PhD position at LOF (Solvay/CNRS/University of Bordeaux)

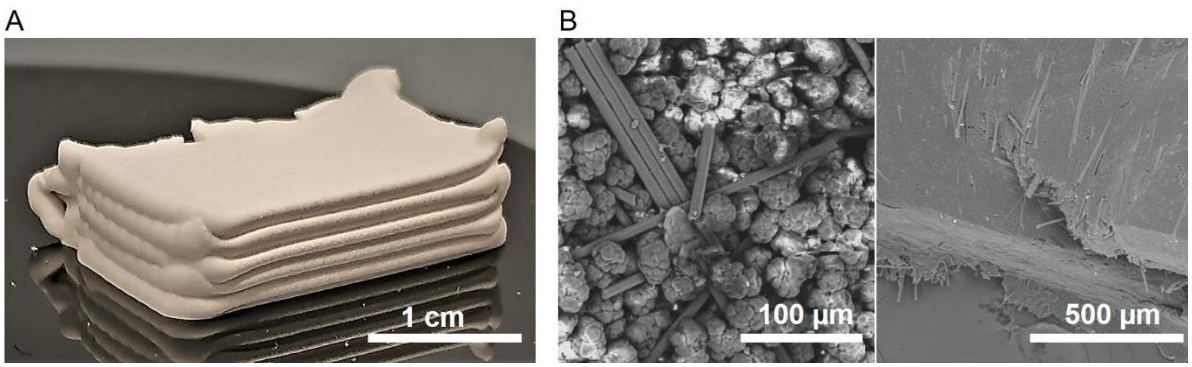
Funded by Solvay (CIFRE) - Starting date: October/November

PhD subject:

Shaping of polymer composites architectured by soft 3D printing

Description:

To give composite materials new properties, but determined a priori (metamaterials approach), it is crucial to adopt a multi-scale approach where the architecture of the material (composition, structural) must be mastered at all scales, from the nanometer to the decimeter. In the context of composite polymer materials, controlling the composition and the local orientation of the functional fillers is then a major parameter in the process of accessing new properties that the conventional processes for shaping composites do not offer.



Principle of direct gel printing: aqueous formulations of thermoplastic powders, fillers and binder form a matrix with specific rheological properties (yield stress fluid) that can be printed in multilayers. (A) Deposit after drying of 5 layers of a dispersion of polymer (confidential) powder (10 µm grains, approximately 2 mm thick layers). (B) Example of formulation of PA12 powder and carbon fibers before and after thermal annealing.

A promising process developed at LOF, called *soft 3D printing*, is a gel printing technique that takes advantage of the specific rheological properties of formulations of concentrated suspensions of thermoplastic particles and fillers to print aqueous-based formulations having a yield stress of flow (for self-supporting systems, see figure above). The printed deposits are subsequently dried and then annealed in order to form a massive polymer composite structure but architecturally tailored.

Such a process, which incorporates know-how in microfluidics, automation, and physical chemistry, makes it possible to continuously control the composition of the printed suspension, and therefore the composition of the final composite and its microstructure thanks to the flow / microstructure coupling. In particular, potentially anisotropic charges included in the interstitial fluid carrying the thermoplastic powder can be oriented locally by the flow and their concentration controlled by a specific microfluidic injection process. It then becomes possible to design new material architectures and quickly test their properties. Thus, the effects of parameters such as the nature of the charges, their local density, their orientation, their distribution in space on a final property of the composite become fully explicable.

The goal of the pHD is to demonstrate the potential of this method for the production of "proof of concept" materials, not necessarily functional parts, which embed new, custom-designed functionalities. In particular, we aim to modify the thermal and electrical conductive properties by engineering the distribution and orientation of charges, conductors of heat or electricity. The work is based on 3 axes:

1. **Formulation and characterization of the suspensions:** the powders and fillers will be formulated in aqueous bases, with the potential presence of a binder, and fundamental questions of surface chemistry (on powders and fillers) arise to reconcile the good dispersibility of the medium and good load / thermoplastic compatibility after annealing. On the other hand, the rheological characterization of the suspensions is a prerequisite for controlling the impression which requires specific rheological values of the suspensions (yield stress, dilatancy, fluidity, etc.) [1].
2. **Printing:** an axis which itself stems from i) a good control of the automation of the direct writing of a gel and ii) a reflection on the design of architectured structures to obtain the desirable macroscopic properties [2]. This could be, for example, layer-by-layer printing of conductive / insulating materials in order to build an anisotropic thermoplastic, or even establishing localized charge or charge orientation gradients to highlight unique properties of thermal or electric conduction.
3. **Thermal sintering of materials:** given their nature, polymers have specific structural properties and the kinetic heating profile to be implemented to ensure the sintering of the powder without degrading the structure or oxidizing the polymer is to be defined according to the targeted polymer. This step is important to verify that the transition from a granular medium to a continuous medium takes place without negative impact on the final properties. In other words, only the loads and the architecture of the composite are responsible for the measured properties.

The characterization of printed materials (micro and macro-structure, mechanics, electrical / thermal properties, etc.) will iterate between the design and shaping stages in order to achieve and optimize the targeted properties.

[1] M'Barki, A.; Bocquet, L.; Stevenson, A. Linking Rheology and Printability for Dense and Strong Ceramics by Direct Ink Writing. **Sci. Rep.** 2017, 7 (1), 6017.
[2] Raney, J. R.; Lewis, J. A. Printing Mesoscale Architectures. **MRS Bull**. 2015, 40 (11), 943–950.

Profile of the candidate:

We are seeking a motivated candidate with a MSc degree, or equivalent, in physical chemistry or materials sciences who is strongly attracted by experimental work; notions of rheology and of programming in Python or in Matlab would be desirable. The selected PhD student will work at the Laboratoire du Futur (UMR LOF Solvay-CNRS-University of Bordeaux) in close collaboration with Solvay's teams. If you are interested in applying for this position, please send your CV and a brief overview of your motivations in this PhD project. All applications will be considered.

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