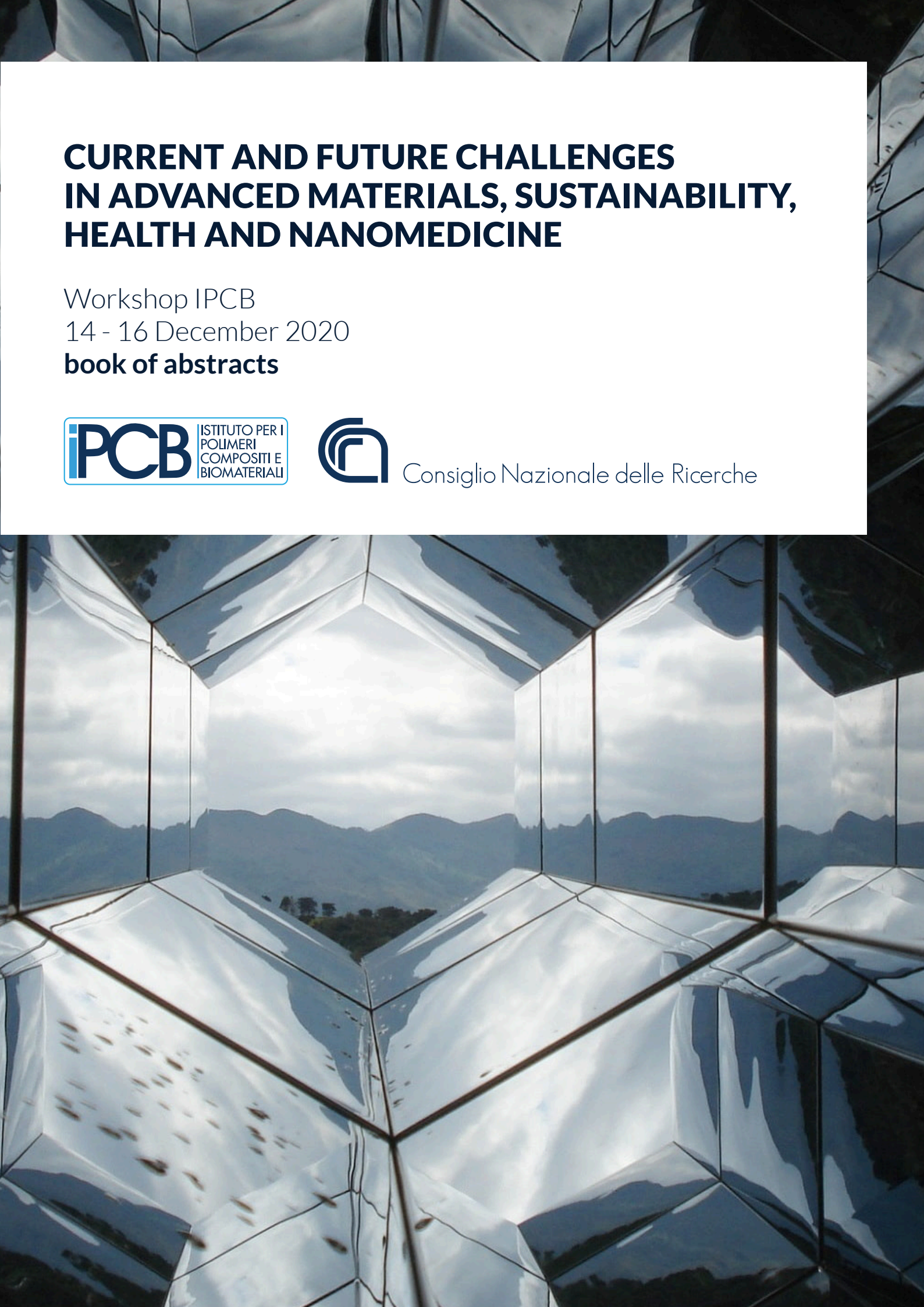

CURRENT AND FUTURE CHALLENGES IN ADVANCED MATERIALS, SUSTAINABILITY, HEALTH AND NANOMEDICINE

Workshop IPCB
14 - 16 December 2020
book of abstracts

IPCB ISTITUTO PER I POLIMERI COMPOSITI E BIOMATERIALI

Consiglio Nazionale delle Ricerche

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Editor Luigi Ambrosio

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EDITORIAL

Dear Colleagues and Guests,

On the behalf of the IPCB's Council, It is my great pleasure to organise and invite you at the first workshop of the Institute aiming to share and discuss the ongoing research activities as well as the transfer technology and outreaching ones. This initiative aims to identify the last achievements in terms of new research topics, to define a platform for new strategies, for finalizing proposals in agreement with regional, national and European programs - Horizon Europe, as well as with international programs (USA, CHINA, etc.), able to satisfy the needs of modern society and the specific dynamic evolution.The Institute of Polymers, Composites and Biomaterials with more 120 staff, located in four locations (Pozzuoli, Napoli/Portici, Catania and Lecco), is the biggest Italian institute performing research on polymer based materials and related advanced technologies. The research activities are organized in three main research platforms: Advanced Materials, Sustainability, Health and Nanomedicine. These activities, developed with a sustainability-based approach, are mainly focused on the synthesis and realization of innovative materials, the development of personalised solutions in nanomedicine and health, the application of chemistry and materials science for the environment and energy, transport, packaging and cultural heritage.

The workshop program includes almost 80 oral and poster presentations plus three main lectures covering the research themes included in the following scientific sessions:

1. Polymers, composites and nanostructures (bio- and synthetic) with multifunctional and sensing properties;
2. Multiphase polymer based materials, nanomaterials and nanostructures (synthetic and natural) for tissue engineering and regenerative/therapeutic medicine. Biointerfaces, drug delivery systems, glycoproteomics;
3. Advanced and sustainable processing technologies of polymers, composites and nanostructures. Additive technologies;
4. Synthesis, functionalization and modelling of polymers based materials. Structural characterization of macromolecule and advanced analysis techniques;
5. Knowledge and technology transfer. Outreaching.

The workshop program is a clear demonstration of the enormous advances of polymers based materials and nanosystems science within the three research platforms reported above. Despite the limitation of the actual sanitary situation due to COVID19, development of new ideas have been presented by implementing the interdisciplinary and multidisciplinary approach as well as inter-sectorial one. This at once presents the young scientists with many challenges, but also with the opportunity to acquire and apply new concepts on scientific knowledge of the highest level as their career progress.

Finally, I would like to invite you to read this abstract book which contains accounts of high quality research and transfer knowledge work performed by the scientists of the Institute.

Luigi Ambrosio

MAIN LECTURES ABSTRACTS

"I'M LOOKING FOR THE LIGHT OF SCIENCE AND ITS BENEFIT"

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The future we're living in is increasingly determined by knowledge, creativity and the ability to produce and use new ideas. We are witnessing and participating in profound transformations that raise new questions but also new awareness. The main one is the fundamental value of Research that becomes an Innovation, understood as an essential driver of economic progress that benefits consumers, businesses, and the economy. Recent epidemics and pandemic threats have shown that scientific Research play a crucial role in combating these crises.
In this context, an analysis of the various performance indicators of scientific research places the Italian system, in terms of innovation and productivity, at the top of all international rankings. However, the knowledge produced has a weak impact on the country's competitiveness system and in industrial terms there is an ineffective transfer of scientific results. Technological transfer represents the tool with which the industry can receive the research results, understand them, process them within their own schemes and deliver a concrete application through the development of innovative products. Materias developed a new business model, to overcome the "Death Valley", through the creation of new business opportunities, by developing science-based technologies in the field of advanced materials and by speeding up the connection between research world and industrial companies.

APPLICATIONS OF NMR METHODOLOGIES TO ELUCIDATE STRUCTURE AND FUNCTIONS OF BIOLOGICAL SYSTEMS

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Nuclear magnetic resonance (NMR) spectroscopy is unique among the methods available for three-dimensional structure determination at atomic resolution of large molecules, such as proteins and nucleic acids, since the NMR data can be recorded in solution [1]. Furthermore, NMR applications allow investigations of dynamic features of the molecular structures, including folding mechanisms, as well as studies of structural, thermodynamic, and kinetic aspects of interactions between proteins and other solution components, which may either be other macromolecules or low-molecular-weight ligands. Here, the solution NMR studies elucidating the structure and dynamics of the Ros87, the first identified member of the prokaryotic zinc-finger family [2], and their relationship with Ros87 tendency to form fibrils will be described. Moreover, the investigation, at atomic level, of the unfolding mechanism of the human prion protein will be also presented, showing the conformational equilibrium between its native structure and a pathogenic β-enriched intermediate state. Finally, an original approach to elucidate mechanisms of action of antimicrobial peptides and derive crucial structural requirements for the design of novel therapeutic agents will be also reported. In particular, the high resolution structure of TB_KKG6A, an antimicrobial peptide designed to amplify the spectrum of action of Temporin B, has been obtained when bound to intact E. Coli cells [3], showing the intriguing potential of the in cell NMR.

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THE CHEMICAL DIVERSITY OF MICROBIAL POLYSACCHARIDES

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Microbial cell surface molecules, such as lipopolysaccharide and exopolysaccharides, are very important cell wall glycoconjugates and act as microbe associated molecular patterns in eukaryotic/bacteria recognition. Besides their general architectural principle, a number of subtle chemical variations are at the basis of the dynamic host-guest recognition that in case of pathogens is followed by the innate response and in case of symbiosis is followed by its suppression. Microbes differently from Eukaryotes have at their disposal an enormous array of monosaccharide structures/derivative with which they built up they external cell surface molecules and drive their recognition by any eukaryotic host. Therefore, the chemical study of such glycoconjugates involved as virulence or beneficial factors in animal or plant interactions is a pivotal pre-requisite for the comprehension at molecular level of the innate immunity mechanisms. [1-4] In this communication, I will show some examples of isolation, structure determination and elicitation and/or suppression of plant and animal innate immunity by cell wall glycoconjugates from pathogen and symbiotic microbes.

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SCIENTIFIC SESSIONS

Polymers, composites and nanostructures (bio- and synthetic) with multifunctional and sensing properties.

Multiphase polymer based materials, nanomaterials and nanostructures (synthetic and natural) for tissue engineering and regenerative/therapeutic medicine. Biointerfaces, drug delivery systems, glycoproteomics;

Advanced and sustainable processing technologies of polymers, composites and nanostructures. Additive technologies.

Synthesis, functionalization and modelling of polymers based materials. Structural characterization of macromolecule and advanced analysis techniques.

Knowledge and technology transfer. Outreaching.

ABSTRACTS

Polymers, composites and nanostructures (bio- and synthetic) with multifunctional and sensing properties.

RECYCLABLE AND SELF-HEALING COMPOSITES BASED ON THERMOREVESIBLE DYNAMIC COVALENT BONDING

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Nondestructive recycle of fiber and resin from cross-linked fiber reinforced polymer (FRP) composites is still a challenge on the way to pursuing sustainable and circular economy. One strategy for promoting sustainability is to design materials with reversible cross-links and allow temporary unwinding of the existing network by incorporating bonds which can undergo reverse reaction pathways by degradable, associative, and dissociative mechanisms, therefore offering inherent recyclability.
Epoxy precursor containing a Diels-Alder moiety can be used to tune the flexibility of the polymer chains [1], the interaction among different polymer segments and the aggregation structure of the network, further influencing the mechanical, self-healing and reprocessing properties [2].
FRP composites based on intrinsic self-healing epoxy resin can only recover the damage related to the cohesive failure of the host matrix while the delamination between matrix and reinforcement would not benefit from the reversible reaction to restore the pristine condition, due to the lack of reversible functional groups grafted onto the fibers. In this work a comprehensive approach combining intrinsic healing of the hosting matrix with the reversible Diels-Alder reaction at the interface [3] has been implemented to promote a mixed-mode recovery strategy for cohesive failures within the hosting matrix and adhesive at the interfaces between polymer and reinforcement.

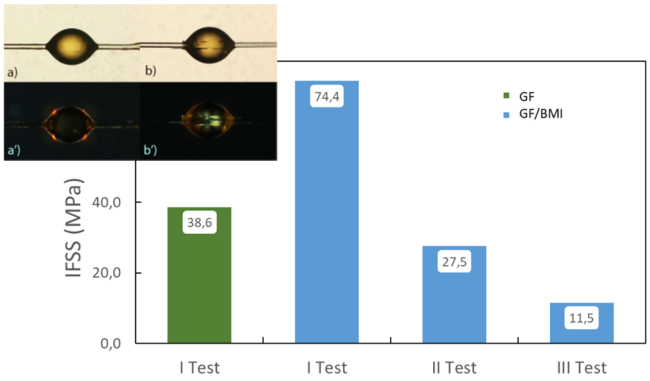

Figure 1. Interfacial strength as function of healing cycle.

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ELECTROSPUN FIBROUS 3D-STRUCTURES

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The feasibility of using electrospun fibrous 3D structures in different fields is due to their many promising properties such as high specific surface area, tailored functional abilities, versatility in material choice, ability to be combined with other techniques, high porosity and small pore size.
In this scenario, our research activity is focused on accurate designing and selecting of materials and morphologies to realize electrospun fibrous structures for different applications ranging from nanomedicine to environmental remediation. Our results reveal that natural extracts are effectively encapsulated in this kind of structures, their bioavailability is enhanced and the release behavior is sustained and tunable in different biological environments [1-3]; as well as, we showed the growth and maturation of stem cells is driven by the 3D fibrous microenvironment that combining diverse cues and factors is able to manipulate biological response [4].
In addition, the highly interconnected porosity of nonwoven three-dimensional structures and the possibility of fine-tuning the porosity and the matrix composition via electrospinning process are intriguing characteristics for air and fluid filtration devices and strongly affect their filtration performance [5].
Lastly, by combining different techniques (i.e. electrospinning, spin coating and solid state polymerization) we effectively succeed in the fabrication of eumelanin based 3D structures with hollow nanofibers [6].

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ANTIOXIDANT AND ANTIBACTERIAL FILMS AND COATINGS FOR PACKAGING AND HEALTHCARE APPLICATIONS

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Due to recent progresses in material chemistry and material science, advanced nanoscale systems used to control the release of active compounds have recently received tremendous attention. In recent years, many inorganic nanomaterials used as nanocarriers have been intensively studied, mainly porous systems which can act as reservoir for the accommodation of drug molecules. In fact, the well-known opportunity to chemically functionalize the surface of siliceous mesostructures with different organic moieties constitutes a route for controlling the drug release by diffusion under specific conditions [2].
The understanding of the fundamental and technological aspects which rule the controlled and triggered release of active compounds from films and coatings with aim to prolong food shelf-life and/or to prevent biological risks in hospitals are the main objectives of this activity. In fact, such approach can be used in the field of food packaging due to the increasing interest in the concept of "active packaging" materials which exhibit a controlled release of active compounds from the film/container to the food with the aim to delay or inhibit the mechanisms responsible for the degradation of the packed foodstuff. A similar strategy can also be used in the field of healthcare. Indeed, the propagation of antibiotic resistance increases the chances of major infections in hospitals. Therefore, the development of nanomaterial-based antimicrobial film and coatings to cover the surfaces in frequently-touched areas in healthcare settings and hospitalization rooms is of utmost importance to prevent the proliferation of pathogenic microorganisms and to protect hospital environment [1].
In this work we present a comparison of different active systems developed by loading various active compounds into/onto inorganic (nano)carriers and then embedding them into low density polyethylene, polycaprolactone and chitosan matrices. The study is mainly focused on the use and chemical functionalization of organic or inorganic (nano)particles to be used as reservoir of active (antioxidant/antimicrobial/antibacterial) compounds and on the study of the structural, functional and mass transport properties of the active materials related to the interactions between active compounds and polymeric matrices.

Acknowledgement: This work has been supported by the NANODISP and HEALTHYPACK projects. Technical support of Mrs. A. Aldi and Mrs. M.R. Marcedula is kindly acknowledged.

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HIERARCHICAL POROUS SYSTEMS CONTAINING HYPER-CROSSLINKED RESINS FOR THE ADSORPTION OF ORGANIC CONTAMINANTS FROM AIR AND WATER

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Porous materials characterized by high specific surface area (SSA) have attracted high scientific attention for their various potential applications in catalysis, separation, gas storage, liquid and gas purification. Among other microporous materials, hyper-crosslinked resins (HCLR) stand out for their low density and for the possibility of tailoring their structure, porosity, and functionality [1].
Recently, we obtained high surface area HCLR by a very versatile synthetic process based on the bulk polymerization of vinylbenzyl chloride (VBC) and divinylbenzene (DVB) followed by Friedel-Crafts reaction. This procedure was effectively exploited to realize tailored high SSA systems, either by grafting specific organic moieties or embedding functional nanostructured fillers within the resin, with the aim of enhancing their adsorption capacity and selectivity towards organic contaminants [2-4].
These functionalized hyper-crosslinked resins and nanocomposites were also engineered in different macroporous polymers and hybrid systems, realizing hierarchical macro/meso/microporous systems that have proven very effective for the adsorption of organic contaminants from air and water (Figure 1).

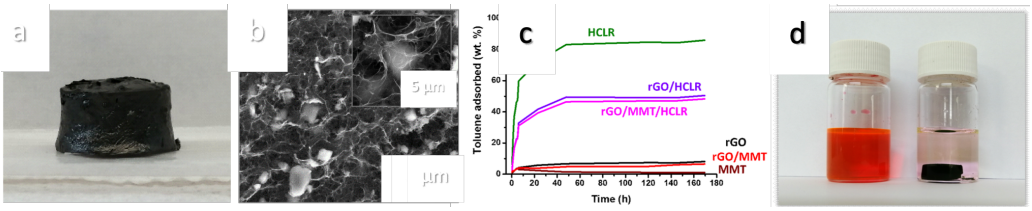

Figure 1. Photographic (a) and SEM (b) images of aerogel based on reduced graphene oxide (rGO) and montmorillonite (MMT) containing HCLR; toluene adsorption graph of rGO/MMT/HCLR systems (c); image of vials showing the rhodamine removal from solution of a rGO/MMT/HCLR hydrogel (d).

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INSIGHTS INTO STRESS TRANSFER MECHANISM IN HIGH FILLER CONTENT COMPOSITES

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Biomimetic composite materials, with brick and mortar architecture are gathering great attention recently due to the outstanding properties of the natural analogues. Thanks to the very high in-plane orientation of nanoplatelets and the low matrix content, these materials exhibit good mechanical performance based on the nanoplatelets characteristics. Key feature of these materials is the presence of a regular nanostructure that consists of alternated nanoplatelet and matrix layers. In the present work, nacre-like graphene nanoplatelets (GNPs)/epoxy films at different filler content have been prepared by a top-down manufacturing technology and their mechanical properties in tension have been experimentally evaluated. The elastic modulus has been found to exhibit a maximum at 50 vol% filler content and then it starts dropping at higher loadings. This is attributed to a discontinuous polymeric matrix layer, and thus to an incomplete GNP surface coverage at high filler content. As a result, the effective area for stress-transfer is considerably reduced at the expense of the reinforcement efficiency. To better understand this behaviour, a model is proposed for predicting the stress transfer characteristics in brick and mortar systems by paying attention to possible non-uniform matrix distribution over the nanoplatelets. The proposed analysis captures well the observed effects also for other materials in other pertinent works [1].

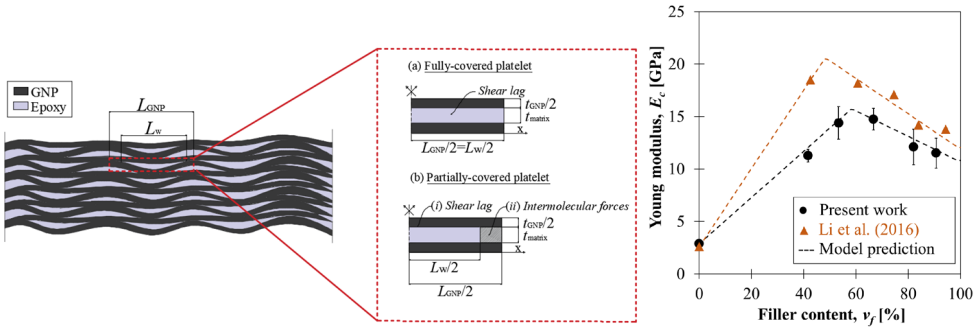

Figure 1. (a) Sketch of resin distribution in GNP/Epoxy film; (b) trend of elastic modulus with filler content

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CELLULOSE WITH TAILORED STRUCTURE AND MORPHOLOGY FOR THE REALIZATION OF SUSTAINABLE AND ADVANCED MATERIALS

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Cellulose has been defined as the most fascinating material, with impressive structure and properties [1]. It represents the most abundant biopolymer on the earth and it is considered an almost endless source of renewable raw materials, able to fulfil the ever-increasing demand for sustainable and circular products. Due to its peculiar characteristics, cellulose, in its fibrous form, has been widely used for a very large number of applications. More recently, cellulose has also entered the spotlight as a nanomaterial (in the form of micro/nanofibres and nanocrystals). Indeed, it is ascertained that by tailoring the crystalline structure of cellulose and its morphology, it is possible to realize cellulose based systems characterized by an extraordinarily wide range of properties and potential applications.
Moving from this background, a research line on the modification of cellulose through mechano-chemical processes and its use in polymer based systems was started a few years ago and the main results obtained are presented in this contribution.
First, amorphized cellulose was easily realized by a dry ball milling process [2] and the obtained material was proven to be a very interesting functional filler in bulk composites based on biodegradable polyesters [3,4] and in polyurethane foams [5]. In these systems, amorphous cellulose particles showed a peculiar behavior with respect to crystalline fibrous cellulose.
Moreover, researches have been focused on the optimization of a wet ball milling process, able to produce micro/nanofibrillated cellulose. In particular, the main goal of this on-going activity is the realization of advanced systems, including porous systems with high adsorption properties [6] and hybrid coatings with high gas barrier properties.

Acknowledgement: This work is partially supported by the project 2017LEPH3M PANACEA – A technology PlAtform for the sustainable recovery and advanced use of NAnostructured CEllulose from Agro-food residues, financed by the Italian Ministry of University and Research, PRIN 2017.

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ELECTROSPUN DEVICES WITH ELASTOMAGNETIC PROPERTIES FOR BIOMEDICAL APPLICATIONS

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This research deals with the optimization of the electrospinning process to fabricate smart devices by the assembly of submicro-fibers with elastomagnetic properties [1].
This purpose was firstly pursued by upgrading coaxial electrospinning process, being succeful in producing NI-PDMS nanofibers [2]. Subsequently, a great improvement was given by realizing an apparatus for magnetic field assisted electrospinning, that enabled the production of Ni-PCU fibres assembled in the form of tubes [3] or wires [4] with preoriented magnetic charge. All the devices showed an high flexural and longitudinal strain under the application of moderate magnetic stimuli, thus suggesting their promising use as bioactuators/biosensors for human implantation.
Recently, PCU ducts incorporating a ribbon-shaped mat of densely packed magnetic nanofibers were manufactured by magnetic field assisted electrospinning via multiple step process [5]. Experimental results show that the confinement of magnetic nanofibers, thus to form a longitudinal magneto-sensitive ribbon (Fig. 1), confer a relative transverse strain of 0.4 to the produced magnetoelastic tubes, under a magnetic field gradient $\Delta=(dB/dX) \leq 30mT/mm$ and at a basic field intensity $B < 0.04$ T. In perspective, this could be very attractive to fabricate magneto-active components for bioactuation and biosensing applications, clinical surgery and endoscopy.

Figure 1. Magneto-elastic electrospun devices: Scheme of the process and tube cross-section contraction, due to the application of a transverse magnetizing field.

Acknowledgement: We are grateful to Dr. Luca Lanotte (INRAE-STLO, Rennes, France) for stimulating discussions.

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NEW PERSPECTIVES IN THE DESIGN AND APPLICATION OF INNOVATIVE NANOCOMPOSITES BASED ON GRAPHENE RELATED MATERIALS

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Graphene and its derivatives, as well as other 2D materials (e.g. hexagonal boron nitride flakes (h-BN), layered chalcogenides, carbides, and oxides), commonly referred as Graphene Related Materials (GRMs) or two-dimensional materials (2DMs), are attracting a great interest from science and industrial comparts for their peculiar physical and chemical properties, such as electrical and thermal conductivity, high aspect ratio, wide versatility of the chemical structure and superficial defectiveness. For these materials, the forefront of the research has moved from the simple preparation and characterization towards the designing and control of quality and optimization of the properties. The last advancements, which have mainly concerned the development of preparation approaches for tailoring both the chemical and physical structure of 2DMs, have contributed to fostering their application in several sectors, up to the production of polymer nanocomposites very promising for future technologies. In this context, 2DMs hybrid structures (organized in 2D and 3D assemblies), polymer-2DMs interfaces and the spatial distribution of 2DMs are the key parameters which need to be optimized for designing innovative, effective and multifunctional polymer nanocomposites [1]. This contribution focuses on the design, preparation. characterization and validation of two different 2DMs-based composites: A) anisotropic composites fabricated by combining the layer-by-layer filtration method with the assembling of carbon nanotubes and hBN on natural rubber (NR) latex particles, which exhibit anisotropic thermal and electrical conductivities and effective EMI shielding (22.41 dB mm^{-1} at 10.3 GHz) [2]; B) lightweight, multi-sensitive porous composite materials based on reduced graphene oxide (rGO) and on an hybrid structure (realized by combining 1D and 2D fillers) of CNTs/rGO/NR, which exhibit low percolation threshold (<0.45 vol%), high sensitivity to compression strain (gauge factor equal to 77.64), sensitivity to liquids (i.e. toluene and tetrahydrofuran) and temperature (range of detectability is 35~90°C) and high electric-heating capability (about 70°C can be reached with an input voltage of 15V, applied for 80sec). The obtained results confirm that the 2DMs-based nanocomposites are very promising for perspective applications such as the production of wearable sensors for monitoring of body-movements and electromagnetic protective shielding structures for electronic devices.

Acknowledgements: The activities have been supported by the following projects: Joint Laboratory for Graphene-based Polymer Nanocomposites (CNR Joint Lab call 2015-2018), GRAPE-MAT (2015-2018), and GINSENG (2018–2020). The authors are grateful to A. Aldi, M. De Angioletti, F. Docimo and M. Marcedula for the technical assistance in research.

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INFLUENCE OF CRYSTAL NUCLEATION ON FOAMABILITY OF POLY (L-LACTIC ACID)

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The influence of aging of glassy poly (L-lactic acid) (PLLA) on foaming is detailed in this contribution.
PLLA is a thermoplastic polyester, widely used in the production of foams.
Aging of glassy PLLA allows formation of crystal nuclei which accelerates subsequent crystallization [1]. The same enhancement in surface free energy is expected to induce nucleation of bubbles in foaming.
Glassy PLLA aged for 0.5, 2 and 4 hours has been foamed with supercritical CO_2. Results demonstrated how the foam density decreases with the aging time. The morphology of the foams confirmed the role of crystal nuclei to promote bubble nucleation. This leads to the conclusion that aging glassy PLLA can be an efficient method to control and enhance foamability of polymers.

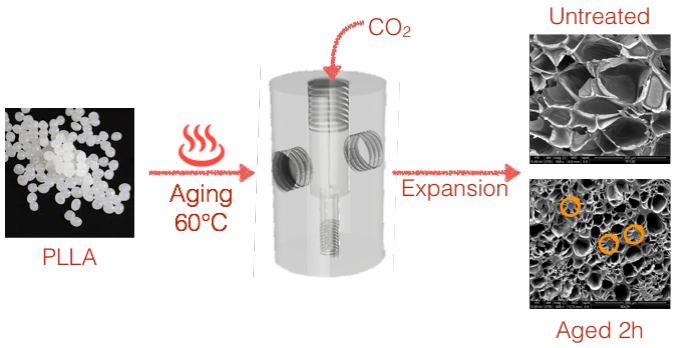

Figure 1. Graphical abstract. Foaming device and foam morphology.

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FUNCTIONALIZATION OF POLYMERIC SUBSTRATES BY GRAPHENE-LIKE COATINGS

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Nowadays, in all technological fields there is an increasing need for specifically designed functional materials. Owing to the variety of their chemical-physical properties, polymers represent the best class of materials for developing advanced devices, and their filling/coating by micro/nano-sized metals, ceramics, glasses, or other types of solid phases surely represents the best way to achieve materials with finely tuned characteristics. The graphite nanoplatelet (GNP) is an electrically conductive type of filler, potentially useful to fabricate innovative electronic conductors. Flexible, optically transparent, thermoresistive, piezoresistive and gas-barrier electrical conductors can be fabricated by coating a thermoplastic polymeric film with a continuous graphite-like layer. These coatings are generated by specifically developed deposition techniques like for example: (i) spreading an alcoholic suspensions of very small graphite crystals (GNP) on the surface of a non-polar polymeric substrate [1], (ii) spraying a GNP-polymer lacquers on the plastic film [2], or (iii) casting a GO-based ink on a thermally unstable substrate (e.g. cellulose) and chemically reducing it [3] (see Figure 1). Depending on the type of substrate, one approach can be more convenient than the others.

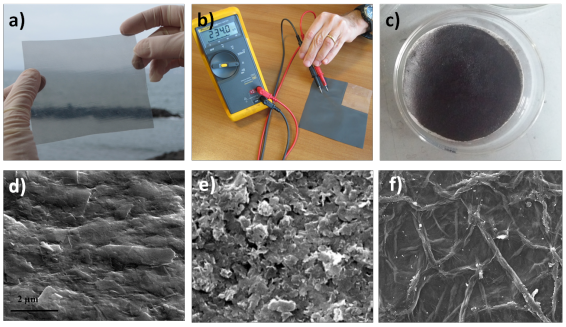

Figure 1. Material images and SEM-micrographs, showing the morphologies achievable by the different approaches (a,d GNP/LDPE produced by GNP spreading; b,e GNP/LDPE produced by lacquer spraying; c,f chemically reduced GO cast on paper).

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PHOTO-TRIGGERED RELEASE OF BIOACTIVE ESSENTIAL OIL FROM NANOCAPSULES-BASED POLYMER COATINGS

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Smart surfaces are a key element for the design and engineering of innovative materials that match the current need for high quality, safety and performance of products and processes. Bioactive coatings with on-demand activation can respond to such standards in food packaging technologies, pharmaceutical and medical applications as well as cultural heritage preservation. Our work focused on the application of photo-responsive nanocapsules containing thyme essential oil as functional coatings for flat and 3D surfaces. Among numerous available natural substances, essential oils stand out for their renowned antimicrobial, anti-inflammatory and antioxidant activity as well as their sustainability when compared to other petrol-based additives [1]. Azobenzene-based nanocapsules were obtained via miniemulsion polycondensation. The nanocapsules response to UV or visible light can be modulated during their synthesis - by adjusting their chemical structure [2] – or in use – tuning the light source wavelength [3]. Coatings were initially obtained by drop-casting of a nanocapsules solution on flat substrates such as PE and PLA films. More recently Matrix Assisted Pulsed Laser Evaporation (MAPLE) was used: a novel technique for the deposition of soft materials on 3D surfaces.

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ENGINEERING OF MESOPOROUS SILICA NANOPARTICLES AS NANOCARRIERS OF CORROSION INHIBITORS

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Mesoporous materials are very interesting for applications in several fields due to their inner porous structure, with pore size compatible with the adsorption of different molecules. In particular, the use of these materials as nanoreservoirs/nanocarriers of active agents is very promising due to their high loading capacity and the possibility of modulating their release.
Amongst mesoporous materials, mesoporous silica nanoparticles (MSN) have been recently exploited for the loading and the pH-controlled release of anticorrosive agent for cultural heritage applications [1].
In this contribution, new results obtained on the synthesis of MSN and their engineering are reported. MSN were synthetized by a facile high-throughput synthesis, with a 98% yield, and two different strategies were optimized to realize smart loading/release systems.
In a first approach, after the optimization of the loading of MSN with benzotriazole (BTA), the loaded nanoparticles were treated with a silver salt to realize new MSN/BTA systems. These nanoparticles showed a pH-controlled BTA blocking/release mechanism that was dependent on the dynamic equilibrium of formation and dissolution the BTA/silver complex.
With a different strategy, MSN were functionalized with aminopropyltriethoxysilane (APTES), then benzoyl chloride (BC) was reacted with the amino groups of APTES. With this method, the benzoyl group was grafted onto the nanoparticles through formation of amide bonds, and the release of benzoic acid was controlled by pH changes that affect the hydrolytic cleavage of the covalent amide bond.
These engineered nanoparticles are very promising to realize smart anticorrosion/antifouling systems for the protection of different substrates, potentially impacting on a wide range of application fields.

Acknowledgement:
This work has been supported by the Project RIPA-PAUN, financed by Regione Campania (POR FESR Campania 2014-2020, CUP B63D18000370007) and by the H2020 Project InnovaConcrete, financed by European Commission (G.A. n. 760858).

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THERMOMECHANICAL MODELLING OF REACTIVE THERMOPLASTIC COMPOSITES

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Joining large and complex polymer matrix composite structures is increasingly important in aerospace industries. This work aims to investigate the welding capability of composites made by a reactive thermoplastic resin, (Arkema Elium). The Elium polymer could be processed by conventional liquid moulding technology, nevertheless it should be reprocessed as thermoplastic.
A comprehensive thermal characterization has been carried out in order to extract parameters for finite element simulation. Differential scanning calorimetry (DSC) and dynamic-mechanical analysis (DMA) analyses were carried out. The viscoelastic characteristic was modelled by extracting Maxwell parameter from Master Curve in the frequency domain. A multiphysic analysis has been implemented to reproduce the behavior of complex shape component subjected to thermal flux, and to investigate the temperature distribution welding and predict residual stresses (Figure 1). The FE model was capable to simulate the continuous induction welding process, accounting for the anisotropy of the composite and the temperature dependence of the material properties.

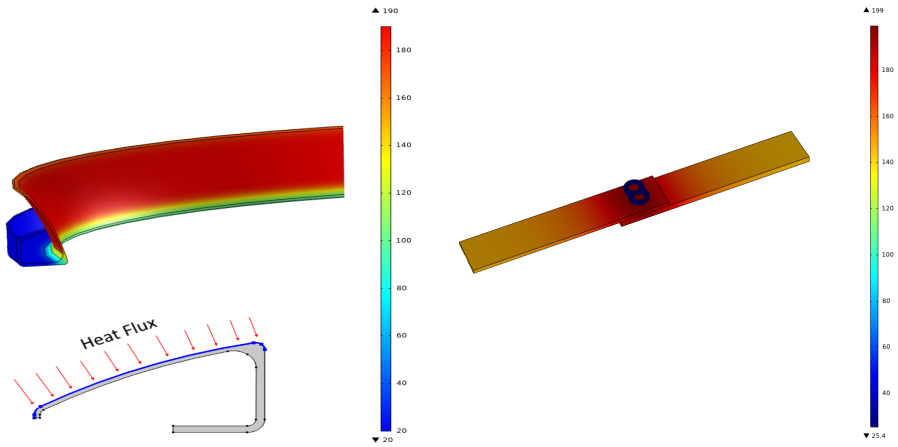

Figure 1. a) Simulated temperature distribution through the component; b) Simulated temperature maps on the welding surface.

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EFFICIENT NANOSTRUCTURED SUBSTRATES FOR THE ANALYTICAL AND BIOLOGICAL APPLICATIONS OF SURFACE ENHANCED RAMAN SPECTROSCOPY

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Surface Enhanced Raman Spectroscopy (SERS) is one of the leading techniques for molecular analysis, with sensitivity up to the single molecule. SERS consists of the enhancement of the Raman scattering intensity by molecules when these are adsorbed or in close proximity to nanometer-sized metallic (usually Au and Ag) particles [1]. The wide applications of SERS depend on the availability of high-performance SERS substrates. In the past few decades, the main challenge has been to fabricate SERS-active substrates with high sensitivity, uniformity, reproducibility and low concentrations detection capability [2, 3]. Owing to its tremendous signal enhancement, SERS has been the object of great interest in many areas of science and technology including chemical analysis, catalysis, biological sensors, nanomedicine, imaging and sensing leading to both diagnostics and therapies. Moreover, the advent of nanotechnology has opened up enormous opportunities in the biosensing area, allowing the fabrication of constructs that are small enough to be targeted in the interior of single living cells (Fig. 1) and their intracellular compartments [4].

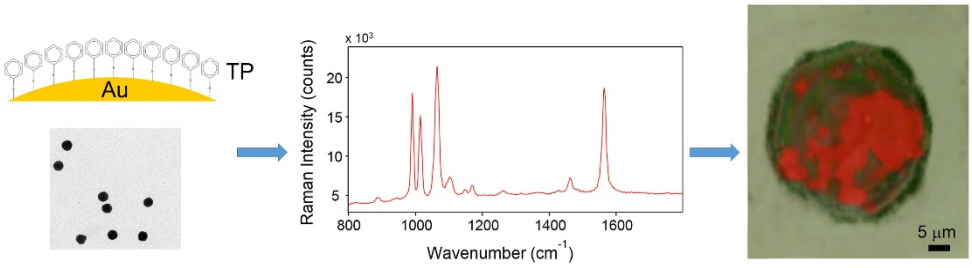

Figure 1. SERS targeting of the nanoparticles internalization in a living cell.

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UV AND SOIL BURIAL DEGRADATION OF MULCH FILMS AND IRRIGATION TUBES FOR AGRICULTURE BASED ON BIODEGRADABLE POLYMER BLENDS

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The disposal of plastics represents a serious problem of environmental sustainability. In agriculture, biodegradable plastic systems can potentially replace the commonly used polyethylene (PE) ones. Several studies have been carried out on commercial biodegradable polymers (BPs) to verify their applicability in mulching or irrigation pipes. However, the effect of UV on their performances and degradation rate in soil has not been investigated in depth. In our recent studies, irrigation tubes and mulch films based on BPs were examined and compared with traditional non-biodegradable materials to verify their biodegradability in soil, before and after UV irradiation. Irrigation tubes were prepared starting from a commercial blend of polylactide/poly(butyleneadipate-co-butyleneterephthalate) (Bio-Flex®) and Mater-Bi® through an extrusion-drawing process and compared to conventional tubes of high-density PE. Mulch films based on BPs (Ecovio® and Mater-Bi®), PE and modified PE with oxo-degradable additive were prepared by film blowing. Irrigation pipes and mulch films were subjected to photoaging with continued exposure to UV radiation and different aging intervals. Mechanical properties, contact angle measurements and soil burial degradation tests [1], at 30 and 50 °C, monitoring the weight loss (WL), were carried out, before and after UV irradiation. Chemical modifications were highlighted by Attenuated Total Reflection-Fourier Transform Infra-Red. The biodegradable tubes showed rheological properties similar to those of traditional ones and mechanical properties compatible with those required by this application. The degradation rate of the Mater-Bi®-based tubes was higher than that of the Bio-Flex®-based ones, but the latter showed greater degradation with increasing temperature. For all the samples, soil degradation appeared to be encouraged by UV exposure. In particular, for the Mater-Bi®-based irrigation tubes the degradation was higher at 30 °C and stimulated after 14 days of UV irradiation. Indeed, the UV irradiation encouraged the disintegration in soil of all the samples promoting a molar mass reduction and hydrophilic end groups, thus increasing surface erosion and WL [2-3]. Predictably, the degradation in soil was higher for BP-based samples than for the PE-based ones.

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THERMOPLASTIC COMPOSITE LAMINATES: A REAL AND SUSTAINABLE ALTERNATIVE TO ADVANCED THERMOSET MATERIALS

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Thermoplastic composites have recently gained exceptional attention from both academic and industrial researchers for their better damage tolerance and impact properties, as well as their inherent recyclability compared to those based on thermoset. Furthermore, the current level of technological readiness of the automated manufacturing processes of thermoplastics has allowed the use of these materials both in advanced sectors such as for the construction of primary aeronautical structures and in high-volume production (e.g. automotive).
Despite these aspects, constituting the main strengths of thermoplastic composites, there is still a great deal of research on this topic to solve many important challenges including processing, the use of additives to improve specific functionalities, properties and outdoor performances and, consequently, to further expand their range of applications.
In this frame, the research at the IPCB Pozzuoli is mainly focused on laminated structures based on thermoplastic matrices reinforced with synthetic, mineral or natural woven fibres, also including hybrid solutions to exploit the well-established advantages expected from the use of the hybridization approach. Specifically, also prompted by specific requests from the automotive and naval sectors, particular interest was addressed to matrices such as polypropylene, polyamides (PA6 and PA11) and thermoplastic polyurethane and to reinforcements consisting of glass, basalt, linen and jute fibres. For this last phase, the use of fabrics has been always considered to obtain products that ensure at least semi-structural performance as well as to enhance their out-of-plane mechanical properties usually verified by low-velocity impact tests.
In all cases, laminates were prepared with the traditional film-stacking technology which involves the stacking, followed by the hot-compression, of plastic films and reinforcing fabric layers according to sequence and processing conditions previously established. Apart from the stacking sequence, the influence of several factors such as weaving architecture, presence of compatibilizing agents, surface pre-treatments of the reinforcement layers and hybridization on the damage behaviour of composite laminates were systematically studied both with mechanical tests and non-destructive analyses carried out in collaboration with other CNR or university research groups.
Furthermore, in the case of composite structures based on advanced matrices with distinctly non-Newtonian behaviour in the range of shear rates typical of the reference technology, specific rheological investigations are underway to optimize the process conditions (i.e. to maximize productivity) while preserving adequate impregnation of the reinforcing fabric.

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PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID BIOCOMPOSITES REINFORCED WITH PECAN NUTSHELL

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Pecan nutshell (NS) has been successfully employed as source of antioxidants [1]. However, the use of NS as filler in polymer composites has been poorly explored [2,3].
In this work, the effect of high loading (50 wt%), and ball milling processing of NS in polylactic acid (PLA)-based composites was studied. The obtained biocomposites were investigated in terms of thermal, mechanical, and thermomechanical properties. NS increased the thermal stability and the stiffness of the matrix. Furthermore, NS acted as heterogeneous nucleating agent (potentially able to control polymer physical aging), which was also able to enhance the polymer viscoelastic response. Finally, the effect of a thermal annealing on thermomechanical properties of the biocomposites was evaluated. This last treatment dramatically increased the Heat Deflection Temperature (HDT) of the biocomposites (Fig. 1). Overall, these results emphasize the potential of NS as a source of sustainable filler materials to tailor the mechanical properties of PLA biocomposites, especially for applications in which stiff, light, and low deformable materials are required.

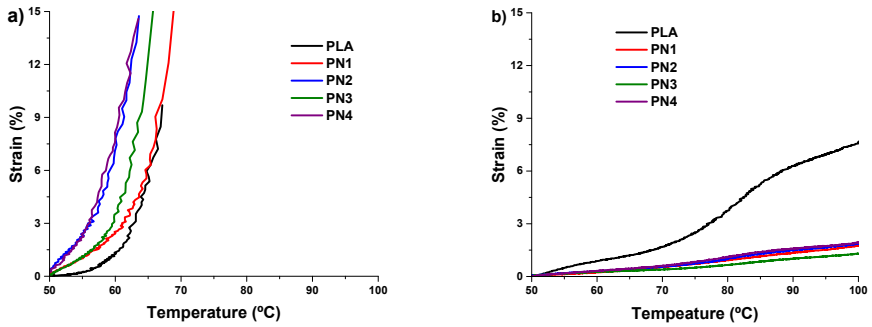

Figure 1. Heat deflection temperature (HDT) of biocomposites, a) before and b) after thermal annealing.

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BIOMASS VALORIZATION BY CIRCULAR ECONOMY APPROACH: FROM BIORESOURCES TO FUNCTIONAL POLYMER BASED MATERIALS

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Biorefineries, defined as the sustainable counterpart of the petroleum refineries, are believed to leverage the turnabout from linear to circular (bio)economy. In this scenario, different parts of non-edible cardoon plant (seeds, leaves and roots) (*Cynara cardunculus* L.) are exploited to obtain biopolymers, plasticizers and bioactive molecules for the development of functional biodegradable materials. Cardoon oil (CO) extracted by seeds was epoxidized (ECO) and used as modifier of poly(lactic acid) (PLA) properties. PLA based films containing 3% by weight of CO and ECO, were prepared by compression molding and the effects of both bioplasticizers on chemico-physical and mechanical properties of the obtained films were investigated. A decrease of PLA Tg was observed, due to the plasticizing effect of the oils, particularly of ECO. Thermal stability of PLA was improved upon addition of the oils and the mechanical properties evidenced the increase of PLA ductility, particularly enhanced in PLA−ECO system.
ECO was used as modifier of PLA/TPS processed films. The effect of ECO on structural, thermal mechanical and barrier properties of the films evidenced the development of physical interaction between oil and polymers, mainly PLA. In addition, no oil migration was detected after two months of film preparation, as evidenced by [1] H-NMR analysis, thus highlighting the well inclusion of oil inside the polymer network. A lean improvement of the interfacial adhesion between the polymers, particularly accentuated in PLA80_ECO composition, was evidenced by morphological analysis of blend fracture surfaces. Epoxidized oil strongly improved the barrier properties of all the films. ECO and post-extraction fibrous wastes, presscake (CP), were recombined for developing PLA functional biocomposites, according to “zero waste” circular economy model. Different compositions of PLA/CP sheets potentially compatibilized with 3% by weight of ECO were prepared and investigated by chemico-physical and mechanical analyses. The poor interfacial adhesion between the hydrophobic PLA and short, hydrophilic and randomly dispersed presscake fibers, were only slightly improved by ECO, but the cellulose residual fraction strongly hastened PLA biodegradation in common soil under environmental conditions. Indeed, biocomposites recovered after 90 days of soil burial tests evidenced a drastic molecular weight dropping down not evidenced in buried neat PLA.

Acknowledgement: grant PRIN–MIUR Bando 2017 – (CARDIGAN)” for the financial support (COD. 2017KBTK93).
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MWCNTS/HAVOH-BASED COMPOSITES FOR 3D PRINTING APPLICATIONS: EFFECT OF FILLER DISTRIBUTION ON STRUCTURAL AND FUNCTIONAL PROPERTIES

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The structural and functional properties of polymer composites, strictly depend on the spatial distribution of fillers, mainly carbonaceous fillers, inside the polymeric matrix [1]. Herein, novel composites have been obtained by embedding multiwalled carbon nanotubes (MWCNTs) into a modified polyvinyl alcohol (HAVOH) matrix, using the ionic liquid (IL) 1-Benzyl-3-methylimidazolium chloride as a suitable compatibilizer. They were prepared by solvent-wrapping (SW) MWCNTs onto HAVOH powders, followed by melt-compounding to produce pellets to be used for Fused Deposition Modelling technology (FDM). The sample printed by FDM, containing 6wt % of MWCNTs and 0.6wt % of IL exhibited a percolating morphology and led to an electrical conductivity (σ) value of $1.2*10^{-2}$ S/m. After annealing at 220 °C for 2h the σ value further improved, increasing up to $7.9*10^{-1}$ S/m. Moreover, HAVOH-based composites are easily soluble in water. However, the thermal treatment induced also the crosslinking of HAVOH, promoted by the presence of MWCNTs, thus obtaining a resulting composite insoluble in water. This reveals the potential of the obtained HAVOH-based composites to be used as raw material for FDM technology to realize post-printing cross-linkable materials.

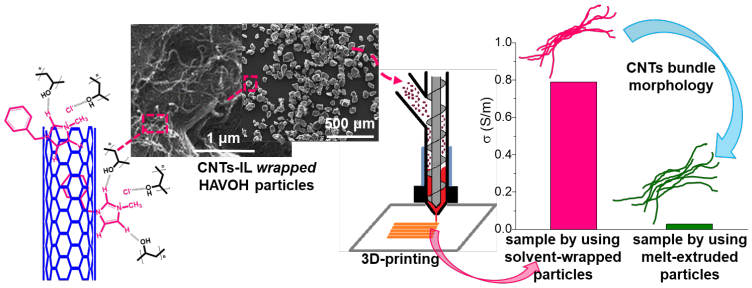

Figure 1. Effect of the SW method on electrical properties of HAVOH-based composites.

Acknowledgement: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D. The authors also acknowledge A. Aldi, F. Docimo and M. Marcedula for the technical assistance in the experiments.

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POLYPORPHYRINS COMBINED WITH GRAPHENE 3D FOR PHOTOCATALYTIC DEGRADATION OF EMERGING POLLUTANTS

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A freestanding hybrid photoactive material based on graphene 3D (G) coupled with porphyrin-polymers (Porph rings) was formulated by using a time-saving strategy to remove Nickel from the final device. Specifically, *"cyclic"* porphyrin polymers were synthetitized to restrain the formation of non-photoactive porphyrin aggregates. Porphyrin copolymers were obtained by interfacial etherification of a mixture of monomers (5,10-di[p-(9-methoxytriethylenenoxy)phenyl]-15,20-di[p-hydroxyphenyl]-porphyrin and 1,20-di-(bisphenoxy-A)-eicosane), in the presence of a large excess of dibromomethane and using tetrabutylammonium bromide (TBAB) as the phase-transfer agent. After, the so prepared polymers were spin coated onto G platform with the double function of visible-light photocatalyst as well as protective agent during nickel etching [1]. The G-Porph rings were characterized by Scanning Electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Photoluminescence (PL). The assembled material explicated photocatalytic activity in degrading different types of contaminants such as the herbicide 2,4 dichlorophenoxyacetic acid (2,4-D), polyethylene glycol (PEG) as ingredient of care and health products, and methylene blue (MB) dye as well. UV-Vis spectroscopy, total organic carbon (TOC) as well as soft Mass spectrometry techniques were used to monitor the photocatalytic process. Data collected revealed that the Ni-free/G-Porph rings showed best performance in terms of photocatalytic efficiency versus MB degradation, respect to the Ni-foam/G-Porph rings previously obtained. Finally, to evaluate the individual contribution of Reactive Oxygen Species (ROS) species produced, free radical and hole scavenging tests were also carried out. A detailed map of the photocatalytic degradation mechanisms was proposed [2].

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DESIGN OF NEW BIODEGRADABLE ALGAE/PHA POLYMERS NANOCOMPOSITES

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In line with the Circular Economy approach [1], compostable and biodegradable-based polymers are currently used in the polymer industry to minimize the amount of wastes and to promote environmental sustainability. Current trends in the healthcare, caused by the increased interest to prevention in the spread of infections, focus on the development of innovative materials capable to combining sustainability properties with antibacterial and/or antiviral ones. Bacterial polyhydroxyalkanoates (PHA) [2] have attracted great commercial interest as biocompatible and biodegradable plastics materials, as they exhibit physical-chemical, thermal and mechanical properties very similar to conventional plastics. Actually, as natural active compound, PHA represents a potential alternative to the synthetic counterpart in order to avoid the adverse health problems (i.e. cancer development, toxicity) from their persistent consumption. Recent articles are demonstrating that *Spirulina platensis algae* (a free-floating filamentous microalgae growing in alkaline water bodies) is potentially capable of inhibiting one of the proteins responsible for Covid-19 replication, in addition to their antibacterial and antioxidant activity [3-4]. Within this scenario, the proposed idea and the preliminary activity we are carrying out, is toward the studying and development of a novel Spirulina-PHA based nanocomposites. Reactive end-groups of PHA could be permit a good interface chemical-physical interaction, useful not only to improve the miscibility between two phases but also to control and to tune the final properties of the obtained systems, in term of mechanical behaviour and biological activity. Furthermore, different potential applications will be explored and attempted in medicine, cosmetic industry and agro chemistry, by taking advantages of tuneable property of Spirulina-PHA based nanocomposites.

Figure 1. Spirulina in spaghetti like form.

Acknowledgement: We are grateful at *Algalia superfood* for the supply of spirulina and for the great collaboration shown in the development of scientific research.

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NANOCRISTALLINE CELLULOSE AS BIO-REINFORCEMENT FOR SUSTAINABLE POLYURETHANES FOAMS

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Nowadays, the chemical industry is looking for sustainable components to synthesize bio-based polyurethane foams, PUs, with the aim to replace the conventional petrochemical raw precursors. Some possibilities to increase the environmental aspects are the use in the synthesis of polyurethane foams of bio-based polyols derived from renewable sources which comprise an increasing wider base raw materials. These represent an excellent approach to help to protect and improve the quality of our environment. Generally, the produced PUs highlight chemical-physical and mechanical properties not comparable with the PUs produced by petrochemical precursors. In order to increase the mechanical and functional performances as well as the bio-based aspect the addition in the polyurethane formulation of sustainable nanoparticles, such as nanocellulose [1], properly functionalized to permit a good interaction with the polymeric matrix and to reduce possible filler aggregation, can be considered. Furthermore, by modifying the surface of nanoparticle with isocyanate functional group the amount of isocyanate can be reduced too. In this respect, nanocrystalline cellulose (CNC) has been modified by linking covalently the bio-polyols on the surface through a two-steps procedure: silylation reaction in water to modify the surface of CNC followed by bio-polyol grafting. The CNC-grafted-polyols has been tested in the preparation of different bio-based PU nanocomposites, in which the sustainable polyol, Cardanol-based [2], is used. The results are compared with PUs nanocomposites obtained by using un-functionalized CNC (milled CNC).

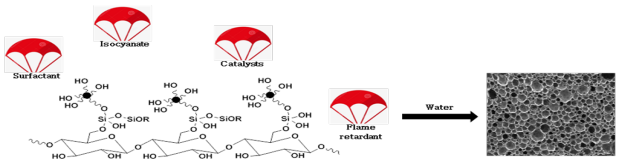

Figure 1. PUF synthesis using CNC-grafted-polyol

Acknowledgement: The work was supported by EU project-REINVENT. The authors are grateful to F. Docimo, A. Aldi, C. Leone and M. Marcedula for technical support within this framework of research.

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PECTIN GREEN EXTRACTION FROM *CITRUS WASTE:* MORPHOLOGICAL AND MECHANICAL CHARACTERIZATION OF PECTIN BIOFILMS

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Every years, the citrus-processing industries generate huge amounts of wastes due to rising consumer demand. The main by-product obtained from *citrus waste* are pectin, flavonoids, carotenoids, dietary fiber, sugars, polyphenols and essential oils (EOs). Citrus residue consist of pectin (~45%), which is its most important along with sugars, cellulose, hemicellulose. In traditional way, pectin is extracted from citrus peels and apple pomace by means of inorganic acid, like sulfuric or nitric acid, or organic acid, like oxalic and citric at high temperature [1]. Therefore, the extraction conditions (temperature, extraction acid, time and pH) should be carefully controlled to achieve the desired pectin quality and yield. In this work, citrus pectin is extracted from the *Calabria citrus waste* through green extraction method using a different concentration of acetic acid (9 and 3% v/v) in water at high temperature and at different times (2, 4 and 6 hours). The different obtained pectin powders were subjected to chemical-physical characterizations (TGA, FTIR-ATR, SEM and GPC). Moreover, chosen the extract liquid for 3% (v/v) acid acetic concentration and time extraction of 6h, pectin biofilms were prepared by casting method also with lignocellulosic residue of the pulp as fillers. These biofilms were subsequently morphologically and mechanically characterized (tensile and puncture tests) [2].

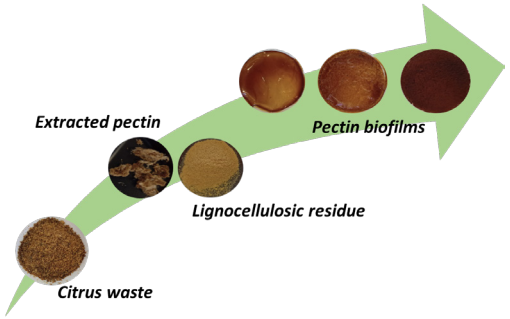

Figure 1. Extraction pectin and preparation of biofilms

Acknowledgement: The authors acknowledge the grant PRIN: Progetti di Ricerca di Interesse Nazionale – Bando 2017 – GoodbyWaste: Obtain ''GOOD products – exploit BY-products – reduce WASTE" (COD. 2017JTNK78)

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THE EXPERIENCE OF "EXTREME" PROJECT: A HIERARCHICAL CARBON/ EPOXY COMPOSITES FOR AN AERONAUTICAL STRUCTURE

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In the last decades, many traditional materials (steel, aluminum, etc.) have been replaced by polymer-based composites in a wide range of industrial field, such as automotive, aerospace, structural and sporting goods. This trend is attributable to different composites advantages compared to conventional materials, such as fast processing/ production, high specific strength and stiffness and above all the possibility of instilling novel functional properties. The development and design of advanced and/or functional composite materials starts with the definition of the appropriate fillers which, based on their physicochemical properties, allow solving the problem under exam. Chemical nature, sizes, interface properties, aspect ratio and physical state are the most important filler parameters. The variation of only one of these features can induce remarkable changes on the composite final properties [1].
Within the framework of the EU project. EXTREME (2015-2019), ad-hoc synthesized nanofiller were employed to improve the fracture and impact properties of an aeronautical graded epoxy matrix. In order to investigate the effect of filler interface properties, silica nanoparticles were coated with an Hyperbranched (HBP) film; the nanocomposites filled with core/shell nanoparticles has revealed a significant improvement of the fracture properties, due to the plasticization effect induced by the HBP shell [2]. Among the other, we report interesting results also for two different hyperbranched polymers, characterized by a glass transition temperature, respectively lower and higher than room temperature; results have shown a higher enhancement of matrix fracture toughness using the last one filler [3]. The developed nanomatrix were employed for the manufacturing of the project prototype i.e. leading edges of an aircraft, realized with a hierarchical carbon fiber reinforced composite whose performance were assessed by a different partner of the consortium.

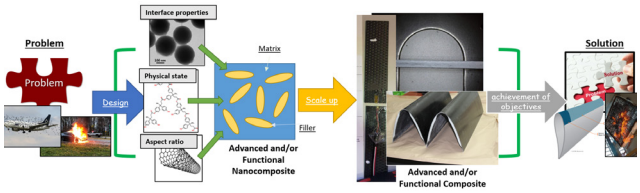

Figure 1. Strategy for development high performance composites using functional fillers.

Acknowledgement: We would like to thank Bernardo Cirillo and Mariarosaria Marcedula for the valuable contribution of the setting of mechanical and thermal tests.

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ABSTRACTS

Multiphase polymer based materials, nanomaterials and nanostructures (synthetic and natural) for tissue engineering and regenerative/therapeutic medicine. Biointerfaces, drug delivery systems, glycoproteomics;

POLYSACCHARIDES BASED BIOMIMETIC DEVICES FOR DRUG DELIVERY APPLICATION

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Biological tissues are multicomponent materials organized in a hierarchically ordered structure from the nano- to the macro-metric scale, which controls the properties and consequently their multiple functions. Their composition and organization, therefore, can be the paradigm for the design of smart devices in the biomedical field [1]. Hyaluronic Acid (HA), a main component of extracellular matrix, is a negatively charged naturally occurring polysaccharide, composed of repeating disaccharide units of D-glucuronic acid and *N*-acetyl glucosamine linked by β(1,4) and β(1,3) glucosidic bonds. HA has been extensively investigated for several biomedical applications due to its unique advantages of non-toxicity, non-immunogenicity, biocompatibility and biodegradability, as well as its susceptibility to chemical modification [2]. In this frame hydrogels able to form micelles based on polysaccharides such as HA and their derivatives, cyclodextrins and natural components such as fatty acids have been designed as smart devices able to prolong the release of an active principles into the joint cavity and, at the same time, able to regenerate the mechanical properties of joints tissue damaged by trauma, disease or ageing [3]. Furthermore, HA based drug delivery systems consisting of nano and microparticles having spherical and non-spherical shape (Figure 1 a,b) have been realized by conventional method such ad emulsion and also by innovative methods such microfluidics. Shape of particles have emerged as a new parameter to control the interaction with biologicals systems. Our results indicate that nanoparticle having elongated shape are internalized in a more efficient way in vitro cell culture systems.

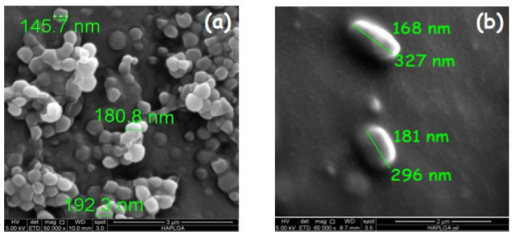

Figure 1. SEM micrographs of a) spherical, b) elongated particles

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SMART DELIVERY STRATEGIES FOR LIGHT-ACTIVATED THERAPIES IN WOUND HEALING

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Wound healing is a global medical concern and there is a pressing need for the development of advanced therapeutic dressings with an active action in the resolution of difficult to heal wounds. The application of the photodynamic therapy in chronic wound treatment, which consists of the localized administration of a non-toxic light-sensitive drug/compound (photosensitizer) followed by exposure to appropriate light to produce singlet oxygen or other reactive oxygen species, could be a promising approach to ameliorate this global health problem [1]. With this research, we want to develop a novel smart delivery strategy for light-activated molecules based on the incorporation of microemulsions (MEs) into a biocompatible hydrogel to fight bacterial infections and enhance wound healing rate. An aqueous titration method was used for the preparation of MEs loaded both with the natural photosensitizer curcumin and with a synthetic molecule able to release nitric oxide, a potential wound therapeutic agent able to regulate inflammation and eradicate bacterial infections. Labrafac lipophile WL 1349 (oil), and Kolliphor HS 15 (surfactant), were selected based on their solubility and maximum nanoemulsion region to encapsulate the two hydrophobic photosensitizers. Stability, dynamic light scattering, and zeta potential studies were carried out to characterize the MEs. Finally, MEs were dispersed into alginate hydrogels prepared by internal gelation [2] using glucono-δ-lactone (GDL) and calcium carbonate to prepare a light-activated wound dressing material. Further studies are in progress to characterize the MEs and the MEs-loaded hydrogel dressing and to evaluate the photodynamic behavior of the light-activated dressings.

Acknowledgement: the authors want to thank prof. S. Sortino (University of Catania) for providing the NO-donor molecule

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COMPOSITE MICROGELS FOR HARD TISSUES REGENERATION: AN *IN VITRO* MODEL FOR DENTAL APPLICATIONS

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In the last years, hydrogels are gaining attention for their ability to support hard tissue regeneration by the presence of calcium phosphates that reply composition and functions of apatites [1,2]. Electro Hydro Dynamic Atomization (EHDA) currently represents a promising technique [3,4] to manipulate bio-hydrogels in the form of microsized carriers - i.e., microgels - for different biomedical use [5,6]. Herein, composite microgels fabricated via EHDA were investigated as *in vitro* model to promote the regeneration of mineralized tissues into dental cavities. Aqueous alginate solution - from 0.5 to 2% wt/v - was atomized by using a commercialized equipment (MECC, Japan) with a customized setup for the fabrication of mineralized microgels. Briefly, a mineral precursor (Na_2HPO_4) was added to the polymer solution, and, then dropped into a Ca^{2+} enriched bath to promote the gelation of the polymer matrix. Narrowly dispersed microgels with sizes ranging from 290 µm to 500 µm and round-like shape were obtained by optimizing the process conditions. Microgels were preliminary characterized by optical and scanning electrical microscopy, Energy dispersive spectroscopy (EDS) and Fourier-transform infrared spectroscopy (FTIR) to confirm the in situ formation of calcium phosphates into the microgels. *In vitro* studies were performed to validate their use as fillers to support the regeneration in dental cavities. Briefly, premolars teeth extracted for orthodontic reasons were cut transversely, washed, and sterilized. Microgels were placed in pulp cavity and human dental pulp cells were seeded to evaluate cell proliferation. *In vitro* cell proliferation showed an increase rate until 14 days, respect to control. At 21 days, a decay of proliferation was recorded independently to the mineral amount, due to the starting differentiation state of cells. According with previous results, we conclude that microgels can be successfully used to support the regeneration of mineralized tissue at the interface of pulp in the dental cavity.

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USE OF MODIFIED NATURAL HYDROGELS FOR TISSUE ENGINEERING APPLICATIONS

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Over the past years, natural polymers have highlighted a great potential in the biomedical field due to their excellent biocompatibility, bioactivity and bioresorbability. Although traditional processing approaches provided interesting opportunities for scaffolds' fabrication, additive manufacturing (AM) has allowed for the fabrication of three-dimensional (3D) site-specific and customisable structures, offering the possibility to control the design in terms of porosity, interconnectivity and mass transport properties. In this scenario, the use of natural materials is attracting a wide research interest as they can work as suitable bioinks for AM (i.e. 3D bioprinting). However, as it is widely recognized, bioinks should be able to: i) be extruded through a thin needle, ii) retain a 3D structure and iii) create a cytocompatible environment, as they can also embed living cells [1-2]. However, their high solubility, high degradation rate and low mechanical properties still limit their use. In this study, hyaluronic acid (HA), gelatin (GE) and gellan-gum (GG) were chemically modified to: i) confer a shear thinning behavior for the extrusion-based process and ii) improve the mechanical properties, also extending the half-life. Furthermore, innovative natural polymer-based double network hydrogels (DNs), a specific class of interpenetrating polymer networks, were developed, for load bearing applications, by a two-step network-formation procedure. To this aim, neat polymers were modified to obtain photocrosslinkable methacrylated HA (HAMA), methacrylated GE (GEMA) and methacrylated GG (GGMA). Spectroscopic analyses confirmed the presence of functional groups onto the polymers. DNs were synthesized by combining a polyelectrolyte as first network (MEHA or GGMA) and a neutral polymer as second one ((poly(ethylene glycol) diacrylate (PEGDA) or GEMA). Crosslinked MEHA or GGMA were immersed in a PEGDA or GEMA solution, respectively, until reaching equilibrium and crosslinked. The effect of the second network on the mechanical properties of the neat hydrogels was assessed by dynamic mechanical analysis, which showed that is possible to tune the properties by varying reaction conditions and material compositions. Moreover, synthesized materials were successfully used for AM of well-ordered structures. Viability/ proliferation of human Mesenchymal Stem Cells was also investigated. The overall results demonstrated the potential use of these bioinks for tissue engineering.

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METHODOLOGICAL APPROACH TO DESIGN ADVANCED PROSTHESES AND SCAFFOLDS FOR TISSUE ENGINEERING

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The advances in design strategies and methodologies of analysis [1-4] have pushed the research towards the development of innovative materials and devices for biomedical applications [1-6]. In this context, over the past few years many efforts have been devoted to the development of advanced prosthetic implants and 3D scaffolds for tissue regeneration, as well as to the design of ortheses and posture correctors – corsets/ braces. Unlike conventional fabrication methods, additive manufacturing technologies allow the direct fabrication of customized and lightweight structures with tailored properties [1, 5, 6]. The potential to design functional porous structures and lattices was demonstrated, with a special focus on the development of orthopedic implants and 3D scaffolds for tissue regeneration (e.g., bone, cartilage, meniscus, intervertebral disc, craniofacial tissues).
In this context, polymers, micro/nano-composites, metals and alloys were properly processed using different additve manufacturing technologies to produce customized devices according to the specific applications. Several studies on bone reconstruction have demonstrated a correlation between pore size and newly formed tissue, as porous devices can offer surface and space favoring cell adhesion and bone ingrowth [1, 5, 6]. The design of porous devices with tailored properties was considered to reduce the implant stiffness and to improve its stability by promoting tissue ingrowth [5]. Accordingly, with regard to the repair, regeneration and reconstruction of damaged tissues, 3D porous devices were fabricated as biodegradable and non-biodegradable scaffolds. In the latter case, the conceived pore geometry and porosity may allow to tailor the structure stiffness and to promote tissue ingrowth, also stabilizing the implanted device. Thus, a current research was also focused on photo-curing 3D printing to fabricate 3D porous composite devices with optimized properties.

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NATURAL POLYMERS BASED INJECTABLE HYDROGELS FOR TISSUE ENGINEERING OF SOFT TISSUES

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Injectable hydrogels have revealed the great potential for use as scaffolds for tissue engineering [1]. The injectable nature of the hydrogels provides the attractive feature of facile and homogenous cell distribution within any defect size or shape prior to gelation at body temperature (Tb). The research activities here presented concern the development of injectable hydrogels for the engineering of soft tissues such as lung and cartilage. As regards the engineering of cartilage tissues, systems based on natural components of Extracellular matrix (ECM) have been developed. It is hypothesised that the hybridization of fibrillar network injectable dense collagen gels (IDC) with the glycosaminoglycan-rich Hyaluronic Acid may result in a scaffold that mimics the physiological conditions in the native ECM. Composite IDC/HA Hydrogels has been fabricated by the gel aspiration-ejection (GAE) method [2] and the results demonstrated that HA in the composites promoted chondrogenic differentiation after 21 days of incubation *in vitro* (Figure 1). Furthermore, HA and collagen-based injectable polymeric biomaterials for the delivery of Mesenchimal stem cells (MSCs) have also been developed as a new strategy in pulmonary tissue regeneration. Results demonstrated that biomaterials were effective in promoting cell viability and more importantly the differentiation in pulmonary lineage. Moreover, the 3D composite biomaterials based on collagen and HA, when scaffold was enriched with HA Low Molecular Weight was particularly effective in promoting the differentiation of MSCs in Alveolar Type II cells.

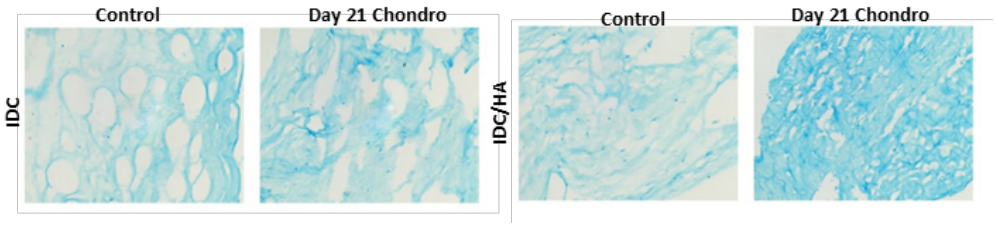

Figure 1. HA enhances MSCs chondrogenic differentiation as indicated by alcian blue staining in histological samples

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EUMELANIN DECORATED POLY (LACTIC ACID) ELECTROSPUN SUBSTRATES: A NOVEL APPROACH FOR SPINAL CORD INJURY TREATMENT

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Spinal Cord Injury (SCI) is characterized by neuroinflammatory processes that are marked by an uncontrolled activation of microglia, which directly damages neurons through the release of several pro-inflammatory cytokines, prostaglandin E2, nitric oxide and superoxide [1]. Current studies suggest natural and synthetic melanins show several biological and pharmacological properties, including antioxidant and immunomodulatory actions. Here, the effect of 3D substrates based on eumelanin-coated PLA aligned microfibers on neuroinflammation in terms of cytokine levels modulation, expression of genes coding for inflammatory mediators, oxidative stress species production and the involvement of inflammation pathways, was investigated. 3D electrospun substrates were prepared combining electrospinning, spin coating and solid-state polymerization processes [2]. Biological investigations on the antioxidant and antinflammatory potential of 3D substrates were performed using an in vitro model of neuroinflammation obtained through the stimulation of microglial cells with lipopolysaccharide (LPS). Cell morphology by using SEM analysis and confocal analysis was assessed. Furthermore, 3D substrates mechanism of action in terms of Toll-like receptor-4 (TLR-4) expression using confocal analysis was investigated. Biological results showed that 3D electrospun substrates were able to decrease nitrite production, ROS levels, NF-κB expression and IL-6 secretion induced by LPS in microglial cells. Additionally, morphological studies suggested that 3D electrospun substrates were able to counteract LPS induced cell morphological changes. Finally, confocal analysis revealed 3D electrospun substrates completely inhibit Toll-like receptor-4 expression selectively activated by LPS signal. 3D electrospun substrates functionalized with eumelanin show promise as new therapeutic strategies for the control of neuroinflammation related to spinal cord injury without adding any antinflammatory drugs.

Acknowledgement
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SIGHTING OF UNUSUAL GLYCANS

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Here we will present three examples dealing with the first description of unconventional glycan structures synthesized by totally or partially different biosynthetic pathways.

Primarily, it will be presented the N-glycans characterization of Paramecium Bursaria Chlorella Virus 1 (PBCV-1) major capsid protein (MCP) Vp54. Chloroviruses have a long evolutionary history, probably forgoing the eukaryotes development, thus it has been hypothesized that they could own a different glycosylation machinery. The structures of the four N-linked glycans attached to PBCV-1 MCP consist of a set of oligosaccharides not previously found in all the three domains of life. Very interestingly, these glycan structures are not located in a typical N-X-(T/S) consensus site [1-3].

A second example will regard the characterization of the lipopolysaccharide synthetized by the photosynthetic Bradyrhizobium strain, symbiont of Aeschynomene legumes. This bacterium synthesizes a unique LPS bearing a hopanoid covalently attached to lipid A. This was the first type that a covalent linkage between a lipid A and a Hopanoid unit was demonstrated [4].

Finally, it will be described the unique case of a patient with multiple genetic mutations that, perhaps interacting, lead to generation of hypersialylated N-glycans structures, never reported before in human serum.

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INTEGRATED DESIGN STRATEGIES TO DEVELOP DEVICES WITH IMPROVED PROPERTIES FOR TISSUE ENGINEERING AND CURRENT THERAPIES IN REGENERATIVE MEDICINE

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Design usually represents the main creative activity of engineering. Over the past few years, polymers and micro/nanocomposite materials have become popular in many applications [1,2]. New advances are being made for the design of novel materials and biomedical devices [1-6]. In this scenario, additive manufacturing allows for the design of advanced devices with complex geometry and architectural features, as well as with tailored biological, mechanical and mass transport properties. Anyway, the engineering design process consists of a series of steps which are generally employed to create functional processes and products. Research, design requirements, feasibility and design for manufacturability, as well as production planning, represent the common steps of the engineering design process [3,7]. The design of biomedical devices involves innovative and creative engineering techniques for generating all possible design configurations, in order to meet design requirements and constraints [3,4,5,7]. The combination of design methods with additive manufacturing, reverse engineering and materials selection/ preparation led to the development of advanced scaffolds for tissue regeneration. As an example, 3D customized scaffolds were designed and additively manufactured for bone, meniscus, intervertebral disc and craniofacial tissue regeneration. Generative design and topology optimization were used to develop 3D biomimetic and advanced porous structures. The solid isotropic material with penalization (SIMP) and the evolutionary structural optimization (ESO) were considered as the most common topological optimization methods. Porosity and architectural features, as well as mechanical and biological properties, were tailored. Theoretical and experimental tests were carried out to analyse the performances of the designed scaffolds. A robotic bioprinting system was also implemented with the aim to improve the capabilities of the additive manufacturing process through the introduction of additional degrees-of-freedom. Integrated approaches involving molecular design and modeling were also taken into account [6].

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NATURAL POLYSACCHARIDES AND BIOACTIVE MOLECULES FROM BIORESOURCES FOR TISSUE ENGINEERING

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Over the past years, natural polysaccharides have been widely investigated for tissue engineering applications since they are non-toxic, biodegradable, biocompatible and adaptable to the different needs due to the presence of several functional groups [1]. Among them, chitosan and sodium alginate are particularly promising for both wound healing and bone regeneration applications.
In particular, chitosan plays a positive role in wound healing due to its strong hemostatic action and antimicrobial properties [2]. Nevertheless, the poor mechanical properties and the lack of long-term stability limit the fabrication of chitosan-based dressings. To overcome these drawbacks, herein chitosan was crosslinked with a low molecular weight diepoxy-poly(ethyleneglycol) (diePEG), and an extract of Opuntia ficus-indica (OPU) was added to prepare an advanced bioactive wound dressing.
Mechanical tests evidenced that the presence of flexible PEG segments caused a decrease of Young modulus, thus approaching the value of the human skin modulus. Finally, a scratch test on a keratinocytes monolayer showed that the rate of cell migration in the presence of OPU-loaded samples is about 3-fold higher compared to unloaded films, confirming the repairing activity of OPU.
On the other hand, alginate is widely used as a biomaterial for bone tissue engineering, due to its ability to form highly porous structures under mild conditions as well as its low toxicity and biodegradability [3]. In this frame, macroporous alginate foams were prepared through the combination of internal gelation technique with gas foaming. Strontium was employed in combination with calcium as both crosslinker and enhancer of osteogenic differentiation. It was demonstrated that the combination of the two techniques allowed to obtain scaffolds with an interconnected three-dimensional porous architecture, with a pore size in the range of 100–400 µm, suitable for bone tissue engineering. Furthermore, biological assays showed that a high strontium content makes scaffolds able to support cell growth and differentiation over long times by promoting the osteogenic marker expression.

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HILIC-UPLC-MS N-GLYCAN CHARACTERIZATION IN THE DIAGNOSIS OF CONGENITAL DISORDERS OF GLYCOSYLATION

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Congenital Disorders of Glycosylation (CDG) are genetic diseases characterized by altered glycosylation of proteins, lipids and/or both. To discover disease-associated biomarkers, as well as to identify changing in N-glycomic profiles supporting diagnosis of congenital disorders of glycosylation, was applied a High Throughput (HT) method based on liquid chromatography (LC) coupled with electrospray ionization (ESI)-mass spectrometry (MS). Before LC-MS analysis, to enhance detection sensitivity, was used RapiFluor-MS (RFMS) that has been developed as a new method for a fast deglycosylation and labeling of N-glycans such as monoclonal antibodies (mAbs). The RFMS protocol was slightly modified extending enzymatic digestion times. RFMS labeled N-glycans were separated and analyzed by Hydrophilic Interaction Chromatography (HILIC)-UPLC-ESI-MS. This strategy allowed us to analyze structural details of patients' serum released N-glycans and, in some cases, to differentiate either structural isomers or isomers differing in the linkage type. In this study, we analyzed N-glycans of serum proteins in some CDG patients (MAN1B1-CDG, ALG12-CDG, MOGS-CDG, TMEM199-CDG). Unusual hybrid N-glycan structures with α-1,2 terminal mannose residue and abnormal oligomannose N- structures were found in serum N-glycosylation profile of MAN1B1-CDG. A similar occurrence was showed in IgG and serum N-glycosylation analysis of ALG12-CDG. Total serum and IgG N-glycome analysis of MOGS-CDG indicated a series of fucosylated and unfucosylated hybrid N-glycans and additional oligomannose species. TMEM199 serum analysis revealed increased amounts of hyposialylated and hypogalactosylated N-glycans as associated with this disease.

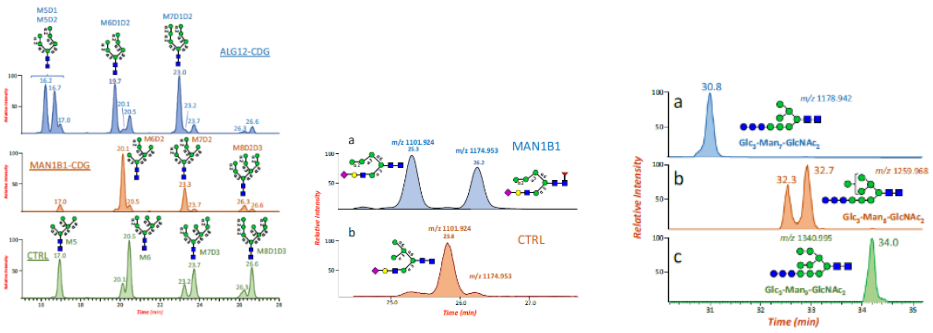

Figure 1. EICs' comparisons of the *Rapifluor*-MS labeled oligomannose serum N-glycans from CDG patients and control

MALDI-MS CEREBROSPINAL FLUID (CSF) N-GLYCAN PROFILES IN NEURODEGENERATIVE DISEASES

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Glycosylation is a key post-translational protein modification in different biological functions such as cellular adhesion, recognition and signalling, and changes in protein glycosylation have been recognized in different neurodegeneration disorders [1].
Alzheimer's Disease (AD) and Parkinson's Disease (PD) are the most common neurodegenerative diseases. Both pathologies are multifactorial diseases presenting clinically heterogeneous symptoms and prognosis and ultimately resulting in neurons loss of functions and death. AD and PD are diagnosed by clinical and neuropsychological criteria, only proved by post-mortem autopsy. Therefore, there is a great need of diagnostic tools able of detecting the diseases in their early stages when preventative therapies could ameliorate patients' conditions before irreversible neuronal damages.
We performed Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) CSF N-glycosylation analysis of released and permethylated N-glycans from a cohort including 21 AD, 11 mild cognitive impairment (MCI), 19 PD patients and 19 control subjects (age- and gender-matched).
PD-CSF spectra denoted a significant increase of high-mannose 5 (M5, m/z 1579.8), agalactosylated biantennary (G0, m/z 1661.8), agalactosylated bisected biantennary (G0B, m/z 1906.9) bisected, agalactosylated core fucosylated N-glycans (G0BF, m/z 2081.0).
Although no unique profile emerged for AD and MCI, principal component analysis (PCA) allows to separate AD and MCI in two categories, according to bisecting-N-glycans relative intensities. AD1 and MCI1 showed significant increase of bisecting structures and an overall decrease of sialylated species compared to healthy controls, while AD2 and MCI2 showed a slightly reduction of those species. Interestingly, the observed divergences in MCI1 and MCI2 glycosylation profiles reflected the different clinical follow-up of the respective class of patients: 5 MCI1 patients out 5 converted to AD within 36 months from diagnosis, while all the MCI2 subjects (6 out 6) remained stable over the time, suggesting that increasing amount of N-glycans with bisected GlcNAc is a biochemical hallmark of AD in the pre-dementia phase [2].
MALDI-MS CSF N-glycome profiling enabled detection of peculiar changes in subject affected by neurodegenerative diseases, helpful in monitoring diseases development and progression, thus representing a source of potential biomarkers and therapeutic targets.

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2D BLACK PHOSPHORUS AS THERAPEUTIC NANOMATERIAL FOR BONE CANCER TREATMENT

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Abstract
Bone is a site of cancer growth either for primary tumour, such as osteosarcoma or Ewing's sarcoma, and also for metastasis derived from breast or prostate cancer. The most common treatment for primary bone cancer or bone metastasis is the combination of different approaches, such as surgical removal followed by chemotherapy or radioisotope treatments. However, these approaches are not able to select the cancer cells from healthy cells. In the last years, more attention is paid for Photodynamic Therapy (PDT) or Photothermal Therapy (PTT) which show high specificity, minimal invasiveness precise spatial-temporal selectivity and able to eradicate cancer cells in primary tumor or local metastatis in lymph node. Emerging 2D nanomaterials, such as graphene, MXenes, molybdenum disulfide (MoS2) and tungsten disulfide (WS2), are frequently used as photothermal transducing agents. In this context, we propose few-layer black phosphorous (2D bP) as an emerging and alternative 2D nanomaterial to be used for bone cancer treatment. In particular, we have developed an *in vitro* model to evaluate the efficacy of 2D bP material with and w/o near-infrared light irradiation (NIR) treatment on healthy (HOb, hMSC) and cancer (Saos-2) cells and we also propose an *in vitro* co-culture model (Saos-2 and HOb cell lines) to study the effect of 2D bP on inflammatory response related to cancer. Our investigations suggested that 2D bP w/o NIR stimulation promoted the HOb viability with the best expression of early marker of osteogenic differentiation at day14, thus inducing higher proliferation values than control. Conversely, 2D bP with and w/o NIR, induced a significant reduction in Saos-2 proliferation and inhibition of ALP activity. We have demonstrated that 2D bP is able to inhibit in vitro cancer cell proliferation and in the same time to stimulate newly forming bone tissue generation after osteosarcoma resection without PTT treatment [1]. Furthermore, 2D bP is able to increase anti-inflammatory cytokines generation on co-culture model and to inhibit pro-inflammatory mediator synthesis thus suggesting the opportunity to prevent cancer-related inflammation. These results inspire the application of 2D bP as a highly promising therapeutic nanomaterial for bone cancer treatment.

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PROVIDING MAGNETIC RESPONSIVENESS TO NANOCOMPOSITES AIMED AT BONE DEFECTS REGENERATION

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Over the past years, the idea of integrating tissue-engineering approaches with nanotechnology emerged as a ground-breaking strategy to ameliorate bone defects regeneration processes. Particularly, magnetic nanoparticles (MNPs) incorporation within biomaterials led to obtain remotely physical-stimulated advanced nanobiomaterials aimed at reproducing the dynamic and mechanical environment of the native tissue. The aim of this work has been to provide a magnetic responsiveness to bone-mimicking nanocomposites, and explore their modular responsiveness with respect to the physiological dynamics of bone-like cells. For this purpose, dextran-grafted maghemite nanostructures (DM) have been synthesized by a green friendly and scalable alkaline co-precipitation method [1]. The superparamagnetic features due to the small dimensions of the cores and the lack of hysteresis in the magnetisation curve have been confirmed. Afterwards, calcium-deficient hydroxyapatite nanoarchitectures (DM/n-HA) have been synthesized by an aqueous precipitation technique in the presence of different amounts of DM. DM/n-HA nanoarchitectures retained the same magnetization profile of DM alone, but with a lower magnetization values due to the presence of the non-magnetic n-HA [2]. Cytocompatibility parameters (e.g. viability, morphological and physical interactions) of DM and DM/n-HAs have been assessed by using a bone-derived human cell line. Finally, the effects triggered by DM and DM/n-Has have been analysed in terms of variation in gene expression of adhesion, proliferation and morphology markers (e.g. FAK, p53 and SLC11A2/DMT1 human genes), to identify possible interplay with physiological cells responses [3]. In this view, the biocompatibility of n-HA together with the magnetic responsiveness of DM represent an optimized combination of structural with functional features of the DM/n-HA nano-tools for bone tissue engineering, for finely acting within physiological ranges.

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ANTI-INFLAMMATORY, PRO-ANGIOGENIC AND OSTEOGENIC PROPERTIES OF CHITOSAN SCAFFOLD FOR BONE FRACTURE TREATMENT

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The realization of bone substitutes for tissue injury characterized by the lack of bone mass, an inflammatory reaction and blood vessels necrosis has a critical role in Tissue Engineering [1]. Research has been given much attention to processes such as angiogenesis and its correlated processes (*i.e.* osteogenesis, inflammation). Here, we highlighted how the bio-activation of chitosan (CS)-based scaffolds by organic and inorganic signals is able to promote osteogenesis, angiogenesis and to modulate the inflammation response. For this purpose, our aim was to investigate the CS-scaffolds role in the inflammation and angiogenesis related to osteogenesis processes by using *in vitro* models aimed to mimic bone fracture microenvironment. The scaffolds by using two different approaches based on inorganic and organic compounds, were bio-activated respectively [2]. The expression of inflammatory mediators and pro-angiogenic markers was estimated in order to assess the anti-inflammatory and angiogenic properties related to osteogenic potential of the scaffolds. The results obtained suggested that bioactive scaffolds show good effect on cellular behavior than neat CS scaffolds. In particular, scaffolds bio-activated by using inorganic signals (hydroxyapatite nanoparticles) inhibit pro-inflammatory mediator's production (IL-1β and IL-6), induce anti-inflammatory cytokine generation (IL-10) and reduce nitric monoxide metabolites (nitrites). Conversely, scaffolds bio-activated by using organic signals (BMP-2 mimicking peptide) were able to decrease pro-inflammatory markers. Furthermore, scaffolds are able to promote angiogenesis by increasing endothelial cell proliferation, migration and tube formation. Bioactive signals on the scaffolds surface allow a desirable effect on inflammation inhibition and angiogenesis and osteogenesis promotion.

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BIOCOMPOSITES AND/OR GRAFT COPOLYMERS FOR DRUG DELIVERY AND COSMETICS

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"Smart" and "*stimuli*" responsive materials can be widely used in controlled-release systems. Some of these materials final properties, e.g. water affinity, may be change, in response to an external stimulus such as temperature or pH. Responsive polymers (i.e. films, capsules and hydrogels) have been widely investigated in nano/biotechnology and they can have potential applications in several fields, such as drug delivery, cosmetics and aerospace. [1,2]. Graft copolymerization might be among the best methods to obtain both synthetic and natural polymers, preserving the properties of biodegradability and bioactivity characteristic to develop "smart" or "*stimuli*" responsive biopolymers. By changing the molar ratio of used polymers and/or their copolymerization conditions, it is possible to study the structure-property correlation potentially tailoring the final performances of the developed advanced materials. [3,4]. Preliminary activity was carried out to synthesize pH-sensitive cross-linked composites by direct reaction of chitosan (CS) and D, L-lactic acid (LA) to achieve graft-copolymers with hydrophobic synthetic side chains and hydrophilic natural main chains. The CS/LA copolymers were chemical-physically characterized and loaded with non-steroidal anti-inflammatory drugs (NSAIDs) solutions to study the kinetic release in simulated intestinal fluid (SIF) at pH 6.8 and 37°C. Graft copolymers, which form pH-sensitive hydrogels in aqueous solution, are of general interest for biomedical applications, such as artificial muscles or switches, in biochemical separation and in controlled-release systems.

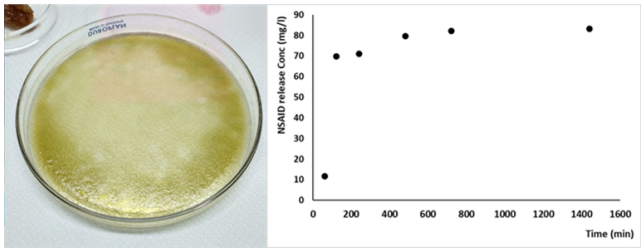

Figure 1. CS/LA graft-copolymers film (left); NSAID kinetic release (right)

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ABSTRACTS

Advanced and sustainable processing technologies
of polymers, composites and nanostructures.
Additive technologies.

PROCESSING AND IMPACT BEHAVIOR OF INNOVATIVE COMPOSITES

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The use of reinforcing textiles in structural applications is a well-established method to produce high performance materials, such as fibre reinforced composites, that have gained significative importance in aerospace and defense applications due to their high specific strength and damage tolerance.
Reducing weight while meeting the structural requirements is of paramount importance in order to minimise fuel consumption in aircraft.
These advanced materials have been also recognized as alternative energy absorbing materials to replace steel and light alloys materials in impact related applications. However, composites materials based on traditional 2D textile fabrics are susceptible to out of plane impact due to the weak bonds between the plies. Low velocity impacts are dangerous for the structure because, even at very low impact energies, can initiate damages, such as matrix cracks, delamination and fibre breakage and the consequent loss of load carrying capability which can fall considerably down the design thresholds leading to catastrophic failures. Thus, in the last years the research attention has been focused on the development of new approaches and technical solutions to modify the damage modes and enhance the impact resistance of composite materials.
This work investigates different strategies that can be adopted in the manufacturing of composites by vacuum infusion process: i) the modification of the resin matrix by rubber addition [1]; ii) the hybridization of the fiber reinforcement by stacking two different kinds of fiber layers [2]; iii) the substitution of 2D fabrics with 3D woven fabrics that have the potential to reduce aircraft weight by 30% and can provide better performances in curved aeronautical components. The mechanical and low-velocity impact behavior of alll realized composites have been experimentally evaluated by performing impact tests up to penetration and at increasing energy levels in order to get complete information on the damage modes and evolution. The esperimental results confirmed the benefits of the investigated solutions over conventional solutions.

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A SUSTAINABLE APPROACH FOR THE RECYCLING OF POST-CONSUMER PLASTIC WASTE

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Environmental sustainability is increasingly seen as a key requirement for polymer-based materials and products. The accumulation of end of life plastic materials into the environment can have dramatic long term consequences and must be avoided by proper material design, waste management and advanced recycling technologies.
Due to the limited efficiency of collection/sorting systems and to the thermo-mechanical degradation and contamination suffered during service, post-consumer plastics (WP) are often heterogeneous materials, which limits their recycling options. The setup of new, sustainable chemo-physical treatments and processing routes, able to manage the compositional variability of waste plastic streams while controlling phase morphology and final properties, is an effective route for the management of end-of-life plastics.
The effects of solvent-free, high energy ball mill (BM) mechano-chemical treatments on recycled materials obtained from different WP streams have been investigated. BM induces an intimate mixing of WP components at the solid state and, in appropriate conditions, high shear and compressive forces can induce localized radical reactions with the in situ formation of graft copolymers, acting as broad range compatibilizers among the different phases. Additionally, size reduction and fine dispersion of rigid contaminants is conveniently obtained in BM, reducing their influence on final properties.
A polyolefin-rich fraction recovered from household plastic waste collection, the polymeric residues of waste paper/cardboard re-pulping process and a plastic fraction retrieved during landfill reclamation/mining activities [1] were pre-treated by BM and processed, obtaining recycled materials with enhanced properties. The influence of waste composition, treatment time and conditions and of simple processing additives on morphology and properties has been assessed, leading to the definition of optimal recycling strategies. The sustainability of the proposed approach coupled with landfill mining has been also demonstrated through a comprehensive life-cycle analysis (LCA) approach [2].

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THE CHEMICAL, STRUCTURAL AND MORPHOLOGICAL EFFECTS OF MECHANO-CHEMICAL TREATMENTS ON POLYMERIC AD LIGNO-CELLULOSIC MATERIALS

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Mechano-chemical treatments are based on the application of high shear and compressive stresses to materials at the solid state through, as an example, the action of high energy ball mills (BM). Developed in the mining and metallurgical fields, these processes allow to obtain a fine grinding and to produce new alloys and metastable compounds. Recently, mechano-chemical treatments have been tested also on organic materials and are attracting a large interest for the development of "green" processes, as they are carried out at room temperature and usually do not require harmful solvents.
In organic materials, the BM treatment can cause both structural and morphological changes (amorphization through disruption of crystalline domains, intimate mixing of immiscible phases with reduction of the domain size) but can also induce chemical reactions, promoting the in situ formation of branched species or even copolymers through mechanically-induced radical formation. In ligno-cellulosic materials (e.g. agricultural byproducts), high energy mechanical treatments can deconstruct the hierarchical fibrous structure, allowing to separate the different fractions (cellulosic materials such as micro-nano fibrils and nanocrystals, partially depolymerized lignin, active natural compounds). This represent a crucial step in the obtainment of secondary raw materials from biomasses.
Mechano-chemical treatments have been employed on polyolefins (polypropylene, polyethylene), aiming to induce chemical modifications, such as branching and/or formation of polar groups at the solid state, avoiding solvents and melt-state reactions. These modifications will be exploited to produce polyolefin blends and composites with improved miscibility/interfacial adhesion without the need for specific compatibilizers.
Moreover, ligno-cellulosic biomasses of different nature (wheat straw, grape skins, rice and sunflower seed hulls) have been treated in BM to obtain a fine grinding and a partial destructuration. The obtained materials will be employed as fillers in biodegradable matrices, exploiting the reinforcement offered by cellulose and the functional properties of natural compounds contained in the biomass (e.g. natural antioxidants from grape skins). As a consequence of destructuration, further extractions and refinements needed to recover secondary raw materials will be carried out with non-aggressive chemicals and in mild conditions.

DESIGN OF BIOMATERIALS VIA ELECTRO FLUID DYNAMICS: CURRENT AND FUTURE PERSPECTIVES

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Electro-fluid dynamics (EFDs) are currently accredited as highly versatile and cost-effective processes to design green materials and/or biomaterials in the form of fibres and/or particles with tailored sizes and functionalities, from macro- to nano-metric scale, by the application of high-voltage electric fields [1].
Bio- active and degradable polymers can be variously processed to fabricate a large variety of instructive platforms (i.e., multicomponent fibres [2,3] micro/nanostructured tubes) serving as conventional scaffolds[4], templates[5] or in vivo-like symmetric[6] or asymmetric models to investigate biological interactions that typically regulate the physiological activity of cells mediated by the in vitro microenvironment. Organic phases with electro-conductive[7]/piezoelectric properties[8] or inorganic nanoparticles with electric, magnetic or optical properties (e.g., nanotubes, iron NPs, nanodiamonds) can be used to design nanocomposite fibres for bio-functional applications (e.g. bioactuation[9], biosensing[10]). Bio-polymers can be functionalized with bioactive phases (e.g. calcium phosphates), molecules (e.g., peptides, proteins) and drugs (e.g. antibiotics, anti-inflammatory, antivirals) to design innovative fibrogels[11] and micro-/nano- carriers[12] for therapeutic treatments in oral delivery[13] and nanomedicine[14]. In this context, the large versatility of EFDs may also serve to define new strategies to modify "*ad hoc*" interface/surface properties, for a promising use of EFDs products as implant coatings[15], antibacterial[16] and functionalized bio-textiles [17].
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SUSTAINABLE INNOVATIVE LIGHTWEIGHT CONCRETE-GRAPHENE NANOCOMPOSITE AS POTENTIAL STRAIN SENSOR

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Nanocomposites Cementitious Graphene-based have been attracted considerable attention from the scientific and industrial community due to the synergistic effects, mechanical, thermal, durability as well as electrical properties, that the Graphene (or its derivatives) is able to induce on the cementitious conglomerates when a percolate and/or segregated path within the matrix is created. Due to their specific surface area, high aspect ratio, intrinsic physico-chemical properties (e.g., hydrophilicity) Graphene and its derivatives are able to affect the chemistry of cement hydration [1]. For instance, their intrinsic properties promote and regulate the formation of a well-ordered crystalline structure, smaller pores and more uniform pore size distribution leading to significant improvements in mechanical performances, durability (including corrosion resistance due to the reduction of penetration depth of chloride), volume stability (including the autogenous, plastic and drying shrinkage) as well as electrical. In this way "sustainable constructions" can be promote with the following potential contributions: a) reduction of cement amount; b) reduction of construction cycle times due to high early strength; c) stimulating novel "multifunctional" architectural and structural design; d) providing strong electromagnetic interference shielding property to reduce electromagnetic emission problems on our health.
In order to achieve the aforementioned goals, different lightweight concrete-based nanocomposites are produced starting from conventional cementitious components (cement) and sustainable aggregates (milled glass, pozzolana, diatomite) as matrix, and different foaming agents (Al powder or foaming protein), in order to obtain an aerated system. Finally, graphene and its derivatives are added in order to give new features (electrical conductivity) to the final materials.

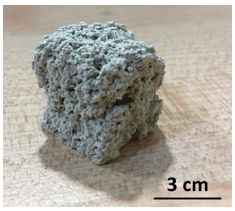

Figure 1. Sample of lightweight concrete/graphene material.

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MANUFACTURING OF COMPOSITES STRUCTURES: DESIGN, SURFACE TREATMENT AND IMPACT CHARACTERIZATION

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The use of fibre reinforced polymeric composites has atttacted significant interest for all applications requiring anisotropic and heterogeneous design coupled to high specific performance. Further, the development of polymers with enhanced physical and mechanical properties has promoted the development of new resin-fiber systems and widened the field of applications of these materials.
However, composite materials are susceptible to damage under dynamic loads that, in presence of through thickness stress, can propagate and leads to failure.
In order to avoid undesired damage and extend the service life of a composite structure, it's useful to modify the external surface of the composite and enhance the compatibility between resin and fibers, that have obviously different physical behavior.
In this work, to enhance the surface characteristics of epoxy/basalt composites, two approaches have been investigated and validated. In particular, plasma treatment and an innovative cold spray metallization have been properly applied on composites [1-2]that have been manufactured by vacuum infusion technology and experimentally characterized by low velocity impact tests. Results evidenced the effectivness of the proposed surface treatments on the impact damage modes and resistance.
The attained benefits open new perspectives also for crashworthy structures that have to be designed to provide significant collision energy absorption aptitudes. In this framework, a preliminary crash study on curved carbon fiber composite laminates has been performed to find the best configuration and technology and design innovative curved crashworthy composites.

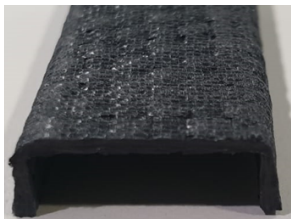

Figure 1: curved structures

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EFFECT OF CARBON NANOTUBES AND GRAPHENE NANOPLATELETS ON PROPERTIES OF ELASTOMER-BASED 3D PRINTED POROUS STRUCTURES

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Elastomer-based porous structures realized by selective laser sintering (SLS) are emerging as a new class of attractive multifunctional materials. Thermoplastic polyurethane (TPU) is a soft and flexible elastomer widely used as raw material for the SLS process. Recently, TPU composites reinforced with nanoscale fillers drew great attention for their enhanced mechanical, thermal, and electrical properties were investigated [1]. In this contribution, two kinds of fillers were used to coat the TPU powders, ie multi-walled carbon nanotubes (MWCNTs), graphene nanoplatelets (GE) and a combination of MWCNTs and GE (70/30 wt/wt). Several 3D mathematically defined architectures, with porosities from 20 to 60%, were designed by using triply periodic minimal surfaces (TMPS) equations corresponding to Diamond (D) and Gyroid (G) unit cells [2]. The resulting three-dimensional porous structures exhibit an effective conductive network due to the segregation of carbonaceous fillers previously assembled onto the TPU powder surface. The composite structures with single fillers show an enhanced thermal stability alongside with interesting mechanical and piezoresistive properties. On the other side, the simultaneous presence of MWCNTs and GE has a synergetic effect with a significant enhancement of electrical conductivity, piezoresistive properties, i.e. Gauge Factor (GF) values -13 with an 8% deformation, and relevant electro-magnetic interference (EMI) shielding properties [3].

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3D PRINTING TECHNOLOGIES IN REHABILITATIVE MEDICINE

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Created over 30 years ago, three-dimensional printing (3DP) has recently seen a meteoric rise of interest in the field of Physical Medicine and Rehabilitation. Currently, two key strategies utilize 3DP to restore both appearance and function to patients: regeneration and rehabilitation. In this work, it has been analyzed the application of different 3DP techniques for regenerative and rehabilitative purpose. For the regenerative approach, chemical modified Hyaluronic acid (HA), in combination with calcium phosphate (CaP) nanoparticles has been processed by 3D bioprinting (3D-Bio) for the realization of scaffolds for tissue engineering application [1]. Furthermore, in vivo studies through subcutaneous implantation in a rat model have demonstrated the potential of HA as patch for wound healing [2]. Similarly, a bilayer scaffold, based on collagen and poly-ε-caprolactone (PCL), has been developed for the regeneration of meniscus with improved bioactivity and suturability of the structure. On the other side, 3DP finds many applications also in the rehabilitative field. Part of this work evaluates the feasibility of producing orthopaedic scoliosis braces by fused deposition modelling technique (FDM), comparing performance and costs with classical thermoforming procedures. The work highlights how 3D printed back brace allows for complete customization, rapid manufacturing time, and the use of a variety of cheap but durable materials as Polylactic acid (PLA) and polyethylene glycol (PETG) [3]. Remaining in the rehabilitative field it has been studied the realization of piezoresistive wearable sensors based on thermoplastic polyurethane (TPU) in combination with Graphene (GE) and multi-walled carbon nanotube (MWCNTs) by selective laser sintering technique (SLS) [4]. Results showed that the simultaneous presence of MWCNTs and GE brings a significant enhancement of specific functional properties of the porous structures with relevant electro-magnetic interference (EMI) shielding properties.

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COMBINATION DESIGN OF ADDITIVELY MANUFACTURED SCAFFOLDS AND NANOCOMPOSITE GELS FOR TISSUE REPAIR

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Tissue engineering and cell-based therapies represent the most challenging fields in regenerative medicine, the aim being to synergistically combine cell population to properly designed scaffolds able to promote extracellular matrix (ECM) analogue deposition. In addition, the combinatorial design of 3D scaffolds and injectable/hydrogel-based systems should help to solve crucial aspects in damaged tissue repair, also trying to overcome the limitation of current practice in reducing surgical invasiveness and in enhancing biomolecular interactions with cells. Natural and synthetic polymers, as well as their combination, have been widely proposed and analyzed in the design of 3D multifunctional, well defined and stimuli responsive scaffolds in hard/soft tissue repair (i.e. bone, cartilage, intervertebral disc, adipose tissue, neural, and cardiac tissue) [1].
In this scenario, customized polymeric and composite 3D scaffolds have been proposed and developed by means of Additive Manufacturing (AM) techniques. Different formulations of collagen and collagen-low molecular weight hyaluronic acid (LMWHA) and their combination with nano- or sub-micro gelatin particles were selected [2] and combined with 3D scaffolds. Biological, mechanical, and chemico-physical performances have been assessed, whilst rheological and injectability tests suggested important information on the functional properties of the injectable systems in terms of viscoelasticity and flow behavior. The proposed collagen-based injectable delivery system has been assessed as a tool for moving toward less invasive effective therapies against neurodegenerative disorders (i.e. Parkinson's disease).
Finally, the proper combination of microfluidic system obtained via AM (lab on chip) and 3D bioprinting of scaffolds for specific tissue cultivation/modeling will lead the functional design and development of a medical diagnostic/prognostic device for the monitoring of a set of signals in cerebral ischemia.

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DEVELOPMENT OF A GREEN METHOD FOR RECOVERY AND REUSE CELLULOSE ACETATE FROM CIGARETTE BUTTS

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Cigarette butts (CBs) have been recognized as toxic residues since may contain contaminants and chemicals produced during combustion. Recycling the CBs for other purposes is difficult as there are no easy mechanisms or procedures to assure an efficient and economic separation of the butts or appropriate treatment of the entrapped chemicals. For this aim, different authors have been concentrating their research on the possibility of using cigarette butts in the most various applications [1-4].

In this study, we proposed a green, low cost, simple, and efficient extraction method of cellulose acetate fibers (CA) from discarded cigarette butts (DCBs). CBs extraction process involved a two-step process. The obtained samples of CA were dried at 60°C for 1h in the oven. The quality and properties of cellulose acetate extracted and purified is comparable to the pure cellulose acetate. The preliminary results obtained on the CA recovered look promising to the use of this recovery material from cigarette butts, to obtain a wide consumption fashion product, such as eyeglass frames.

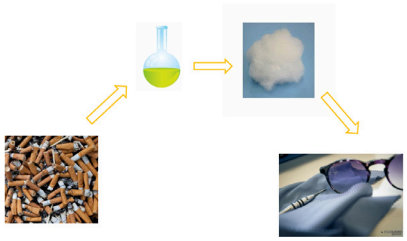

Figure 1 Scheme of recovery CBs

Acknowledgement: The Authors thank to Essequadro eyewear for providing cigarette butts, funding for the 'green' exctraction study and testing support for material development.

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SHAPING THE MAGNETO-ELASTIC RESPONSE OF FIELD-STRUCTURED SMART FOAMS

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The mechanical and magneto-elastic response of magnetic field-structured smart materials is imparted by assembling magnetic reinforcing particles in form of aligned aggregates during the production process [1]. Magnetic field strength and particles content are the main parameters that affect the final elastic and magneto-elastic responses. Conventional polymeric field-structured materials are characterized by a density higher than 1 kg/dm^3. To overcome this limitation, smart polymeric foams with density lower than 0.2 kg/dm^3 have been developed as composite lightweight and multifunctional materials [2]. Smart foams have been produced by applying the magnetic field during foaming until the end of the process. Unlike in conventional composite foams, the mechanical response is anisotropic, thus the reinforcement potential is fully exploited along a single direction, and it is obtained by means of a very low volume content of reinforcing particles. The use of this process have the additional advantage of preserving the homogeneity and regularity of the cellular morphology at the end of the foaming process. Furthermore, a wide range of densities is allowed.
In case of soft polymeric matrix, an additional feature of field-structured foams is their smart behaviour. In fact, they have the capability to interact with the magnetic field, and respond with a change in apparent elastic modulus (positive ΔE-effect). Such behaviour is due to the geometrical features of the aligned aggregates.
This paper present a development of the field-structuring process, which takes advantage of the implementation of a time-variable magnetic field during foaming. In particular, magnetic field strength, switch on and switch off times have been varied to tailor the geometrical characteristics of the aligned aggregates and their effects on the mechanical and smart performances have been investigated. It has been proved that length and aspect ratio of the aggregates allow to shape the stress-strain curve in compression and the enhance the sensitivity to the magnetic field of the smart foams.

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THERMAL, GAS TRANSPORT AND ANTIMICROBIAL PROPERTIES OF PEBAX®RNEW FILMS LOADED WITH IMIDAZOLIUM IONIC LIQUIDS

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The incorporation of imidazolium ionic liquids (ILs) in flexible films is useful to take advantage of ILs remarkable properties [1] in many industrial applications. Poly(ether-block-amide) (Pebax®Rnew) membranes were prepared by *controlled solvent evaporation* loading, up to 5 wt.%, two ILs 1-octyloximethyl-3-methylimidazolium hexafluorophosphate [OOMmim][PF_6] and 1-hexadecyl-3-methylimidazolium dimethyl-5-sulfoisophthalate [Hdmim][DMSIP] [2]. The ILs were synthetized and characterized by ^{1}H NMR, MALDI-TOF spectroscopy, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The miscibility, morphology, wettability, gas transport, spectral and thermal properties of the obtained blends were investigated. TGA evidences a good thermal stability (>200 °C) for the membranes, while DSC reveals phase separation in the IL-loaded films, in accordance with the island-like surface morphology observed by Scanning Electron Microscopy (SEM) and with Fourier Transform Infrared (FTIR) analysis. Gas permeability tests shows that the films are defect-free, maintaining the original selectivity of the neat polymer with a reduction in the gas permeability due to the impermeable nature of the solid ILs crystals. The blend antimicrobial activity, tested against both Gram- (*Escherichia coli*, *Pseudomonas fluorescens*, *Salmonella enterica*) and Gram+ (*Listeria monocytogenes* and *Bacillus subtilis*) bacterial strains, depends on the chemical structure of the incorporated ILs. The smaller [OOMmim][PF_6] only slightly lowers the hydrophobicity of the neat polymer and is readily released from the films. Instead, the [Hdmim][DMSIP], having a cation bearing a longer alkyl chain, induces a promising antimicrobial activity in the blends together with good hydrophilicity, permeability and thermal stability. Data on ILs release and biocompatibility/cytotoxicity suggest their application as antimicrobial coating on furniture for sterile environments/rooms, as filters for aerating systems and, at low concentrations of ILs (≤1%), in biomedical field.

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INSIGHT THE DEVELOPMENT OF BIOPOLYMERS AND FUNCTIONAL GEOMETRY BY 3D PRINTING

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In recent years, additive manufacturing (AM) has increasingly gained more attention both in scientific and industrial fields; this growing interest can be attributed to different reasons such as the reduction of material waste, possibility of using suitable materials for a specific application and the potentiality to achieve complex geometry with inherent functionalities. Among the AM techniques, fused deposition modelling (FDM) is one of the most flexible 3D printing techniques for neat or filled thermoplastics and, very recently, also for long fiber composites. The versatility of FDM 3D printing allows to exploit a twofold approach: firstly, the bulk feeding material can be fed to the process also considering suitable filler loadings to improve specific properties; secondary, complex geometries can be opportunely designed to meet performance needed in structural application unachievable by the standard thermoplastic.
Poly-L-lactic acid (PLA) is one of the main biodegradable materials copiously processed and investigated but it is also potentially employable for structural elements [1], in both medicine (i.e. substitute of metallic fixations stem in osteosynthesis [2]) and structural engineering (i.e. absorbing energy structures). The present contribution will present results and preliminary activities toward: a) the development of filled PLA system for 3D printing for medical applications to overcome its recognized limitations as slow degradation, thermal conductivity and brittleness [3] (i.e. orthopedic elements); b) modelling of 3D printing processing and configurational parameters affecting the final mechanical performance and c) manufacturing of complex shape components as for shock absorbing and predictive simulation for design porpoises [4].

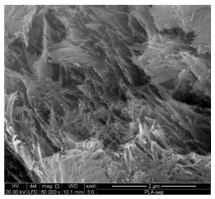
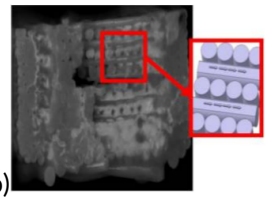
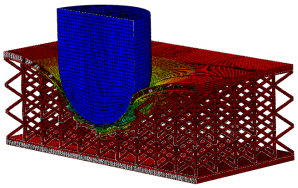
a)  b)  c) 

Figure 1 a) Filled PLA b) 3D printed cell; c) energy absorption

Acknowledgement: We would like to thank Bernardo Cirillo, Fabio Docimo and Mario De Angioletti for the valuable contribution of the setting of mechanical and thermal tests.

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ABSTRACTS

Synthesis, functionalization and modelling of polymers based materials. Structural characterization of macromolecule and advanced analysis techniques.

DESIGN OF ACTIVE FUNCTIONAL INTERFACES FOR SENSING MATERIALS

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In recent years there is a clear trend in materials science to shift research effort from "passive" to "active" materials, leading to breakthroughs in realization of sensing platform. This approach became feasible by means of the synthesis of materials and nano-engineered surface, leading to the development of micro- and nano-structured interfaces based on bottom-up approaches.
Active materials show properties that can be altered after their synthesis, by either inherent autonomous mechanisms or by enforcing an external stimulus, which could conduct to a reversible change of structure, porosity, permeability and conductivity
A well-built strategy to obtain active interfaces is represented by the functionalization of materials with active molecular components which can translate a molecular signal in the change of a macroscopic function. Moreover, it should be underlined that in addition to the interface chemistry, also the interface topology is a fundamental key factor determining the material properties.
The design of sensing materials represents an interesting research topic which requires a multidisciplinary approach grounded on chemistry, materials science, engineering, biology and medicine.
The present contribution will present results and future perspective.

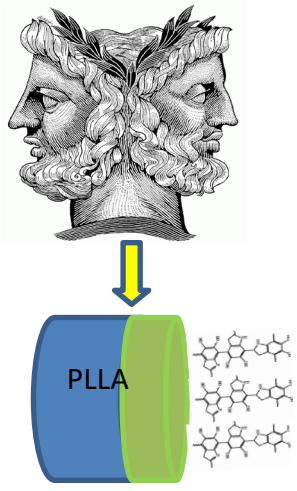

Figure 1. Janus structure of PLLA aerogel with surface coated of polydopamine

NEW METHODS AND ALGORITHMS FOR THE *"FOURTH PARADIGM OF SCIENCE"* IN THE ERA OF DELUGE OF DATA AND COMPUTING POWER

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The plenty of data available, as never before in history, in many scientific contexts, is imposing what many now define the *"fourth paradigm of science"* [1]. At the same time, some projects (e.g., *The USA Exascale Computing Project* [2] and *The European Technology Platform in HPC* [3]) that plan to create *"computing ecosystems"* capable of guaranteeing computational powers of the order of 10^{18} operations per second, are beginning to bear fruit.
In order for scientific research to concretely take advantage of all this "abundance", it is necessary to rethink the tools that have up to now supported scientific computing, for example: 1) (re) designing the algorithms which, in the light of the new infrastructures for supercomputing characterized by a very high number of components and a great heterogeneity [4], must respond to high levels of granularity and locality (e.g., the *communication-avoiding* algorithms for the solution of linear systems [5]); 2) implementing methods that can make use of full decomposition of the models 's space-time domain (e.g., the *"parallel in time"* algorithms for the solution of the differential equations describing evolutionary phenomena [6]); 3) overcoming the classic techniques of *"data assimilation"* [7] in correction/definition of the models to develop new integration strategies between these and the data (e.g., the use of *"machine learning"* techniques for data-driven discovery of partial differential equations [8]).

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POLYMERIC SPONGES FOR CONTAMINANTS REMOVAL FROM WATER

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Novel adsorbents sponges based on poly-2-hydroxyethyl methacrylate (PHEMA) and/or (4–vinyl-benzyl)–N–methyl–D–glucamine (VbNMG) to remove organic or inorganic contaminants from water were formulated. Ice templating approach via traditional radical polymerization was used to obtain the macroporous structures. Going into more synthetic details, sponges designed to remove heavy metals take advantages from the use of N-methyl glucamine as grafting group (NMG) for the vinyl benzyl monomer. The cryogel containing 100% of VbNMG (VbNMG-100) showed excellent ability in fast water uptake, removing arsenic (76.3 mg/g) as well as chromium (130.9 mg/g) metal ions from it. Reusability up to six cycles was also demonstrated. Furthermore, exploiting its spongy nature, only 5 mins are needed to absorb contaminated medium releasing purified water by a simple squeezing. The sponge can be easily regenerated and reused again up to three times without the depletion of its efficiency [1].
To obtain a photocatalytic material able to permanently degrade organic pollutants, hydroxyl pendant groups present on HEMA were used to link ZnO by using Atomic Layer Deposition (ALD). This step provides them the ability in photodegrading organic molecules via UV light after the adsorption process. Conversely, acrylate porphyrin units were added as comonomer to HEMA, to test also their photodegradation efficiency under visible light irradiation. Furthermore, during syntheses, graphene oxide was added to the reactants with the aim to increase the sequestration of organic pollutants. PHEMA-ZnO nanostructures produced, are able to degrade methylene blue in water, by regenerating themself for subsequent reuses. Up to three cycles of regeneration were successfully tested [2].

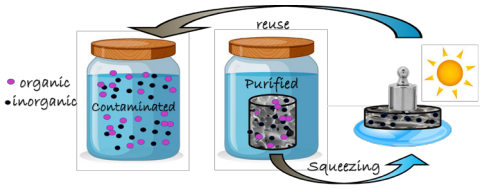

Figure 1. Working action of polymeric sponges.

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AMPHIPHILIC THERMORESPONSIVE POLYMERS FOR DRUG RELEASE AND WATER PURIFICATION

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Thermoresponsive polymers are amphiphilic macromolecules which display reversible lower or upper critical solution temperature transition (LCST or UCST), above or below which they self-assemble forming micro- or nano-assemblies according to their hydropobic to hydrophilic balance. Herein, copolymers (PFG) of pentafluorostyrene (PFS) and oligoethyleneglycol methacrylate (OEGMA) are synthesized at variable compositions by free and controlled radical polymerization. These copolymers display tunable self-assembly properties as a function of the PFS content. In particular, the LCST values and the size of assemblies range from 26 to 50 °C and 80 to 2000 nm, respectively, with increasing the PFS molar content [1]. The controllable thermoresponsive self-assembly behavior makes these polymers attractive as high efficiency loading agents which are suitable both for controlled delivery and water remediation applications (Figure 1) [2].

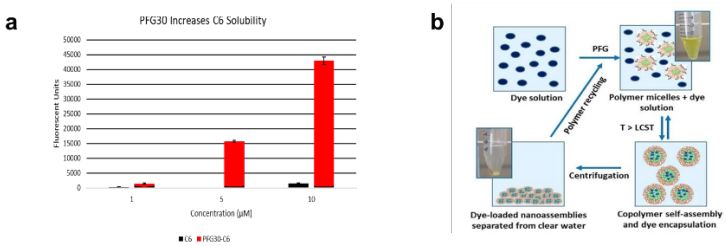

Figure 1. (a) PFG30 encapsulation significantly increases the water solubility of coumarin-6 (C6). (b) Use of PFG copolymers to remove dyes from contaminated water.

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ADVANCES AND CHALLENGES OF MICRO- AND NANOPLASTIC POLLUTION IN DIFFERENT ENVIRONMENTS

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During the last decade, microplastic pollution, and more recently nanoplastic pollution, has become a relevant global problem due to the direct impact these pollutants have on the environment and to their effects on biota and potentially on human health [1]. Microplastics (>100 nm and <5 mm), or nanoplastics (<100 nm), could enter the environment as primary particles, if they are intentionally produced in micro/nanometric size either for direct use or as precursors to other products, and secondary particles if they are generated in the environment from degradation of larger plastic items. Due to their high surface area, they could sorb contaminants and act as their potential vector, translocating them in organisms or uncontaminated environments. These particles are challenging to isolate, quantify and identify in environmental samples due to their size and surface alteration caused by biofilm formation or by chemical/biological substance adsorption. In this scenario, new approaches to determine microplastics/nanoplastics in environmental matrices are under investigation. The results will allow to correlate particle types, sources, occurrence, transport and fate, and their interactions with organisms in different compartments. Promising results have been obtained in determining microplastic pollution in complex matrices such as freshwater, seawater and biological tissues by combining morphological, thermal and spectroscopic techniques. The TGA/FTIR analysis of a collection of microplastic samples, prepared at lab scale, will allow the development of a database, which can be used to identify and quantify polymers in environmental samples. Furthermore, different analytical procedures have been set up to identify and quantify microplastics of fibrous shape, released from synthetic fabrics during their washing and wearing [4-5]. The obtained results have also allowed the correlation of microplastic release with different textile structures, laundering detergents and additives, washing conditions and parameters.

Acknowledgements:
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THE "MOLECULAR APPROACH" TO STUDY THERMAL, THERMO-AND PHOTOOXIDATIVE DEGRADATION OF PA11 NANOCOMPOSITES

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Most of the degradation studies regarding polymer nanocomposites were focused to evaluate change in mechanical properties. Herein, we focalized our attention on the assessment of precise modification on skeleton chains caused by an external stimulus (light, heat, oxygen exposure ect).To this purpose, Matrix-Assisted Laser Desorption Ionization Time-of-Flight mass spectrometry (MALDI MS) was used to determine the macromolecular structures of stimulated samples; the formation of peculiar degradation products even in trace amounts, were detected and correlated to (Size Exclusion Chromatography) SEC data. This original "molecular" approach can be applied in several fields of polymer chemistry. In this case, our goal was to differentiate the contribution of clays and impurities on degradation of PA11 matrix.
Specifically, the thermal, thermo and photo-oxidative degradation processes of bio-based PA11 nanocomposites containing montmorillonite (MMT) and the organo-modified Cloisite®30B were investigated to discriminate the influence of organo-modified components on the polymer durability. Indeed, despite the extensive studies reported, there are still ambiguous points to be clarified from the chemical point of view. As expected, the addition of organo-modified nanoclays strongly affected the PA11 light durability, triggering the macromolecular chains scission due to the typical αH, Norrish I and II mechanisms. However, the main contribution in boosting the photooxidative degradation is induced by iron impurities contained into the clays. Conversely, thermo-oxidation process performed at 215°C, was unambiguously affected by the presence of the organo-modifiers whose presence determined an enhancement of crosslinking reactions [1].

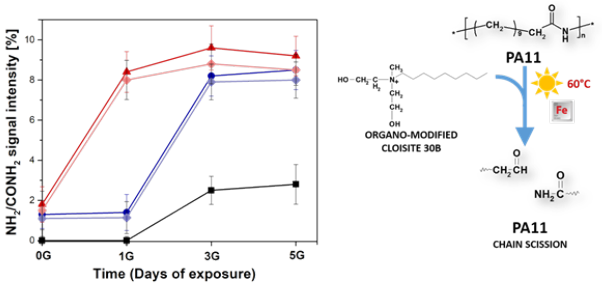

Figure 1. Intensities of MALDI peak related to $NH_2/CONH_2$ oligomers plotted as a function of exposure time for PA11 (black square), PA11-CC3 (blue circle), PA11-CC9 (red up triangle), PA11-MMTC3 (violet diamond) and PA11-MMTC9 (rose diamond) samples.

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SELF-ASSEMBLING TRIBLOCK COPOLYMERS FOR ANTICANCER COMBINED THERAPY

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Polymeric nanoparticles (NPs) have a key role in drug delivery as nanocarriers for small hydrophobic molecule drugs and as non-viral vectors for gene delivery (plasmid DNA or siRNA). Combination of these properties in a single NPs formulation can be helpful in cancer treatment. In this topic, block copolymers, capable to self-assemble in NPs, offer a wide range of opportunities due to the possibility of fine tuning the structure (nature, length and ratio of blocks) and surface properties of final NPs. The aim of this work concerns synthesis and characterization of amphiphilic triblock copolymers based on polyethyleneglycol (PEG)-poly(dimethylaminoethyl-methacrylate) (pDMAEMA)-polycaprolactone (PCL) with different blocks length with the purpose of realize NPs for a combined anticancer therapy. The structure of triblock copolymers is shown in **Figure 1.**

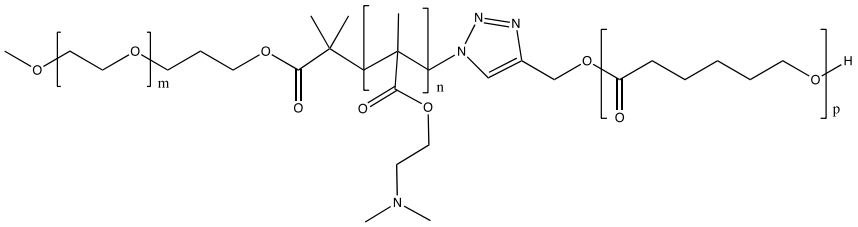

Figure 1. Structure of triblock copolymers

PEG was chosen as hydrophilic block for its stealth properties; pDMAEMA cationic block, introduced for siRNA complexation, was synthesized via atom transfer radical polymerization (ATRP); finally, PCL was conjugated via "click" reaction through copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) as biodegradable hydrophobic block. Copolymers were characterized through ^{1}H-NMR, FTIR and GPC. NPs were obtained by nanoprecipitation and characterized for size, polydispersivity index, surface charge, stability and critical micellar concentrations (CMC). NPs were loaded with docetaxel (DTX), and a non-targeting siRNA was adsorbed. The complexes were characterized by electrophoresis on agarose gel. The final NPs showed narrow size distribution, good loading efficiency and adequate release profiles. *In vitro* transfection experiments of siRNA-loaded NPs showed good ability to transfect for selected formulations, demonstrating that the blocks length and ratio have a big impact on the final properties of NPs.

DICLOFENAC REMOVAL BY USING MOLECULARLY IMPRINTED POLYMER BASED ON ACRYLIC ACID

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In the last few decades, environmental issues are posing serious threats to human health, receiving growing attention from civil society and major international organizations as well. Contamination of natural systems derives from organic and inorganic chemicals introduced into media by a large number of ancient and novel human activities. In addition to pesticides and other well-known organic pollutants, pharmaceuticals, veterinary medicines, and personal care products have been recently detected in surface water, groundwater, and also drinking water, constituting new insidious concerns. Even if present in trace amounts, the so-called emerging pollutants can cause bio-accumulative, persistent, carcinogenic, mutagenic, and detrimental effects on the survival of aquatic organisms, flora, fauna, and human health. To resolve restrictions derived by traditional wastewater treatment plants, we implemented a molecularly imprinted polymers (MIPs) as valid tools for selective adsorption and removal of these drugs from water. Specifically, we have prepared diclofenac-selective MIP by a simple bulk synthesis. The binding abilities of the produced materials were evaluated in detail *via* the capture of diclofenac in aqueous medium and compared with the corresponding non-imprinted polymer used as a reference. Owing to the templating effect, the as-prepared MIP adsorbs with high selectivity the template molecule, i.e. the diclofenac. This specificity was tested by measuring the adsorption efficiency versus acetylsalicylic acid as well as trimethoprim. Furthermore, MIP reusability has been proven by a simple regeneration procedure, allowing its reuse more and more time [1].

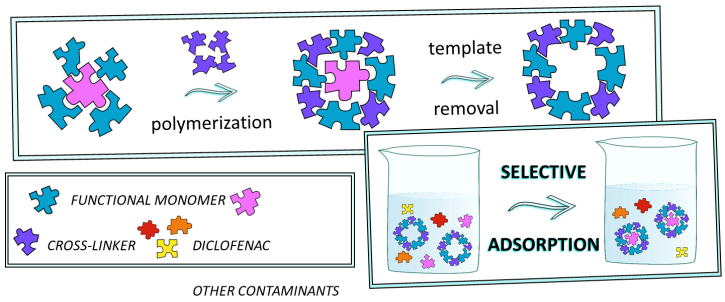

Figure 1. Polymer templating scheme

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MITIGATION OF MICROPLASTIC RELEASE FROM SYNTHETIC TEXTILES

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The washing and use of synthetic textiles like polyester, polyamides and polyacrylonitrile, represent one of the main sources of microplastic pollution. In fact, microplastics of fibrous shape are ubiquitous pollutants that have been detected in the most various environmental compartments, from seas and oceans to soil and atmospheric deposition [1]. The release of microplastics from the textile structure is a complex process and depends on several factors. Therefore, the mitigation of the release requires a comprehensive approach that includes actions at all levels involved in the release, from textile design and production, to laundry and wastewater treatment.
For this purpose, with a first approach, we developed eco-sustainable innovative finishing treatments suitable for the implementation at textile production level. Such treatments create a thin and uniform layer on fabric surface, protecting the textile during washing without altering its characteristics. The first treatment was based on the grafting of a natural polysaccharide, pectin, on the surface of polyamide 6.6 by using a two-step synthetic route [2]. The second treatment was based on the deposition on fabric surface of biodegradable polymers like poly (lactic acid) and poly (butylene succinate-co-butylene adipate), whose degradation behavior in a simulated marine environment was also studied, by using an electrofluidodynamic method [3,4]. Both treatments showed promising results, reducing the amount of microfibres released during washing by more than 80%.
With a different approach, as mitigation measures applied at laundry stage, we tested a filtration system for household washing machines, composed by a pre-filter, a membrane and a replaceable filter cartridge. The system showed an efficiency of 70% in retaining microplastics from wastewater. Finally, we are currently developing new porous materials based on cross-linked polyvinyl alcohol, in order to use them as membranes for microplastic removal from wastewater.

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ADVANCED THERMAL ANALYSIS OF BIODEGRADABLE POLYMERS

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Advanced thermal analysis is the most powerful technique to investigate the metastable nanophase structure of semicrystalline polymers, as it is established during processing: advanced thermal analysis allows to clarify the interplay between transitions of crystalline and amorphous chain portions, including quantitative analysis of the two main amorphous fractions: the mobile amorphous fraction (MAF) that mobilizes at the glass transition temperature (T_g), and the rigid amorphous fraction (RAF) that includes portions of macromolecules whose mobility is hindered by the near crystalline structures. Main results achieved at IPCB-CNR via advanced thermal analysis are summarized below, with most investigations carried out on biodegradable and biobased polymers.

- A discontinuity in crystallization kinetics of PLLA, caused by crystal polymorphism, was evidenced for the first time at IPCB-CNR; this finding started new research lines by several other groups worldwide.
- The influence of crystal polymorphism on thermal, mechanical and barrier properties of PLLA was clarified, which favored design of EMAP biodegradable food packaging.
- The effect of chain parameters, including molar mass and stereoregularity, on crystallization kinetics of PLLA, was rationalized in terms of nucleation and crystal growth rates, for both α'- and α-polymorphs.
- The melting enthalpy of both α'- and α-forms of PLLA was quantified.
- ICTAC guidelines for collecting thermal analysis data were defined.
- Influence of mobility of MAF and RAF on crystallization kinetics was proven (Fig. 1).
- Interplay between RAF mobilization and crystal melting was demonstrated for a number of polymers, with focus on crystal annealing and RAF enthalpy relaxation.
- The influence of RAF on material properties was demonstrated.

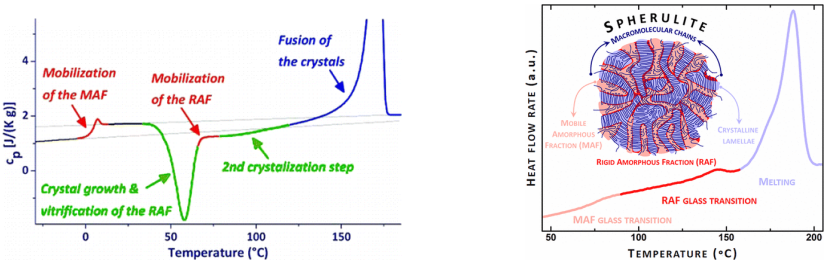

Figure 1. Left, poly[(R)-3-hydroxybutyrate]; right, poly(L-lactic acid)

Current research is focused on glass transition and enthalpy recovery of the RAF (Fig. 1), improved crystallization kinetics of PLLA, thermal treatments for tailored foaming/ nanofoams of PLLA, biodegradable materials containing active molecules (eg. mosquito repellents, or natural additives with antibacterial properties).

INTERFACE/INTERPHASE IN MULTICOMPONENT POLYMER SYSTEMS: INSIGHTS FROM SOLID STATE NMR

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Solid State Nuclear Magnetic Resonance (SS-NMR) is among the most powerful and versatile techniques for the study of complex solid systems. It provides information on molecular and collective phenomena over large length and time scales allowing to study structural and dynamic parameters at a molecular level.
In the field of polymer based multicomponent materials, the understanding and the control of interfacial phenomena is an important challenge to design innovative materials with tailored properties considering that the features of the interphase can influence or even dominate the behavior of the whole material.
To this aim, SS-NMR proved to be a very precious tool allowing to highlight mechanisms of interactions occurring at the interface as well as their effect on mobility, orientation and organization of the molecules in this region.
Here, SS-NMR analyses of polymer/nanofiller interactions occurring at the interface and prompted by different reactive preparation strategies are presented.
In particular, PMMA and PET based nanocomposites have been investigated.
PMMA/silica nanocomposites were prepared by in situ polymerization via a free radical mechanism. Silica nanoparticles were modified with methacryloylpropyl trimethoxysilane (MPTMS), due to the presence of vinyl end groups able to partecipate to the radical polymerization. NMR analysis proved the grafting of PMMA chains onto silica particles (PMMA-g-SiO_2), defined the average chain length of the grafted PMMA and highlighted the mechanism of silica and growing macromolecular reactions. The silica/MMA system was further investigated through a combined experimental/theoretical approach, highlighting the strong effects of monomer/oligomer molecular weight on the interfacial interactions during the first stages of polymerization.
PET based nanocomposites containing precipitated $CaCO_3$ nanoparticles (PCC) were prepared by melt mixing. A trimellitic anhydride end-capped PET (T-PET) was synthesized and added during the processing as interfacial agent exploiting the reactivity of carboxyl and anhydride groups with calcium ions at the surface of PCC particles. SS-NMR demonstrated T-PET/PCC particles interactions. Moreover, as a consequence of the interactions with the inorganic surface it was also evidenced an unusual chain conformation and a marked perturbation in the relaxation behavior of PET chains, thus underling strong changes in molecular dynamics.
The insights obtained through the study of interfacial phenomena have been of crucial importance for the setup of preparation strategies and the development of materials with controlled properties.

Acknowledgement: This contribution is dedicated to the memory of dr. Donatella Capitani.

HIGHLY SENSITIVE BIOSENSOR BASED ON 2D GRAPHENE OXIDE COATED ON A LONG PERIOD GRATING FIBER

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Biological recognition elements have attracted extraordinary interest in recent years, because of the key role they play in the development of highly sensitive and selective chemical and biological analysis. Specificity and sensitivity should be the main properties of any biosensor. Moreover, microengineering technologies give us some opportunities in developing high-tech sensing systems that operate with low volumes of samples, integrates one or more laboratory functions on a single substrate, and enables automation [1-4].

In this work, we report an ultrasensitive fiber-optic biosensor realized using a single-ended Long Period Grating (LPG). The LPG working point is tuned in the highest sensitivity region of mode transition, through a thinner layer of 2D Graphene Oxide (GO). Due to the coexistence of hydrophobic domain from pristine graphite structure and hydrophilic oxygen-containing functional groups, GO exhibits good water dispersibility, biocompatibility, and high affinity for specific biomolecules. These properties of GO provide many opportunities for the development of novel biological sensing platforms.

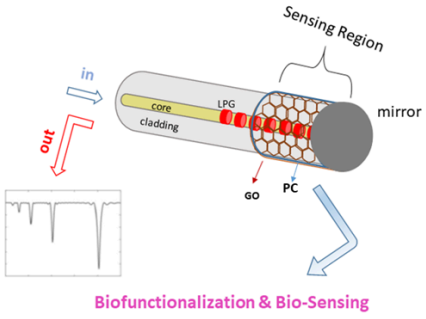

Figure 1 Scheme of 2D GO-LPG

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STRUCTURAL CHARACTERIZATION OF NOVEL PRANOPROFEN-POLY (Ɛ-CAPROLACTONE) CONJUGATES SYNTHESIZED BY MICROWAVE-ASSISTED TRANSESTERIFICATION

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Pranoprofen (PPF) is a non-steroidal anti-inflammatory drug (NSAID) prescribed to treat arthrosis and rheumatoid arthritis both in acute and chronic diseases. It is also used in ophthalmology as a powerful anti-inflammatory postoperative treatment of strabismus and cataract surgery, to relieve dry-eye symptoms, and in cases of uveitis and cystoid macular edema. Unfortunately, as is the case for other NSAIDs, oral administration may cause deleterious side effects and gastric disorders, and eye-drop preparations have limited efficacy. Biodegradable polymers are used in many biomedical devices, such as implants, cellular scaffolds, and drug delivery systems. To improve drug delivery capability and to reduce systemic toxicity, the interest in polymer-drug conjugates has increased remarkably. In this prospect, PPF was conjugated to poly(ε-caprolactone) (PCL) *via* microwave-assisted transesterification acid-catalyzed by p-toluenesulfonic acid (pTSA). This synthesis represents an adaptation of that proposed previously [1, 2], which produced copolymers starting from the respective homopolymers. The procedure involves three steps: first, a concentrated solution of the polymer in toluene/chloroform 4:1 in the presence of pTSA and a small amount of water is heated at reflux temperature in a microwave reactor. Partial hydrolysis of the polymer proceeds during this stage, as shown by the appearance of signals of the PCL -CH2-OH terminal group in the ^{1}H NMR spectra of the hydrolysis products. In the second step, PPF is added to the reaction mixture, and the solution is heated at reflux temperature for 4 h, at the same conditions as above. In the third and final step, water is removed through a Dean-Stark-trap from the refluxed mixtures. As a consequence, an increase in the molecular weight of the polymer (due to the self-condensation of the end-groups of PCL chains) and the transesterification reaction between PCL and the carboxylic moiety of PPF occur. The obtained products were characterized by NMR, MALDI-TOF mass spectrometry, and GPC, which gave proof of the covalent link between PPF and PCL, and by thermal analyses. The conjugates were found to contain up to 4.3 % w/w of PPF, and molecular weights ranging from 5 to 12 KDa.

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A MULTISCALE APPROACH TO UNVEIL THE INTERPLAY BETWEEN STRUCTURE AND DYNAMICS IN SOFT MATERIALS

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Complex fluids, such as gels, suspensions, and biological fluids, to name just a few examples, have dynamics related to the structural details of their constituents. Unveil the interplay between dynamics and structures is of paramount importance for understanding these systems, and has relevant implications for various practical aspects (e.g. stability over time, relaxation under constraints, etc.). Typically, the structures present in such fluids have lengths ranging from tens of nanometers up to millimeters, while the associated times vary between millisecond and hours (or even days). To properly study such wide range of lengths and times a multi-scale approach is on demand. An example of such an approach for an alginate gel is shown in Figure 1. Here, unconventional dynamic light scattering (multi-speckle DLS), rheology, and microscopy (SEM) are coupled to reveal the aforementioned link [1].

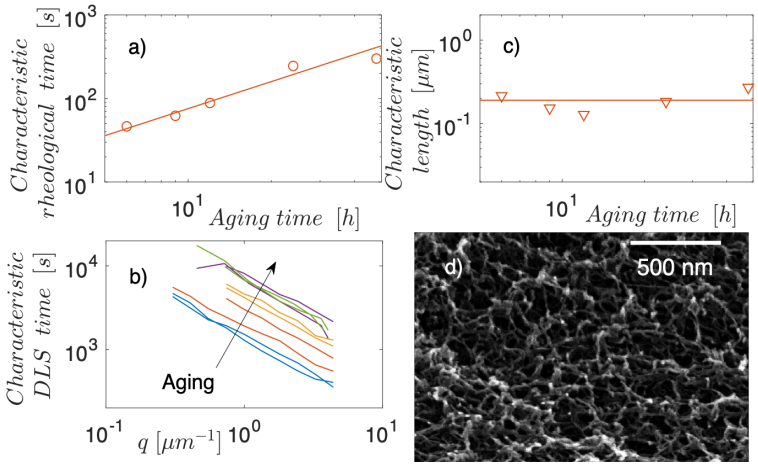

Figure 1: a) Characteristic relaxation time as a function of aging time. b) Characteristic de-correlation time as a function of the wave vector (q) at different aging times. c) Characteristic length, defined as the inverse of the wave vector at which the rheological and DLS times are equal. d) SEM image of the alginate aerogel showing the typical pore size of the gel.

Linear rheology and multi-speckle DLS, performed on samples with different aging times, enable to extract the gel rheological and de-correlation times (fig.1a,b). The comparison between the rheological time and the DLS time-scales (time as a function of the wave vector), allows to define a characteristic dynamic length (fig.1c). This length does not change with aging time, and represents the length that controls the gel initial relaxation. SEM analysis (fig.1d), performed on an aerogel, allows to identify this length with the pore-size of the gel, linking the structure to macroscopic relaxation.

Acknowledgement: Thanks to F. Docimo and C. Leone for technical assistance, and C. Del Barone for SEM analysis.

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SYNTHESIS OF SELF-ASSEMBLING COPOLYMERS FOR THE REALIZATION OF NANOPARTICLES FOR ANTICANCER THERAPY

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In the field of nanomedicine, core-shell nanoparticles (NPs) are already a clinical reality for the treatment of cancer, due to their capability to overcome physiological barriers and to accumulate into tumor tissue. Nanotechnologies in cancer medicine aim to optimize the pharmacokinetics of chemotherapeutics, preserve them from *in vivo* degradation, reduce toxicity, direct towards the target organ, and allow the delivery of two or more drugs in association. The diversity of available nanoparticles for drug delivery is considerable and includes polymeric nanoparticles, dendrimers, carbon nanotubes, quantum dots, metallic nanoparticles or lipid-based systems, such as micelles or liposomes. Amphiphilic biodegradable block copolymers able to self-assembly in aqueous solution to form core-shell nanostructures are particularly attractive, due to the possibility to be synthesized *ad hoc* by controlling nature and length of blocks and copolymer architecture, and to covalently bound target, diagnostic or therapeutic agents. It is so possible to realize multifunctional NPs, that present a surface decorated with functional groups for active targeting, diagnostics or therapeutics.
In the present communication, several examples of synthetic strategies of block copolymers based on poly(ethylene glycol) (PEG) as hydrophilic block and poly(ε-caprolactone) (PCL) as hydrophobic block are presented. The copolymers are functionalized either with target units (folate, which is recognized by the specific receptor overexpressed on the surface of the majority of solid tumor cells), or peptides with antiangiogenic or tumor-penetrating properties. NPs were prepared by nanoprecipitation and fully characterized for size, polydispersity and surface properties. Possible strategies to enhance surface exposition of the covalently bounded functional groups are also discussed. Biological studies performed on KB carcinoma cells to highlight the potential of NPs in cancer treatment showed promising results [1-3].

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SORPTION INDUCED SWELLING OF POLYMERIC MEMBRANES: A NEW APPROACH BASED ON IN SITU FTIR VIBRATIONAL SPECTROSCOPY

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In the perspective of zero emission and low energy technologies envisaged by the new European Green Deal, polymeric membranes are thought to be a good alternative to thermal based separation processes. However, sorption of small molecules in polymeric membranes often results in dilation of the host matrix. This type of structural modification adversely affects the polymer separation performances (e.g. in organic solvent nanofiltration) but is not easily measured with common techniques.

In this contribution, *In situ* FTIR vibrational spectroscopy in transmission mode is used to measure swelling of two polymers i.e. polydimethylsiloxane (PDMS) and polybenzimidazole (m-PBI or Celazole®) due to sorption of carbon dioxide and methanol respectively. The specimen thickness can be varied from a few micrometers to a few millimeters. The technique resolution is 0.1 % and the limit of detection (LOD) is 0.5%. The accuracy is easily modulated by modifying the instrumental parameters. The swelling calculation procedure is straightforward [1-2].

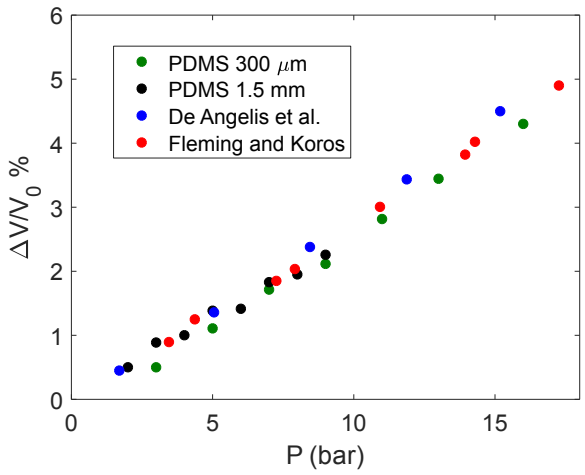

Figure 1. CO_2 sorption induced swelling of PDMS

References:
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AN OVERVIEW ON THE ROLE OF THE MALDI-TOF MS IN THE CHARACTERIZATION OF THE CONJUGATED POLYMERS

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Conjugated polymers are an attracting class of materials that owing their semiconducting properties finding application in optoelectronic devices as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), organic photovoltaics. A lot of experimental and theoretical studies are devoted to research field of several classes of the conjugated polymers. Several synthetic procedures have been developed to reach the highest control over both polymerization and analytical methodologies (i.e MS, NMR, SEC, FTIR) allowing an in-depth and straightforward characterization of the polymer synthesized without any required doubt. We have opportunely synthesized several conjugated polymers as polyfluorenes, functionalized polythiophenes (homopolymers and copolymers), polycarbazoles, amphiphilic P4VP based copolymers, which were deeply characterized either by NMR and MALDI-TOF MS methods.[1,2] For each class of polymers synthesized, the MALDI-TOF MS analysis proved the formation of different end groups, and permitted also to identify side reactions, regio-irregularity and in the case of copolymers the formation of homosequences due to homo-chain coupling. The combination of SEC-MALDI-TOF MS data with the optical properties of each SEC fraction allowed to evaluate the changes the optical properties as a function of the chemical composition and of the average molar masses (Figure 1) [1].

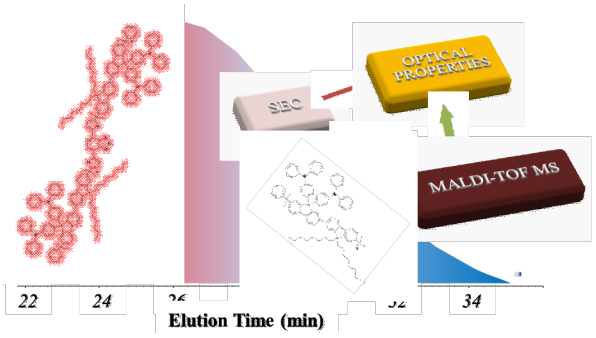

Figure 1. Combination of SEC, MALDI-TOF MS and Optical analyses of a polyfluorene.[1]

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SYNTHESIS AND CHARACTERIZATION OF POLYMERIC MEMBRANES

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Aromatic poly(ether sulfone)s (PES)s are engineering thermoplastic materials with excellent chemical and thermal stability as well as high glass transition temperature, excellent strength and flexibility, transparency, as well as a good film forming properties. PESs have obtained wide use in many fields, both scientific and industrial: separation membranes (solid-gas, solid-liquid), metal-metal adhesives, composites, toughening agents for thermosetting resins [1, 2], membranes for proteins recovery. Lack of hydrophilic groups and the closing arrangement of macromolecular chains lead to the poor hydrophilicity for PES. One way to avoid this could be to make the membrane partially hydrophilic. A wide range of PES based copolymers was synthesized and characterized, exploiting various reaction paths. The insertion of carboxyl and sulfonic groups and their effects on the behaviors of the polymers was verified and applied to the engineering of different kind of membranes for different applications.

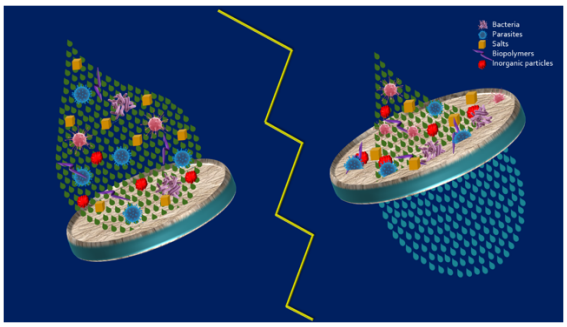

Figure 1. Water Treatment Scheme

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ARTIFICIAL INTELLIGENCE AND NATURAL INSPIRATION: WHAT FUTURE FOR POLYMER SCIENCE?

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In recent years, a growing sensitivity toward environmental concerns and an increasing demand for renewable and bio-inspired solutions have driven the research in materials science towards the development of more eco-friendly polymeric materials. Unfortunately, the variety and variability of these materials and their complex morphological organization makes any progress in their development susceptible to a complex process of trial and error, guided by the experience of experts, human intuition and conceptual insights. Unfortunately, such an approach has become too slow and costly for modern society. Over the past decade, we have become accustomed to an exponential growth in innovation, especially in the world of information technology. One of the reasons for such progress is undoubtedly the widespread application of artificial intelligence (AI). AI is a technology that can analyze data, synthesize new knowledge, and continue learning as it acquires and uses new information. AI provides the opportunity to find the hidden pattern between these data to tailor final products' properties and realize full benefits. It can enhance productivity and increase energy efficiency. AI can also help reduce human errors in defect detection and quality control as well as speed up the process.
Despite the growing success of AI-assisted solutions, materials scientists and engineers have not yet fully understood the benefits of accelerating research and development, predictive maintenance and process optimization. They are probably still too frightened by the idea of an excessive "artificial" computerization.
This paper will present recent experimental, computational and theoretical advances in this expanding field. Topics of particular interest include the AI-assisted discovery and design of innovative polymers, data-based methods for the design, synthesis and characterization of polymers and their composites, the structure-property-performance relationship of processed polymers, process development and optimization, and the multiscale modeling approach for polymer composites.
The goal of this contribution is to bring together researchers from a variety of backgrounds to exchange ideas, identify and address major challenges, and initiate new areas of research in this expanding field.

HYBRID FUNCTIONAL NANOCOMPOSITE STRUCTURES

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The growing interest in nanotechnology has been driven research activities to develop hybrid nanocomposite structures capable of performing multiple tasks and functions [1]. To this aim, the synthesis of multilayer nanostructures is one of the most suitable strategy to induce or to improve specific functionalities onto substrate material (i.e., nanoparticles, fibres, etc.) and it can be achieved by in situ surface modification and/or nanocoating deposition. Core/shell nanoparticles represent a specific hybrid nanostructured configuration which integrate into a single geometry two or more functions, related to both the inner core and the outer shell coating [1].

Among our recent works, the design and the synthesis of inorganic core/polymeric shell nanoparticles (~270 nm) as toughenersfor epoxy resin were carried out. A one-step modified Stöber method to obtain amino-functionalized silica core was developed along with a hyperbranched polymer shell growth onto the core surface [2]. Hence, in order to improve properties at filler-matrix interface, the bio-inspired polydopamine was recognized as suitable candidate not only for its adhesive characteristics but also for the simple formation/deposition method. The effect of these core/shell nanoparticles in the final nanocomposites have been assessed in terms of structural properties withinin the EXTREME EU project [3].

Conversely, this kind of hybrid nanoparticles are promising and versatile platforms for other different applications. Hence, future works will focus on design and develop of ad-hoc inorganic core/polymer shell nanoparticles to enhance specific functional properties useful in perspective in the field of environmental pollutants degradation.

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ABSTRACTS

Knowledge and technology transfer. Outreaching.

TECHNOLOGY TRANSFER OFFICE

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The Technology Transfer Office was created in 2005 (prot.169/05) with the aim to support the research community for all the activities related to the promotion and the protection of the research results, the support for spin-off creation, the Intellectual Property Rights management and exploitation, the building partnerships with companies and institutions public and/or private. At about 15 years from start-up has experience in the development, organization and management of Research, Development and Innovation Projects thanks to the Open Innovation Model used. Although the importance of Technology Transfer is well accepted at National Research Council, there isn't an Office dedicated in each Institute and the role and the skills of the staff TTO in IPCB is not well allocated. It would be appropriate for the TTO to work closely with its department, as well as with the CNR central government offices and the Office for International Relations. Here are a SWOT analysis emerged during the activities of TT conducted in this years [1].

SWOT ANALYSIS	
STRENGTHS • TTO in IPCB • Self-motivated, trained and dedicated staff (Project Management certificated) • Multidisciplinary backgrounds • Good relationship with researchers also of other Institutes • Strong scientific network • Growing number of research project	**WEAKNESSES** • No organisation chart in TTO/IPCB • Understaffed in TTO • Lack of an internal plan decision making • No internal periodical staff meeting • No Communication Area in IPCB • Low number of patent applications • Low exploitation of granted patents • Low number of Spin-off • No strategic plan from Central administration of CNR
OPPORTUNITIES • Sharing • Development of an internal strategic plan "who does what" • Accredited scheduling • Data usage for institutional effectiveness • Using specialized database for state of art • Using data as a compass for growth and other opportunities	**THREATS** • Lack of resources allocation • Lack of data usage for planning at different level • Lack of data usage for decision making at different level

Figure 1 SWOT ANALYSIS

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CO-DESIGN, RESEARCH, INNOVATION AND TECHNOLOGY TRANSFER FOR IMPROVING QUALITY LIFE: FROM LABS TO PATIENTS WITH NEUROMUSCULAR DISEASES

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The Unit of Lecco of the Institute of Polymers, Composites and Biomaterials (IPCB-CNR), supports the design and the implementation of NeMO Lab S.r.l. start-up. This lab, which is originated from NEMO Clinical Centres already present in 8 Italian Regions, is a multidisciplinary technological hub for the development of innovative projects in the field of neuromuscular diseases; the hub has established, through direct investments, participation in funded projects and involvement of private companies several research laboratories with the scope to bridge the market and assure that innovations arrive to the patients.
Among these labs, IPCB-CNR scientifically leads the ORTHO LAB, mainly addressed to innovation of Aids, Orthoses and Prostheses, with a specific focus on innovative materials and rapid prototyping, in order to improve the functional and aesthetic characteristics, increase comfort and readiness for use of the several biomedical devices.
ORTHO LAB, that involves also the SME Ortopedia Castagna and the Department of Design of Politecnico di Milano, is establishing a multifunctional laboratory with facilities that will be complementary with the ones located in IPCB lab in Lecco. The goal is to create a virtuous pathway to bring advantages in terms of quality of life and timing for patients and general cost-savings for the National Health Service, by incorporating the research results and innovations on materials developed by IPCB both in its labs in Lecco and the leaded ORTHO LAB.
In this fruitful context, IPCB will be the scientific partner for the development of innovative, functional and sustainable materials mainly for 3D printing e for personalising devices, and it will be further involved in the other labs cooperating with Research Centers, like IIT, Campus Biomedico. Research Centers, Clinicians Patients, Companies and Government with a focus on sustainability, makes this a great Best Case of quintuple helix approach to accelerate the transfer of research and innovation results.
The IPCB collaboration with NeMO Lab S.r.l. is ruled by an Agreement addressed to reach the following goals: 1) Developing and coordinating research and development programs of mutual interest in the field of innovative materials applied to aids, orthoses and prostheses through 3D printing techniques. 2) Encouraging knowledge sharing, patent registration and the technological transfer from research to the patients; 3) Facilitating and encouraging contacts and exchanges between researchers, collaborators, postdocs and doctoral students; 4) Developing industrial PhDs programmes.
Currently a thesis project which has brought to the preparation of a customized prototype for cervical orthosis is at patient evaluation stage. Furthermore there are many project calls that IPCB has or will submitted together with NeMO Lab, and a sharing of Students and personnel is in progress.

KNOWLEDGE TRANSFER IS A BEST PRACTICE FOR THE WHOLE SCIENTIFIC COMMUNITY

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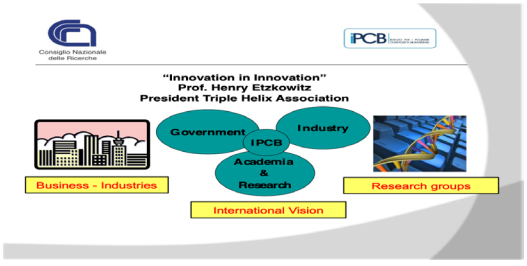
Europe, despite hosting only 7% of the world's population, boasts 20% of the world's investment in research and innovation, producing a third of all high-quality scientific publications. It is a world leader in the innovative sectors such as the chemical industry and the innovative materials used within the heath industry for health, the environment, cultural heritage conservation, renewable energy, textile engineering and regenerative medicine. It is therefore Europe's job to turn excellence into success in new imaginative markets. This is particularly true for innovations based on radically new technologies (pioneering innovations) or radically new markets (disruptive innovations). In this context, the theme of technological transfer and, more generally, the theme of the transformation of knowledge into productive value, has always been at the heart of research and innovation policies. The fully globalized dimensions of today's dynamics are increasingly pushing us to see innovation as the real determining factor on which to base the competitive capacity of an international scientific/economic system. This competitive capacity appears increasingly structurally assured by an innovation that sees scientific research as its fundamental engine, its characteristic element. The ability to produce knowledge and at the same time the ability to quickly transform that knowledge into an economic value and thus to quickly produce high-quality innovation, is the key to a country's competitive growth and success. The process of creating innovation is a precise linear sequence, ranging from scientific discovery, to experimental verification in applied science, to subsequent inventions, to imitative and diffusive processes. In this model, clear and well-defined areas of expertise are identified between basic research, applied research, technological transfer, industrial development, and consequently the areas of action of universities, public and/or private research centers, institutions, companies creating that inspirational model of the Triple Helix [1] studied around the world (figure 1).



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THE RELEVANCE OF INTERNATIONAL UNIONS FOR THE ADVANCEMENT OF SCIENCE AND SOCIETY

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After 10 years of serving Italy in IUPAC (International Union for Pure and Applied Chemistry) and in ISC (International Science Council), I am convinced that the role of International Unions is essential for Science as well as for all human activities. The explosion of web as source of information has changed completely the way in which knowledge is delivered to persons, in particular in a period like this, when the entire world faces the effect of a pandemic disease. As scientists, we have the responsibility to deliver a correct information to citizens, debating science and technology with colleagues from all the world and taking part to scientific Unions not just as spectators but as active participants. Young scientists in CNR are prompted to candidate themselves for the Unions through the National Representative (CNR), starting as observers, then submitting projects [1,2] or taking part in projects proposed by other scientists [3]. This is essential for a wise and equilibrated growth of their human and scientific personality.

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ADVANCED MATERIALS. METHODOLOGY FOR THE VALORIZATION OF RESEARCH RESULTS

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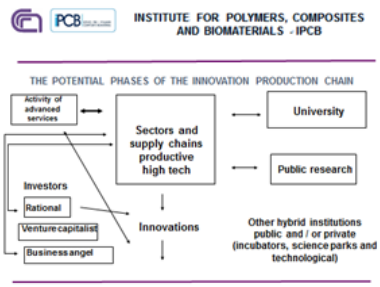
The need to promote the transfer of technological innovation from the world of research to that of industry has become increasingly pressing, especially in the last fifteen years, in which the globalization of markets has been affirming. Therefore, for small and medium-sized enterprises (SMEs), which in Italy make up about 70% of the production of goods and services, and which generally do not have valid research facilities, the acquisition of new technologies is of vital importance in order to to be able to achieve or maintain a competitive position on the national and international market.
The great technological changes we are experiencing have often originated from the use of results achieved in academic laboratories, enhanced and developed in a context of venture capital investments, which have proved to be effective tools for the development of the economy in many countries. Western countries (USA, Great Britain, Holland, Israel), especially in those high-tech sectors, such as information technology, telecommunications, biotechnologies, medicine, new materials.
The IPCB operates in the field of innovation and technology transfer with priority of using the laboratories for industrial research, prototype development and services related to the direct and / or indirect use of the scientific instrumentation supplied to the laboratories.



The network of collaborations in the scientific, technological and economic fields allows the Institute to propose itself as a dynamic interface between the supply of technology (scientific research system) and the demand for technology (business system), and to provide a series of services useful for a complete realization of the transfer of technology in the different phases in which this takes place.
However, innovation and technology transfer are processes that may not be activated, although in the presence of relevant inventions or important possible repercussions of scientific research results. The realization of a technological innovation therefore goes beyond the genius of an idea, often because the daily activity in a company takes time and resources away from the study of innovative technological solutions. This strategic choice of the Institute to transfer the research results obtained has only one objective: to compete in innovation, to choose, with rigorous criteria, the fields in which it is possible to excel, to focus the objective of facilitating a concentration of interventions and resources that aims to enhance the strengths of our production system on the international market.
The intervention is aimed at carrying out specific projects based on defined criteria for evaluating concrete results, so as to always have a clear vision between invested resources and results.
This strategy must take into account the competitive pressures weighing on Europe not only by the United States, which invest about twice as much in scientific research, but also by other emerging countries that have skipped the traditional phases of economic development (agriculture, industry heavy, high-tech industry) by focusing on innovation.
Investments in research; and state aid, must arrive at a new definition that overcomes the differentiations now existing between basic research, industrial research and precompetitive research.
It is a difficult path, but when the synergy between the world of research, the world of production and local authorities is achieved, great results are achieved which in any case pass through:
the creation of public and private partnerships in the area of high technology sectors;
promoting the transfer of innovation between research and businesses and the creation of efficient networks for technological dissemination; credit and venture capital facilitation for innovative SMEs, young businesses and start-ups; the development of risk capital / venture capital also through greater complementarity between the EIB (European Investment Bank) and EIF (European Investment EIF (European Investment Fund) and national initiatives.

A VIRTUOUS EXAMPLE OF TECHNOLOGY TRANSFER FROM A PUBLIC LABORATORY TO AN INNOVATIVE SMALL COMPANY

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The interaction between public research institutions and small companies generally arises from the need of the productive sector to develop new technologies or new products. Often, small companies are very innovative and creative but lacks infrastructure, scientific knowledge and modern technology laboratories. This case study will describe all the steps necessary to convert a good idea into an international patent. The Gamastech is in the top ten list of the companies that produce and commercialize elastomeric infusion pumps. The elastomeric pumps are disposable devices that exploit the swelling principle of an elastomeric component to put the fluid contained inside under pressure. Typically, commercial elastomeric pumps comprise, a reservoir made of elastomeric material in which the fluid to be administered is housed, and an external shell that protect it. Current commercial products have some disadvantages, first of all the elastomeric reservoir made in silicone are not compatible with a long lasting contact with some drug requested from the market; secondly, the external shell is often not ergonomic and looks like a plastic bottle with a transparent balloon inside. The main idea of the company was to solve these two problems by totally changing both the used material and the design [1].

Figure 1 E.pump CNR Gamastech

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