Post-doctoral project :
Biosourced epoxy foams for thermal and elasto-acoustic insulation

Institut de Chimie et des Matériaux Paris Est (ICMPE) - UMR 7582 CNRS-UPEC Laboratoire Modélisation et Simulation Multi-Échelle (MSME) - UMR 8208 CNRS-UGE Laboratoire Navier - UMR 8205 CNRS-ENPC-UGE		
Co-responsible ICMPE: Agustín Ríos de Anda agustin.rios-de-anda@u-pec.fr	**Co-responsibles MSME:** Fabrice Detrez, Camille Perrot fabrice.detrez@univ-eiffel.fr, camille.perrot@ univ-eiffel.fr	**Co-responsibles Navier:** Sébastien Brisard, Michel Bornert sebastien.brisard@univ-eiffel.fr michel.bornert@enpc.fr

Context

Polyurethane-based foams have been largely developed and studied for thermal and acoustic insulation for buildings, automotive, transport and aerospace applications [1,2]. In the past several years there has been a great interest for developing alternatives such as porous polyethylene or polypropylene in which an external porogeneous agent (*i.e.* isopropanol or supercritical CO_2) is introduced during their processing. This approach has also been considered for thermoset polymers such as epoxy resins, nevertheless it has several drawbacks such as the control of the resin's hardening and the obtaining of homogeneous materials [6,7]. Thus, having the porogeneus agent already in the starting formulation can be a solution to overcome these issues for fully biosourced epoxy resins. A preliminary study was conducted by chemically attaching CO_2 into the monomers [8-10]. This was done by using biosourced amines developed at ICMPE [11] which are able to "trap" CO_2 via a chemical reaction undertaken between 25 and 40°C, and yielding carbamate functions as shown in Reaction 1 of Figure 1.

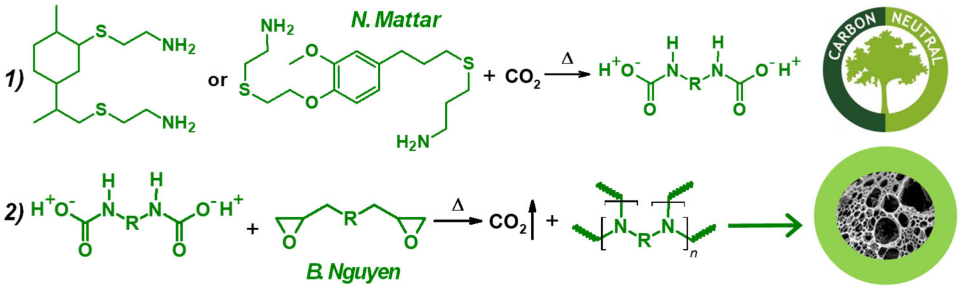

Figure 1: Chemical reactions ultimately yielding porous époxy-amine materials.

These carbamates are formulated with biosourced epoxy monomers [12]. The formulations are heated up between 80 to 150°C so as to "liberate" the trapped CO_2 within the carbamates. At the same time, the reformed amines harden the epoxy monomers as shown in Reaction 2 of Figure 1. The liberation of CO2 and the resin's hardening occurs at the same time, which allows CO_2 to act as a porogeneous in situ agent [8-10]. Preliminary investigations on such materials showed that the porosity was of 30% with a pore size distribution between 250 and 500 µm. This relatively low porosity is explained by the latent hardening of the considered biosourced epoxy-amine formulations, leading to a loss of CO2 which does not contribute to the material's foaming. These obtained materials could be considered for aerospace applications [10] but their low porosity does not allow them to be considered for building and automotive applications.

To overcome this issue, mineral porous agents such as potassium carbonate and sodium bicarbonate (*i.e.* K_2CO_3 and $NaHCO_3$ respectively) have been added to the aforementioned formulations. These porogeneous agents are a good renewable alternative to further increase the material's porosity. Moreover, the materials processing can be easily transposed onto a pilot scale, which can be of interest for industrial applications. The latest trials considering these mineral agents have shown that it was possible to obtain thermoset resins with a porosity of 70 to 85% with a pore size distribution of 50 and 500 µm. Two internships (bachelors and masters interns) allowed to optimize the hardening and foaming processing for these materials (*i.e.* 24h à 100°C). These internships also lead to conclude that sodium bicarbonate exhibited better foaming properties than potassium carbonate. By varying the amount of mineral agent (between 10 and 60 parts per hundred resin), foams of varying porosity were thus obtained (0.70 – 0.85).

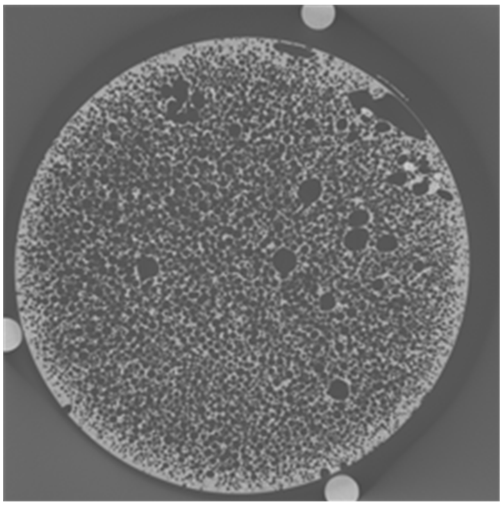

Figure 2: X-ray micro-computed tomography image illustrating the porous structure of the biosourced epoxy-amine foam under development (samples of 40 mm in diameter).

These previous studies resulted in a reproducible manufacturing process of biosourced epoxy foams. The present post-doc will be focused on the characterization of the resulting material (mechanical, acoustic and thermal macroscopic properties), in a two step process: (1) analysis of the microstructure by X-ray microtomography and (2) numerical evaluation of the homogenized properties. Since the smallest pores are barely resolved (see Figure 2 that shows a first microtomography image of one of the already generated biosourced epoxy-amine foam samples), step (1) in itself is a scientific challenge. Indeed, owing to their high specific surface area, it is anticipated that these materials will be extremely sensitive to the so-called "partial volume effect" by which a heterogeneous voxel [e.g. crossed by interface(s)] is assigned a uniform gray level after reconstruction.

Indeed, in a traditional use, microtomography images are somehow non-precise with regard to the exact position of the interface between the solid and fluid phases of the porous medium, this is termed the "partial volume" effect (a voxel of the reconstruction is assigned a uniform gray color level, even though the corresponding zone may be heterogeneous at the sub-voxel level). Given their high specific surface area, it is anticipated that these foam microstructure images may be affected by this effect.

Objectives

The objectives of this project is to link the foaming process, the associated microstructural morphology, and the mechanical, acoustic, and thermal properties of this novel class of bio-sourced foams [13-16] in order to propose a new eco-responsible material/processing approach for insulating functional applications.

Scientific challenges and novelty

Now that the pertinence of using mineral foaming agents to obtain bio-sourced epoxy-amine foams has been demonstrated, we need to face the following two challenges:

- Develop a numerical method taking into account the partial volume effect, either at the image reconstruction technique itself, or during the post-processing stage of the reconstructed images.
- Establish structure-property relationships for these foams (mechanical, acoustic, thermal) from the experimental characterization of their microstructures (pore size and spatial distributions, inter-connection sizes, connectivity).

Scientific program

The project follows a multiscale approach aiming to develop relationships between the manufacturing process, the resulting microstructures, and the macroscopic functional properties. Based on some preliminary work where biosourced foamed materials have been obtained, the main tasks of the current project will be developed during 3 *work packages* (**WP**):

WP1: Analysis of the obtained microstructures by X-ray tomography (lab and synchrotron) and methodological developments to overcome the current limitations related to the partial volume effect. Besides simple mixing rules (possibly followed by a phase-field spatial regularization) that relate the gray level of the reconstructed voxels to the volume fraction of the heterogeneous voxel constituents, techniques that account for partial volume effects *during* reconstruction (rather than *after* reconstruction) will be explored.

WP2: Experimental characterization of the macroscopic properties: geometrical (specific surface, porosity); mechanical (compression, DMTA); elasto-acoustic (porosimetry, permeability, impedance tube with three microphones, resonating mass-spring, Oberst beam); and thermal (DSC, TGA, thermal conductivity).

WP3 : Multiscale modeling so as to estimate the mechanical, elasto-acoustic, and thermal properties by solving boundary value problems at the Representative Volume Element (RVE) scale through numerical methods, such as the finite element discretization for the less time-consuming problems, and the FFT, LBM, or pore-network methods for larger domain sizes. These simulations will use explicitly the morphological information arising from the WP1. They will aim not only to predict the multi-physical properties of a specific microstructure (WP2), but also to identify the most influent morphological parameters on the overall macroscopic response in order to address the optimization problem *via* the process.

Candiate

We seek a post-doctoral fellow with an interest for methodological developments with the application to real engineering materials (12-mounths secured, with possible extension to 24-mounths). Background knowledge in imaging techniques, image analysis, numerical methods (including numerical homogenization) are required. Programming skills would also be appreciated. Applications (cover letter, electronic copy of PhD thesis and all publications, at least two referees) should be sent to A. Rios.

References

[1]. A.H. Landrock, *Handbook of Plastic Foams*, Noyes Publications, New Jersey, **1995**.
[2]. A. Kausar, *Polymer-Plastics Tech. & Eng.* **2018**, 57, 346-369.
[3]. D. Raps, T. Köppl, A. Rios de Anda, V. Altstädt, *Polymer* **2014**, 55, 1537-1545.
[4]. D. Raps, N. Hossieny, C.B. Park, V. Altstädt, *Polymer* **2015**, 56, 5-19.
[5]. C. Okolieocha, D. Raps, K. Subramaniam, V. Altstädt*, Eur. Polym. J.* **2015**, 54, 44, 11056-11064.
[6]. P. M. Stefani A. Tejeira Barchi J. Sabugal A. Vazquez, *J. Appl. Polym. Sci.* **2003**, 90(11), 2992-2996.
[7]. O. Takiguchi, D. Ishikawa, M. Sugimoto, T. Taniguchi, K. Koyama, *J. Appl. Polym. Sci.* **2008**, 110(2), 657-662.
[8]. Q. Ren, H. Xu, Q. Yu, S. Zhu, *Ind. Eng. Chem. Res.* **2015**, 54, 44, 11056-11064.
[9]. Q. Ren, S. Zhu, *ACS Macro Lett.* **2015**, 4 (7), 693-697.
[10]. C. Bethke, S. A. Sanchez-Vazquez, D. Raps, G. Bakis, S. Bard, U-L. Du Ngoc, V. Altstädt, *Polymers* **2019**, 11(5), 793.
[11]. N Mattar, A. Rios de Anda, H. Vahabi, E. Renard, V. Langlois, ACS Sust. Chem. & Eng. **2020**, 8, 34, 13064-13075.
[12]. Q.B. Nguyen, N.H. Nguyen, A. Rios de Anda, V.H. Nguyen, D.L. Versace, V. Langlois, S. Naili, E. Renard, *J. Appl. Polym. Sci.* **2020**, 49051.
[13]. C. Perrot, F. Chevillotte, M. T. Hoang, G. Bonnet, F.-X. Bécot, L. Gautron, A. Duval, J. Appl. Phys. **2012**, 111, 1, 014911-16.
[14]. M. T. Hoang, G. Bonnet, H. T. Luu, C. Perrot, J. Acoust. Soc. Am. **2014**, 135, 6, 3172-3185.
[15]. V. Langlois, V. H. Trinh, C. Lusso, C. Perrot, X. Chateau, Y. Khidas, O. Pitois, Phys. Rev. E **2018**, 97, 053111-10.
[16]. V. Langlois, V. H. Trinh, C. Perrot, Phys. Rev. E **2019**, 100, 013115-12.