**Composite materials based on self-assembly strategies and FDM techniques: versatile tools to realize innovative hybrid materials for energetic, environmental and biomedical applications**

Massimiliano Gaeta

*Dipartimento di Scienze Chimiche dell’Università degli Studi di Catania.*

*massimiliano.gaeta@unict.it*

Scientists have been fascinated by the challenging syntheses of nature-inspired materials. In this regard, over the last decades, a fascinating development in material science is the construction of engineered nanomaterials by self-assembly of small molecular building blocks [1]. Among them, porphyrinoid molecules can be employed as interesting molecular synthons. However, these molecules hide manifold trouble; even if the peripheral charged groups make these macrocycles water-soluble, nevertheless, porphyrins remain mainly hydrophobic molecules, preserving the well-known tendency to aggregate. This “dichotomy” is worthy of special attention because (i) it plays a central role in the non-covalent syntheses and, interestingly, (ii) in conjunction with inorganic -or polymeric- structures to arrange quite complex hybrid composite materials for energetic and environmental applications.

Therefore, in this keynote, I intend to describe the guiding principles about that and some interesting cases of engineered composite materials based on the self-assembly approach which we have realized [2-4]. In addition, new bio-composite suitable for Fused Deposition Modelling (FDM) methods will be also discussed [5-6].

For instance, from an energetic point of view, polyaromatic membranes, such as sulphonated polyetheretherketone (sPEEK), can be considered as a low-cost alternative to PFSA (i.e., NafionTM) based membranes for portable fuel cell applications. However, sPEEK membranes do not own sufficient performance to tackle the NafionTM [2].

Thus, in order to improve the characteristics of such sPEEK membranes, we succeed in synthesizing new composite membranes by adding meso-tetrakis(4-sulfonatophenyl) porphyrin, TPPS [2]. In particular, we obtained hybrid TPPS/sPEEK materials with peculiar behavior in terms of good proton conductivity, chemical stability, and fuel cells performance. To get better insight into the specific interaction responsible for the improved quality of the materials, we have conducted a detailed spectroscopic investigation and physical-chemical characterizations of the composite membranes.

Furthermore, the electrochemical accelerated degradation test on PEFC single cell, simulating the typical operative conditions for portable applications, highlighted the improved stability of the composite membrane compared to that of the pristine sPEEK [2].

From another point of view, antibiotics represent essential drugs to contrast the insurgence of bacterial infections in humans and animals. However, their overuse can implicate a risk of water pollution and related antimicrobial resistance. As a consequence, innovative strategies for successfully removing antibiotic contaminants have to be advanced to protect human health. In this respect, a growing interest is arising in the degradation of antibiotics by heterogeneous photocatalysis using suspended TiO2 nanoparticles. With the attempt to increase the photocatalytic efficiency of TiO2, we decided to functionalize it with porphyrins [3]. Thus, we tested the photocatalytic efficiency of our hybrid organic/inorganic porphyrin@TiO2 materials to degrade, in water, oxolinic acid (OXA) and oxytetracycline (OTC), two of the most extensively used antibiotics in aquaculture [3]. Accordingly, our porphyrin functionalized TiO2 nanomaterials can represent an innovative tool for depuration of water and wastewater by OTC contamination, aimed to improve the reduction of bacterial resistance to antibiotics and, finally, to reduce the health outcomes related to the inefficacy of current pharmacological therapies against these diseases [3].

Concerning the safe water matter, another challenging problem of public health is the pollution due to dye-contaminants. Inspired by adhesive proteins secreted by mussels for attachment to wet surfaces, melanin-like materials result in efficient adsorbents for entrapping organic water-pollutants via synergic non-covalent interactions [4]. So, in order to enhance the adsorption performance, the strategy is to form melanin-coated nanomaterials having a higher specific surface area. Consequently, we employed a synthetic porphyrin–spermine derivative, namely H2TCPPspm4, to realize a new functionalized DOPA-melanin film, self-assembled film onto a commercial glass substrate, through a viable synthesis in aqueous medium at room temperature [4]. Our H2TCPPspm4/L-DOPA-melanin@glass device displayed an increased adsorption capacity against aqueous solutions of methylene blue dye. Furthermore, the possibility to reuse our prototype for continuous adsorption/desorption cycles enable us to have a smart device for water remediation technology on a larger scale [4].

Finally, from a different perspective, by exploiting the Fused Deposition Modelling (FDM) methods, we have recently realized novel bio-composites useful for biomedical prototypes [5,6]. In fact, FDM techniques have promoted the extension of 3D printing technologies to new applications ranging from the biomedical, aerospace, and submarine fields, to some specific applications in manufacturing and civil fields. The expansion of the fields of application, generally, entails considering peculiar characteristics, such as complex geometries or requirements as low density. Furthermore, the breathability, the pleasantness to the touch, aesthetic appearance and a strong visual identity, that can be achieved by means of 3D printing, are especially requested for some applications such as biomedical. Thus, the development of purpose-dedicated filaments can be considered a key factor to successfully meet all these requirements.

In this respect, we fabricated and analyzed five new thermoplastic materials with fillers [5,6]: they are organic bio-plastic compounds made of polylactic acid (PLA) and organic by-products.

We preliminarily studied the main properties of these materials with a major emphasis on their strength, lightweight, and surface finish. In addition, experimental tests were performed in order to assess the suitability for FDM printing. The interesting final properties make these materials suitable for biomedical and, indeed, we reported the production of two different biomedical devices with one of the analyzed thermoplastic materials. In addition, such innovative bio-composite materials allow reducing the cost of environmental impact as well as the production management costs.

**References**

[1] J.A.A.W. Elemans, R. van Hameren, R.J.M. Nolte, A.E. Rowan, Adv. Mater. 18 (2006) 1251-1266; C.J. Medforth Z. Wang, K.E. Martin, Y. Song, J.L. Jacobsenc, J.A. Shelnutt, Chem. Commun. (2009) 7261-7277.

[2] A. Carbone, M. Gaeta, A. Romeo, G. Portale, R. Pedicini, I. Gatto, M.A. Castriciano, ACS Appl. Energy Mater. 1 (2018) 1664-1673.

[3] M. Gaeta, G. Sanfilippo, A. Fraix, G. Sortino, M. Barcellona, G. Oliveri Conti, M.E. Fragalà, M. Ferrante, R Purrello, A. D’Urso, Int. J. Mol. Sci. 21 (2020) 3775.

[4] M. Gaeta, M. Barcellona, R. Purrello, M.E. Fragalà, A. D’Urso, Chemical Engineering Journal 433 (2022) 133262.

[5] M. Calì, G. Pascoletti, M. Gaeta, G. Milazzo, R. Ambu, Procedia Manufacturing 51 (2020) 698-703.

[6] M. Calì, G. Pascoletti, M. Gaeta, G. Milazzo, R. Ambu, Appl. Sci. 10 (2020) 5852.