UNDERSTANDING THE PHOTOCHEMICAL MECHANISMS INVOLVED DURING AND AFTER 3D PRINTING BY VAT PHOTOPOLYMERIZATION

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The recent developments of easy-to-use 3D printers has enabled the 3D printing sector to move away from a niche market towards mass-market or very high value-added applications. Among the different additive manufacturing (AM) processes, vat photopolymerization (stereolithography (SLA), digital light processing (DLP)…) related to a spatially controlled photopolymerization is recognized to give access to printed objects with the highest resolution and surface quality. An increasing number of patents and publications demonstrates the interest of this field. Among the 454 articles published since 1985 on the topics "photopolymer and 3D printing", 443 have been published the last 10 years.

Significant progress has been achieved these last years in terms of resolution, shrinkage limitation, compatibility of the binder with fillers and enhanced printing process. These advances have allowed 3D printing to be used in semi-industrial production such as for the manufacturing of objects by the lost wax method in dentistry, jewelry, etc. However, challenges are still remaining to establish AM as a large scale production tool. They are mostly related to the performances of the materials during use. Understanding and controlling the thermomechanical properties, shrinkage, toughness, porosity, safety, etc… becomes of high importance and recent studies have addressed some of these topics. Surprisingly, the long-term stability of the currently build materials remains understudied. Yet, the durability of polymeric materials is becoming an essential aspect in the development of new objects. It will depend on the duration and the extent of interaction with the environment. Solar radiation (especially 300–400 nm) is one of the major factors contributing to polymer degradation. Unlike thermosets obtained by a thermal process, photopolymers contain chromophoric species resulting from the presence of residual photoinitiator or corresponding photoproducts. The photostability of the photopolymers will be much more affected by solar radiation as it can induce further photoinitiator decomposition and/or other side photoreactions. In view of the future growing applications of materials made by 3D printing, the issue of the long-term stability should receive a special attention, and the comprehension of the photodegradation mechanisms will be crucial for allowing stabilization strategies in order to achieve durable materials. This topic appears to be one of the recent concern of the Photopolymer Additive Manufacturing Alliance.

This project is part of the 3Durable project, founded by ANR, which benefits from the complementary expertise of three recognized academic partners in the fields of 1) macromolecular photochemistry and photopolymerization processes (LPIM, Université de Haute-Alsace), 2) organic photochemistry (IPCMS, Université de Strasbourg), and 3) photochemical ageing of polymers (ICCF, Université Clermont Auvergne).

The PhD candidate will have to develop fundamental knowledge that combines:

- A mechanistic study of photoinitiating systems (PIS) frequently used in 3D printing, the full identification of the photochemical mechanisms involved during the irradiation of the photoinitiator as well as the photoproducts.

- A precise in-depth characterization of the monomer conversion of 3D printed samples. Particular attention will be paid to assess its evolution during the different steps of the fabrication process (printing and post-photocuring). The results will be combined to the consumption profile of the PIS within the sample thickness to predict the presence of possible extractables (monomers, residual PIS, photo-products).

In addition, strong interaction is expected to take place with other partners through:

- The preparation of samples for photoageing (in ICCF) and discussion on the results.

- The collaboration with ICPMS in order to identify and analyze the photoproducts created during irradiation.

This study will combine different aspects:

- Photochemical approach through fluorescence (steady-state and time-resolved), laser flash photolysis, time-resoved ESR (CIDEP)

- Photopolymerization process analysis through Real-Time FTIR and confocal Raman microscopy

- Photoproducts analysis through HPLC, LC-MS and NMR.

Working environment: The doctoral student will be enrolled in the Doctoral School of Chemical Sciences at the University of Mulhouse (ED222).

Application process: We are looking for a candidate with a master's degree in chemical sciences. Knowledge in photochemistry, photopolymerization and polymer science is of interest. Written and oral communication skills, organizational skills and an interest in taking an active part in the day-to-day life of the laboratories are also expected. The candidate should have a team spirit and an interest in conducting research with colleagues from other scientific and cultural backgrounds. The candidate will acquire expertise in conducting research projects centered on polymer science through his/her thesis topic, but also through training courses, seminars and the use of electronic resources.

The candidate must provide a letter of motivation, a detailed CV including a list of grades and the contact details of one (or two) reference(s) to xavier.allonas@uha.fr or celine.croutxe-barghorn@uha.fr