UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

Two Phd fellowships funded by the Department of Materials Science on

Materials for Energy

The student can choose for his Phd thesis any of the experimental or theoretical activities carried out at the Department of Materials Science on the study of materials for solar cells, solid state batteries and supercapacitors, fuel cells, electrochromic devices, hydrogen production and storage.

These activities are described at the webpage
https://www.mater.unimib.it/en/research/research-areas
within the research areas of "Environment and energy materials", "Organic and polymeric materials" and "Microelectronics and photonic materials".

The Consortium Corimav in collaboration with Pirelli Tyre

finances 3 fellowships for the

Phd Program in Materials Science and Nanotechnology

on the projects

1) Novel fillers for enhancing thermal conductivity of rubber nanocomposites

2) New functionalization approaches of lignocellulosic feedstock to obtain reinforcing fillers tailored to rubber compounds

3) New biotechnological approaches to the modification of natural micro- and nano- fibers to obtain efficient reinforcing fillers for rubber compounds

The project will be carried out both in the University labs of the Department of Materials Science and in the laboratories of Pirelli Tyre under the joint supervision of University and company tutors.

For information please contact

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- Dr. Raffaella Donetti, PIRELLI TYRE (raffaella.donetti@pirelli.com).

A description of the three projects is given below.

Novel fillers for enhancing thermal conductivity of rubber nanocomposites

University Supervisor: Prof. Massimiliano D'Arienzo (massimiliano.darienzo@unimib.it)

Rubber nanocomposites generally exhibit poor thermal conductivity, which has been partially enhanced by the addition of thermally conductive fillers, i.e. graphite, carbon black, carbon fibers, ceramic or metal particles. High filler loadings are typically necessary to achieve this target; however, this dramatically alters the mechanical behavior and the cross-linking density of the final materials. Further, the filler systems currently employed are not able to fulfill the key requirements of high thermal conductivity and remarkable performances, simultaneously.
In this context, the PhD research activity aims at design novel fillers suitable for developing rubber nanocomposites with high thermal conductivity and satisfactory mechanical performances. A survey of different conductive nanofillers will be carried out, by investigating in depth the correlations between nanoparticles structure, morphology, dispersion and distribution in the polymer matrix, and final composites properties. The best formulations will be selected and possibly up-scaled in order to provide real technological applications.

New functionalization approaches of lignocellulosic feedstock to obtain new reinforcing fillers tailored to rubber compounds

University Supervisor: Dr.Luca Zoia (luca.zoia@unimib.it)

Lignocellulosic materials are the most abundant class of renewable materials available on earth, with a long history of industrial use, the most recent development being the use as substrates of "biorefinery" approaches leading to valuable chemicals, ultimately aiming to substitute oil-derived materials.
Attempts to use lignocellulosic materials, including by-products of pulp&paper industry as lignin, for the reinforcement of rubber compounds were not very successful up to now, mainly because of the scarce compatibility of the hydrophilic lignocellulosic materials with the hydrophobic dienic polymers constituting the backbone of rubber compounds.
The target of this research is to investigate innovative ways to obtain surface-modified lignocellulosic materials capable to be efficiently dispersed in rubber compounds by thermomechanical means and to effectively reinforce such compounds. Preferably, the process of surface modification should follow a "green chemistry" approach. The activity will include laboratory synthetic work to functionalize selected lignocellulosic materials, compounding activity to formulate compounds with such materials and laboratory characterization work of the prepared modified lignocellulosic materials and of the corresponding compounds.

New biotechnological approaches to the modification of natural micro- and nano-fibers to obtain efficient reinforcing fillers for rubber compounds

University Supervisor: Prof. Paola Branduardi (paola.branduardi@unimib.it)

Biosourced micro- and nano-fibers have been investigated as alternative reinforcing fillers in polymer composites, with the aim of reducing their ecological impact related to raw materials utilization. In this context, a particularly attractive material is nanocrystalline cellulose (NCC) for its nano-size and high aspect ratio particle. However, few studies are available on rubber reinforcement with natural micro- and nano-fibers, possibly due to the lack of a dedicated surface modification strategy able to efficiently bridge the natural fibers with the complex environment of the rubber compound.

Aim of this research shall be to fill this gap by elaborating an energy-efficient, ecological and scalable bio-modification of micro- and nano-fibers to enhance their dispersibility in rubber compounds and to optimize their interaction with the polymer in the final compound. Activity will include the development of a biotechnological approach to the preparation and/or surface modification of micro- and nano-fibers, compounding activity to formulate compounds with such materials and laboratory characterization work of the prepared fibers and of the corresponding compounds.

Phd fellowship funded by ENI Spa

Developing of new fluorophenazine and fluoroacridine based molecular acceptors for tandem organic photovoltaic cells

University Supervisor: Prof. A. Papagni (antonio.papagni@unimib.it)

The new generation of heterojunction photovoltaic cells based on donor-acceptor polymers with new acceptors alternative to fullerene-based acceptors (PCBM) allows efficiency over 10%. The research project will explore new molecular acceptors different from those currently used, easy to prepare at grams scale from commercially available starting materials and showing electronic properties (HOMO and LUMO levels) and thermal and photochemical stability similar or better than those of fullerene acceptors. From this point of view, fluorinated electron-poor heteroaromatic systems are interesting. Indeed, fluorinated phenazines and acridine show interesting electronic properties with HOMO and LUMO levels comparable with fullerene derivatives and potentially exploitable as n-type semiconductors and acceptors in organic photovoltaic cells. As an example, the octafluorophenazine shows HOMO and LUMO levels of -7 eV and -4.12 eV, respectively, comparable to fullerene (-6.2 and -4.5 eV). In addition, the fluorination of aromatic and heteroaromatic systems normally increases both the thermal and oxidation stability. Starting from commercially available fluorinated materials, the research project, to be developed during the PhD program, is addressed to the synthesis of new and selected phenazines and acridine to employ as starting materials in metal mediated cross-coupling reaction with suitable counterparts in order to optimize their electronic properties, n-type semiconducting behaviors and solubility. The activation of phenazine C-H bonds by cross-coupling reaction will be considered together with the other possible protocols including Suzuki, Stille and Ulmann-like cross-coupling reaction.

Phd fellowship funded by RSE

(Ricerca Sistema Energetico)

Development of earth abundant chalcogenide thin films for photovoltaic applications

University Supervisor: Prof. Simona Binetti (simona.binetti@unimib.it)

Photovoltaic (PV) is the most promising renewable energy source that can meet the global energy demand while producing low emissions of CO_2 in the atmosphere. To become a major energy source, module costs should be reduced significantly and abundant materials should be employed. In particular, to reduce the module cost, thin film solar cells are a viable option due to their lower material usage, implementation on flexible substrates and inexpensive manufacturing implementation/design(tandem). These aspects are fundamental to assure the development of a large scale built-in PV production. However, current materials for thin film (TF) solar cells (e.g CdTe and CIGS) suffer from concerns over low resource availability (e.g. Te and In) and toxicity (e.g. Cd) respectively, and are therefore limited to sub-terawatts deployment.
On this basis, attention will be devoted to alternative materials based on Earth-abundant metals, like chalcogenides belonging to the family $Cu_2M(II)M(IV)S_4$ (with M(II) = Mn, Fe, Co, Ni, Cd, Ba; M(IV) = Si, Ge, Sn). This experimental activity aims to investigate and prove the breakthrough offered by $Cu_2M(II)M(IV)S_4$ chalcogenides as PV absorbing materials.
In this regard, RSE (Ricerca Sistema Energetico) is collaborating with researchers of the Materials Science Department on the deposition and characterization of Cu_2MnSnS_4 (CMTS) and Cu_2FeSnS_4 (CFTS) TFs. A two-step approach (sputtering + sulfurization) has been identified as a deposition technique to offer a good trade-off between the control of deposition parameters and in-plane scalability. This activity aims to fill the gap on the chemical-physical properties of these new compounds (fundamental research), offering, at the same time, useful PV data for immediate industrial scale-up (applicative research).
To optimize the deposition set-up for each material, the main properties of these TFs will be studied by several experimental techniques and will be correlated with PV performances. In accordance with the extended literature on the more known chalcogenides (e.g. CIGS, CZTS), the effects of innovative post-deposition treatments and new buffer layers will be also tested to improve the final solar efficiency. A more complete view on the potentialities of these chalcogenides get also through the optimization of deposition parameters as a function of substrates; for example, transparent supports are fundamental to test their potentiality as a top layer of high efficiency Si based tandem devices.

Phd fellowship funded by Istituto Italiano di Tecnologia (IIT)

Preparation of new keratin-based bioplastics

Supervisor: Dr. Giovanni Perotto – Istituto Italiano di Tecnologia, Genova (GE), giovanni.perotto@iit.it

University Tutor: Prof. Roberto Simonutti

New bio-sourced and biodegradable materials that can replace plastics are needed to reduce the plastic pollution of the environment. For a circular economic process, the conversion of proteins in bioplastics can be very advantageous because proteins are a renewable source of materials that are also completely biodegradable and compostable. In the framework of the PROTHEIFORM project, founded by Fondazione Cariplo, new protein bioplastic using keratin as a source of raw materials will be developed. In this PhD activity, a hybrid nanotechnological and chemical approach will be employed, with the aim of overcoming the performance limits of keratins and to facilitate their processing. The focus of the activity will be the development of the new processing technologies and material technologies needed to successfully exploit keratins, extracted from wool or feathers, in materials that will have useful properties for packaging. The research activities will be performed at the Italian Institute of Technology, located in Genova.

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Phd fellowship funded by Regione Lombardia in collaboration with ENEA

Metal additive manufacturing (3D printing) based on Digital Light Processing

University Supervisor: dr. Carlo Antonini (carlo.antonini@unimib.it)

Additive manufacturing technology (also known as 3D printing) has opened unprecedented opportunities to manufacture and customize objects with complex geometry with minimal waste. One of the most interesting fields of application is metallurgy, due to rapid prototyping and the possibility to overcome limitations of classical "subtractive" techniques. In this project, the PhD candidate will work on an innovative DLP (digital light processing) technique for metal powders. The system is based on light-curing resins suitably loaded with metal powders (steel, Inconel, etc.), for printing complex objects. The technology enables to print a resin loaded with metallic powder. Through photopolymerization, the resin polymerizes and hardens to construct layer-upon-layer objects with a complex geometry. Finally, the object can be inserted into a furnace, for resin removal and metal sintering. The advantage of DLP, compared to SLS (selective laser melting) technique, is the decoupling of shaping, from material properties tuning through the sintering process. During the research project, the PhD will first investigate and subsequently develop the entire printing process (design, printing, sintering), using custom powders and resins, with the goal of advancing the DLP based metal 3D printing.

The project activities will be based mainly in two laboratories:

- “Surface Engineering and Fluid Interfaces”, led by Dr. Carlo Antonini, a Rita Levi Montalcini Fellow at the Department of Materials Science, University of Milano-Bicocca.
- Enea Laboratory ““Materiali e processi industriali sostenibili 4.0 - MaPIS4.0” (Sustainable industrial materials and processes) at the Kilometro Rosso innovation district, in Bergamo.

The project will be characterized by strict collaboration with the Enea Laboratory “TEcnologie dei Materiali” in Faenza (SSPT-PROMAS-TEMAF). Collaboration with the startup ApiTech, a consulting company supporting innovation in SMEs, is also envisioned to promote the use of the technology within the metal district in the area of Lecco.