzle exit.

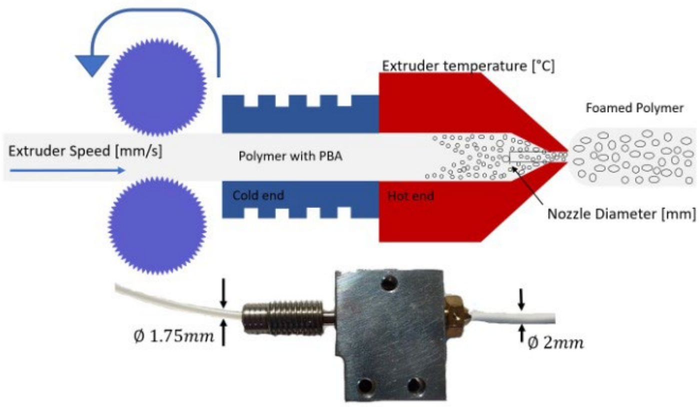


Fig. 1 - Additive Manufacturing of foams extruder: sketch (top) and real picture (bottom).

In this research it was chosen to validate the AM of thermoplastic polymer foams with a custom-made polylactic acid filament, to have control of the thermal history and the rheology of the filament. Each foamed strand was then characterized in terms of microstructure with SEM images, mechanical properties via mini-tensile tests and finally in terms of density and cross section size measurements. The polylactic acid (PLA) used in this research is the PLA 710 grade M by Bewi Synbra bought as microbeads, whose characteristics are reported from the manufacturer [31]. The carbon dioxide pure at 99,95% from the Sol Group S.p.a was used as a blowing agent.

The strand densities were measured using the Gibertini Eternity Balance, which employs Archimedes' principle by comparing the weight in air and in water. Foamed strands were examined using a Hitachi High-Technologies Corporation TM3000 electronic microscope (SEM) to investigate the micromorphology of the foam. The specimens were prepared by cutting and flash-freezing with liquid nitrogen using an Astra Platinum blade. Metallization of the specimens was achieved using a K650X Sputter Coater from Quarum Technologies with gold as the filler material for surface conductivity. The mechanical behaviour of each foamed strand was analysed using micro-tensile tests conducted with a Deben Microtest 200N instrument. Custom jaws were designed and fabricated to securely grip the strand with epoxy resin during testing. In **Figure 9**, it is possible to see 3 cross section images made by scanning electron microscope of the strands realized at different extruder temperatures keeping constant the others process parameters. It can be noticed how, as the temperature increases, the bubbles tend to coalescence and escape as gas from the polymer. The strand realized with the lowest temperature has a final diameter of 2.6 mm and the one realized with the highest temperature has a diameter of 1.2mm. This put in evidence the need to accurately control the temperature during the printing to obtain a product with the desired microstructure.

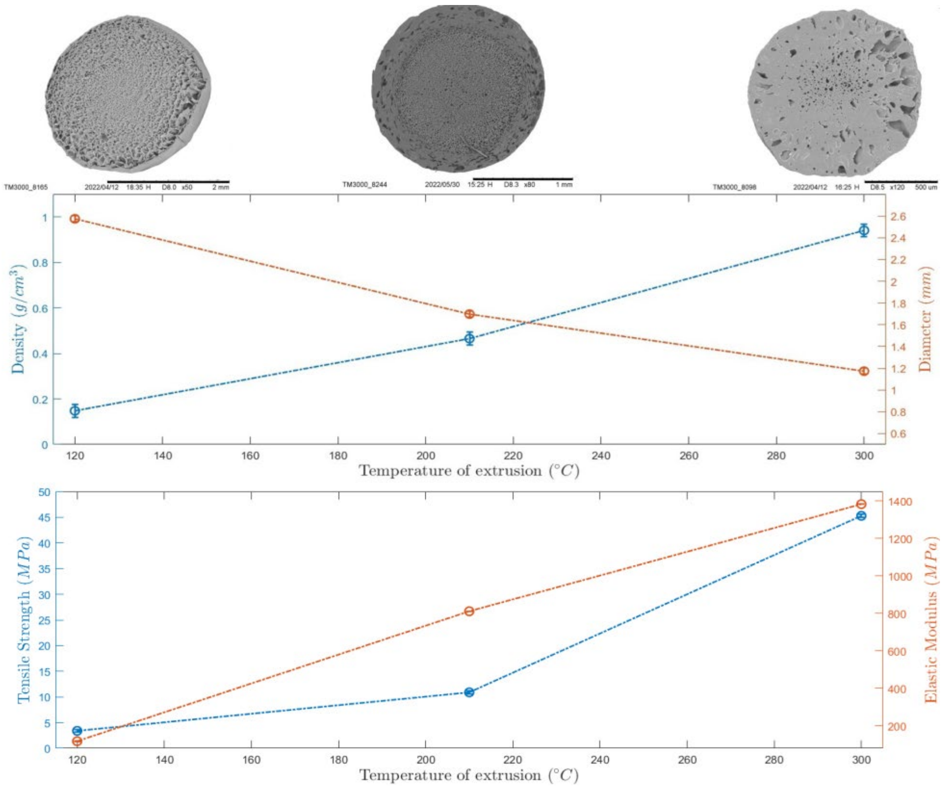


Fig. 2 - Influence of the temperature on the foam properties. P_a=32.5bar; T_a=33h; T_d=138h; N_d=0.7mm; S_e=675mm/min

The final density and diameter of the foamed strand strictly depends on bubbles size and location, as reported in **Figure 9**. In the same figure, tensile strength and elastic modulus of foamed filaments are reported versus extrusion temperature. By screening the foam production of various thermoplastic polymers, the feasibility of the process could be verified with a series of tests. As examples, the properties and morphologies obtained for various polymers are shown in the following **Figure 10**.

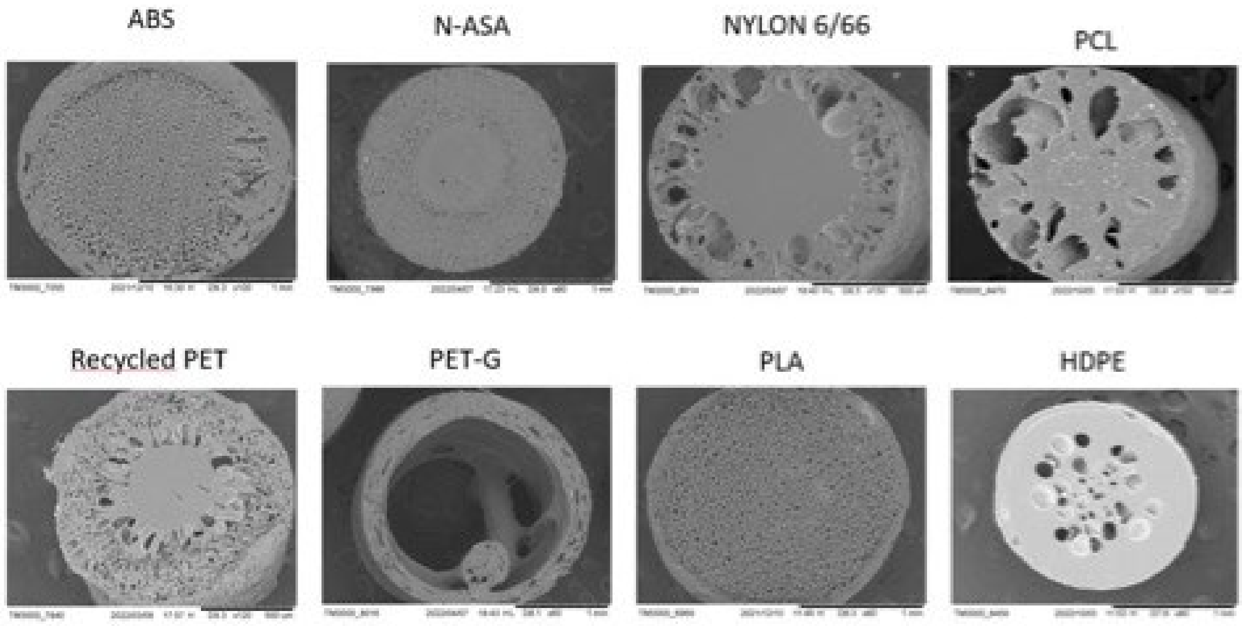
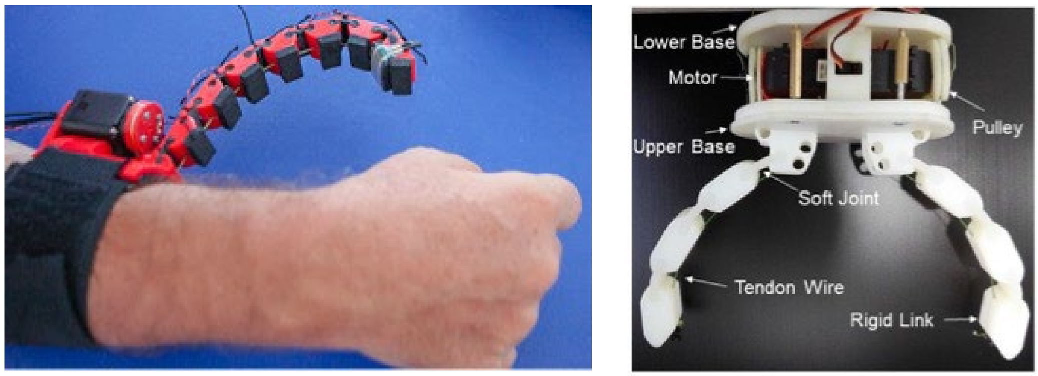


Fig. 3a - Different thermoplastic polymers foamed with FAM technology

With the process just described, the research group involved intends to propose the manufacturing of robotic systems such as sixth fingers (see **Figure 10b**) or exoskeletons that are lighter (thus benefiting from the advantages of expanded structures), monolithic (thus benefiting from the advantages of processability and sustainability of monomaterials), in which the ability to articulate one part over all the others is not due to the classical joints, but rather to soft joints thanks to the intrinsic flexibility of foamed thermoplastic or elastomeric polymers.

Here are some interesting examples of possible benchmarks:



a) b)

Fig. 10b A sixth finger consisting of several components and joints (a) and a monolithic gripper with soft joints (b)

On the premises of these first results, it can be stated that:

- FAM is promising for the creation of complex structures with intricate internal geometries that would be difficult or impossible to achieve with traditional manufacturing methods.
- Precise control over printing parameters is necessary to produce high-quality objects with FAM. This includes the extrusion temperature, pressure, speed, and die geometry, which can significantly affect the expansion of the polymer and the resulting foam morphology.
- Future steps in FAM should focus on further improving control over the printing parameters and developing new materials and printing techniques to expand the range of possible foam structures and properties.

1.1.2.2 Development of soft active coatings

PHOTORESPONSIVE CROSSLINKED POLYMERS FOR THE SWITCHABLE RELEASE OF SMALL MOLECULES AS WEARABLE ROBOT COATINGS

Tactile sensations are usually triggered by external objects interfering with receptors and other ion channels of the Transient Receptor Potential ion channels (TRP) family, located on the plasma membrane of numerous animal cell types. Usually, ion channels included in this family are responsible of primary functions for the cell, modulation of calcium oscillations, insulin secretion, cold (TRPM8), heat, and pain sensations (TRPM3), magnesium reabsorption and cell adhesion.

In normal conditions, cold and heat sensations are usually caused by the local variation of temperature, but those sensations can also be chemically triggered using a group of small molecules that could interact with TRPM channels, such as menthol for cold, capsaicin for heat or pain, lidocaine for numbness.

The project aims to the incorporation of these small molecules into a switchable photo responsive matrix, which can ultimately release the selected compound through light-activated mechanisms. The synthesis of the photo-responsive crosslinked polymeric matrices is still in progress. First, the photo-responsive linkers should be synthesized, then they will be used to crosslink linear polymer/polysaccharide chains to obtain photo-responsive matrices for the switchable release of small active molecules To achieve this final product, the E/Z photoisomerization process of azobenzene moiety will be exploited, using them as crosslinkers of linear polymeric and biocompatible matrices, such as Polyvinyl Alcohol (PVA) and polysaccharides. The crosslinking reaction will be achieved when azobenzene moieties are functionalized with a reactive group (such an aldehyde or an amine) to react with the polymeric backbone and achieve a final ether or amide moiety. To obtain a selective wavelength for the cis-trans isomerization, this crosslinker will be further functionalized even according to mesh size and optimal release conditions.

As benchmarks, the reactions are performed with a di-aldehyde crosslinker for PVA (to obtain an ether crosslinking bond) and a di-amino crosslinker for polysaccharides matrices, to assess the yield of EDC/NHS coupling and amide formation with the selected polymer matrices, while the synthesis of a library of photo-responsive linkers is in progress.

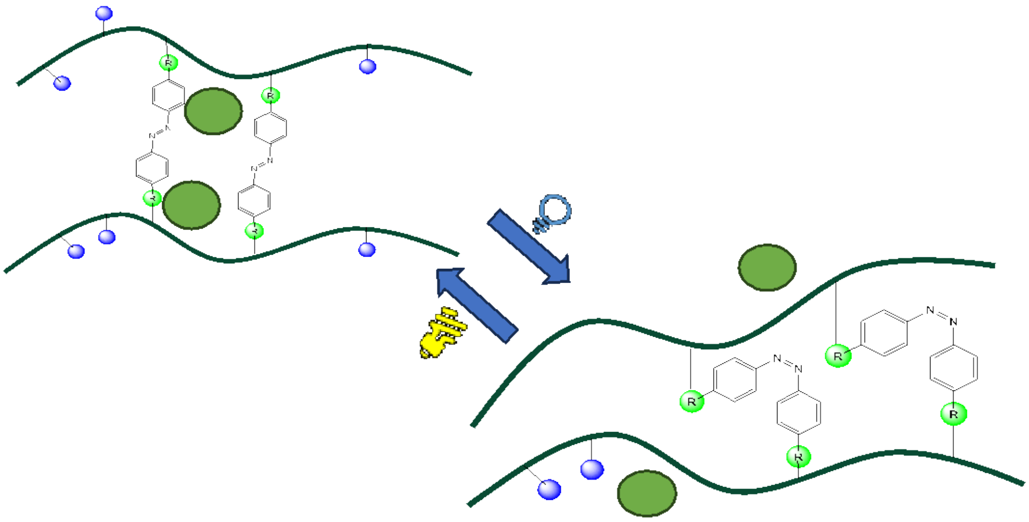


Fig. 41 - Scheme of cargo release from polymer matrices crosslinked with azobenzene moieties under UV light stimulus.

1.2 POLIECO-BAT: REPORT ON RESULTS

FIT4MEDROB addresses the issue of powering biomedical devices by considering modern and no longer deferrable eco-sustainability needs. For this reason, within the MISSION3 dedicated to support basic research related to the physical and computational aspects of robot bodies, robot intelligence, and interfaces with the patient, specific studies on innovative and eco-sustainable materials for new batteries are also envisaged. In addition, since biomedical devices designed under FIT4MEDROB are intended for frail people or people with limited physical capabilities who are particularly vulnerable in the event of imminent danger or accident, the new batteries powering these devices should also be safe. In this context, the sub-project POLIECO-BAT aims to realize safe and eco-sustainable batteries, focusing the research on the case-study of innovative metal-air batteries to power disposable sensors of glucose in sweat.

Currently, robots are mainly used in elderly health care to provide direct physical assistance, companionship, or health and safety monitoring [62]. The future goal of the assistive robots will be to focus on rehabilitation or telerehabilitation with a direct sensorial support on therapy effects (biomedical parameters monitoring). In the past, the use of technology to promote diabetes care has mainly focused on healthy eating and medication [63]. Telerehabilitation, which carries health services through telecommunication systems is an important treatment option for improving continuity for patient care and health care [64]. About the modulation of physical activity in cardiac rehabilitation, it was demonstrated that, if glucose levels tended to be >8.0 mmol/L, a middle intensity aerobic exercise could be started first, while if glucose levels were <5.0 mmol/L, a carbohydrate-based snack could be provided, or an intensive but brief aerobic activity could be initiated first [65]. So, the development and the availability of energy autonomous sensors for glucose monitoring during rehabilitation exercises is highly desired and recommended.

The technology on which glucose sensors are based is the glucose oxidation reaction, catalysed by the Glucose oxidase (GOx) enzyme, which produces hydrogen peroxide which, in turn, is reduced by Prussian blue producing a current signal. Therefore, the current measured by the device is proportional to the concentration of glucose in sweat. The sensor is small and presents significant technical challenges. In fact, it should be able to measure electrical currents of the order of magnitude of microamperes, distinguishing the glucose signal from that of other compounds present in sweat, and guarantee sensitivity levels of at least tens of µM/L. In turn, the battery that powers this sensor, to be physically integrated into the device, must be small and deformable, but without short-circuiting the electrodes, and with the required electrochemical performance. In addition, since these sensors are disposable devices, the battery should also be low cost, as well as eco-sustainable and safe. Al-air batteries, assembled with neutral gel polymer electrolytes (GPEs) made of natural polymers and with metal-free cathodes of vegetal origin, have been proposed as the most suitable electrochemical cell to power these sensors.

This case study, although focused on low-power batteries, offers the opportunity to study the electrochemical properties of new materials to extend their applications: It suffice to mention the electrochemical stability of solid electrolytes and the electrocatalytic properties of cathode materials towards oxygen reduction and evolution reactions (ORR and OER), fundamental for defining possible cell applications at higher powers, including the possibility of charging the cells.

During the first year of the project, in accordance with its scheduled activities/deliveries, the most suitable biomedical sensors and batteries to power these devices have been identified. They rare glucose sensors and Al-air cells. Although preliminary, interesting studies have also been carried out on both sensors and batteries. Thus, the small glucose sensor realized by CNR-IMM has shown a detection limit of 30 µM/L, while the experimentation conducted by CNR-STEMS on materials for electrochemical applications has highlighted the potential of GPEs produced from natural polymers and wood-derived cathode materials, even tracing new paths to obtain better performing cells.

1.2.1 Glucose sensor (µM range in sweat)

CNR-IMM has proposed a device for the indirect monitoring of blood glucose through the detection of glucose in sweat [66-69]. New glucose sensors, utilizing an enzymatic layer deposition process with Prussian blue mediator, have been developed. Moreover, the sensor has been integrated in a medical patch and calibrated with typical sweat glucose concentrations. The concentration of glucose in human sweat is 0,06-0,2 mM which corresponds to 3,3-17,3 mM in the blood. The operating principle of the sensor is represented in the following **Figure 12**:

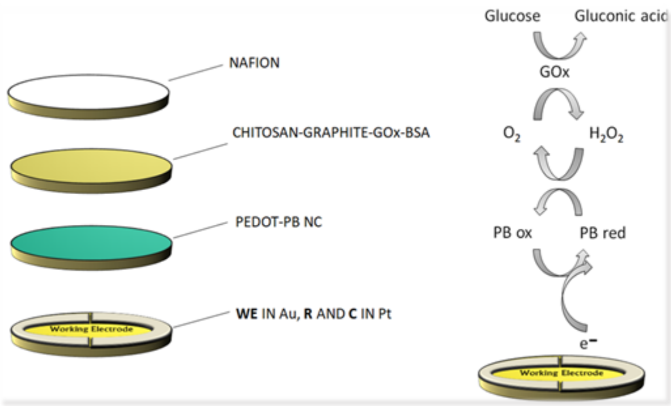


Fig. 52 - Operating principles of glucose sensor

Briefly, The Glucose oxidase (GOx) enzymes embedded in a polymeric layer, catalyses the production of hydrogen peroxide (H2O2) in proportion to the glucose concentration. The H2O2 is then promptly reduced by Prussian Blue (PB) layer of the sensor generating an amperometric response.

In **Figure 13** some sensor pictures, its response curve to glucose concentration and the calibration curve are reported.

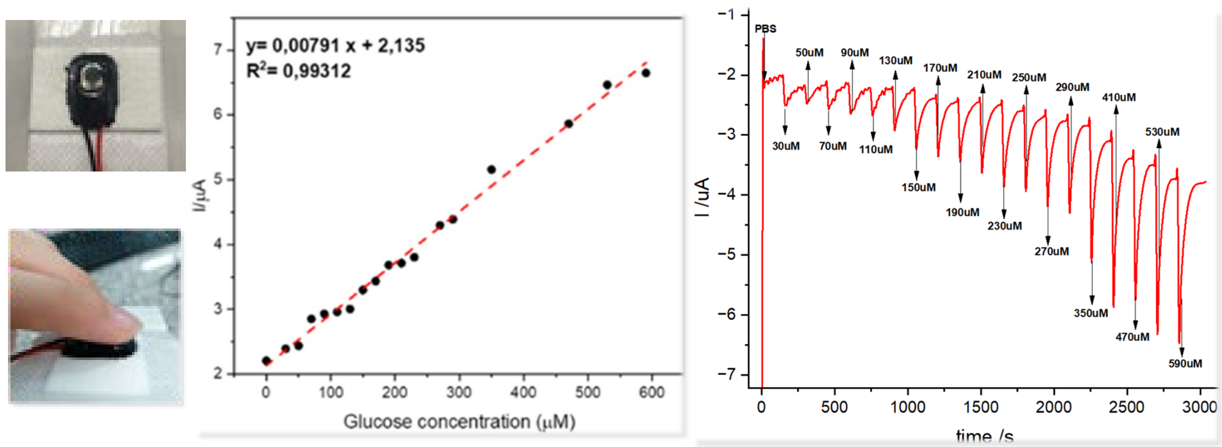


Fig. 6 - Sensor pictures (left), sensor calibration curve (center) and sensor response curve to glucose concentration (right). The glucose quantities in figure refer to 1 liter of solution.

The calibration curve results approximately linear up to glucose concentration of 600 µmol/liter, with a sensitivity limit of 30 µmol/liter. The right curve evidence the response rapidity of the sensor also at low glucose concentration.

1.2.2 Materials for sustainable electrochemical cells: the electrolyte and the wood-derived carbons for metal-free cathodes

A Gel Polymer Electrolyte GPE for Al-air cells has been prepared starting from xanthan gum and neutral aqueous solutions (in the following indicated as NX-GPE). Xanthan gum is a nontoxic natural polysaccharide and an important industrial biopolymer, produced by the bacterium Xanthomonas Campestris. GPEs made of xanthan and aqueous solutions, at any pH value, show electrochemical properties suitable for practical applications [70, 71]. Neutral KCl aqueous solution based electrolytes exhibit higher operational safety and superior environmental benignity, with respect to acidic and/or alkaline solutions. They are more suitable to be used as power sources for devices working closely to the human body., as glucose sensors but also strain sensors detecting facial expressions which can be coupled with a rehabilitative device to help people with mobility issues [72]. The NX-GPE is gummy with a marked stickiness, as shown in **Figure 14**, left, useful for ensuring good contact with the electrodes. The NX-GPE conductivity values, depending on the xanthan concentration, is in the range 1-2 mS cm-1 (Figure 17, right)

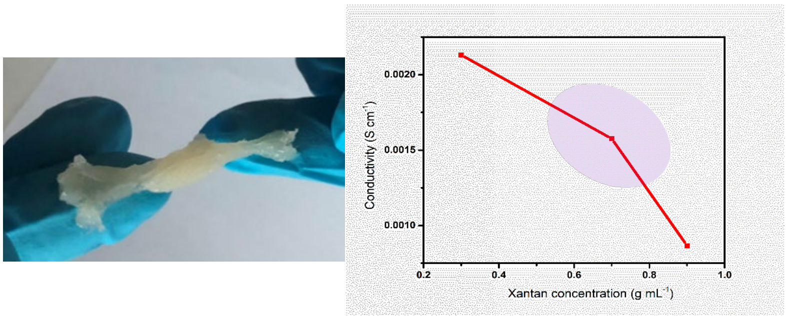


Fig. 7 - NX-GPE (left) and the ionic conductivity of the electrolytes prepared with different xanthan concentration (right). The conductivity values have been retrieved from Electrochemical Impedance Spectroscopy measurements. The pink oval identifies a useful

Activated carbons obtained by pyrolysis of biomass (b-AC) have been chosen as cathodic material as they are known to be characterized by catalytic activity for oxygen reactions [73]. The electrocatalytic activity of these carbonaceous materials seems associated with the presence of defects in the graphite layers, such as edges or point defects caused by vacancies or impurities [74]. Furthermore, the natural hierarchical porous structure of some biomasses, for example wood, partially preserved during the pyrolysis process, is an ideal template both for the effective diffusion of oxygen towards the interface with the electrolyte and for the high accumulation of the metal-air battery reaction products [75]. Cathodes have been prepared by coating carbon cloths with inks of b-AC or of benchmark Pt/C cathodic material (Figure 18, left). Linear sweep voltammetry (LSV) measurements of the b-AC and Pt/C cathodes contacted with NX-GPE were also carried out. As shown in Figure 15, a more marked inflection and a significant increasing of the current is obtained at more positive potential with b-AC cathode, indicating a more active material for the Oxygen Reduction Reaction (ORR).

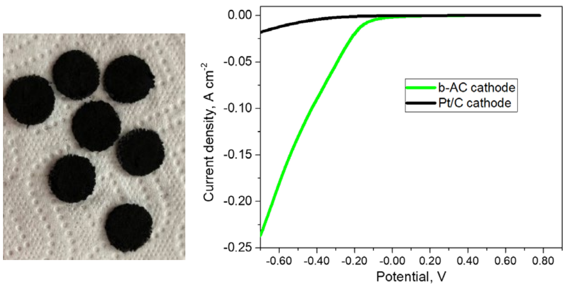


Fig. 8 - Cathodes for 1 cm diameter Al-air cells (left). LSV measurements effected on cathodes contacted with NX-GPE (right)

Anodic efficiency (AE) measurements allow to evaluate how much metal is used in the electrochemical reaction of metal-air cells, with respect to metal consumed in parasitic reactions. The higher this value, the more efficient the cell and the closer its gravimetric capacity (in Ah gMe-1) is to its theoretical value, that in the case of Al-air cell reaches the remarkable 2.98 Ah g-1 (77% of Li-air cells).

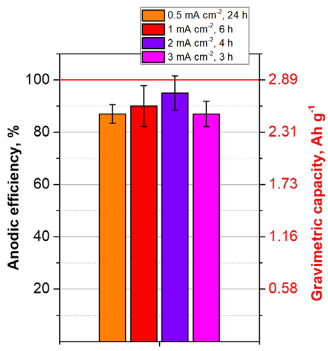


Fig. 9 - Anodic efficiency/gravimetric capacity vs discharge current of cells assembled with NX-GPEs and b-AC cathodes

In **Figure 16**, the anodic efficiency of Al-air cells assembled with NX-GPEs and b-AC cathodes is reported. The AE values are retrieved from anode weight loss measurements after discharge tests. As Figure 16 shows, the anodic efficiencies are between 80 and 90%, indicating that cells made with NX-GPE and b-AC, in addition to being benign for health and the environment, are also rather efficient electrochemical cells.

DISSEMINATION

- M. Fraldi, S. Palumbo, A. Cutolo, A.R. Carotenuto, D. Bigoni, “Bimodal buckling governs human fingers’ luxation”, PNAS, 120 (44) e2311637120, 2023
- International conferences “Eurosensors” 2023 in Lecce, 10-13 September and “Processes in Isotopes and Molecules- T3 Green Energy and Innovative Technologies” in Cluj-Napoca, Romania, 19-22 September 2023.

List of Abbreviations

AC	Activated Carbon
AE	Anodic efficiency
AM	Additive Manufacturing
BBPD	Bond-based perdynamics
C-PIL	Cross-linked PIL
ER	Electrorheological
FE	Finite Element
FAM	Foam AM
FFD	Fused Filament Deposition
GPEs	Gel polymer electrolytes
Gox	Glucose oxidase
HEC	Homogeneous Equivalent Continuum
IL	Ionic Liquid
LSV	Linear Sweep Voltammetry
MCF	Magnetic Compound Fluids
MEMS	Micro-Electro-Mechanical Systems
MILs	Magnetic ionic Liquids
MR	Magnetorheological
MRE	Magnetorheological Elastomers
MRF	MR Fluid
MRPG	Magnetorheological Polymer Gels
NEMS	Nano-Electro-Mechanical Systems
OER	Oxygen evolution reaction
ORR	Physical Blowing Agent
PBA	Oxygen reduction reaction
PC/ABS	Polycarbonate/AcrylonitrileButadieneStyrene
PCL	Polycaprolactone
PD	Perdynamics
PDE	Partial Differential Equation
PEEK	Polyetheretherketone
PEI	Polyetherimide
PEO	Poly (ethylene oxide)
PILs	Poly(ionic liquid)s

PLA	Polylacticacid
PVA	Polyvinylacohol
RTILS	Room temperature Ionic Liquids
RVE	Representative Volume Element
SEM	Scanning electron Microscope
TRP	Transient Receptor Potential

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