MIT Visit Report

In the first plan of the 3DPMTP project (submitted with the project application files) it is possible to observe that the MIT Visit was expected to happen for a 3 months period from the beginning of March until the end of May of the present year.

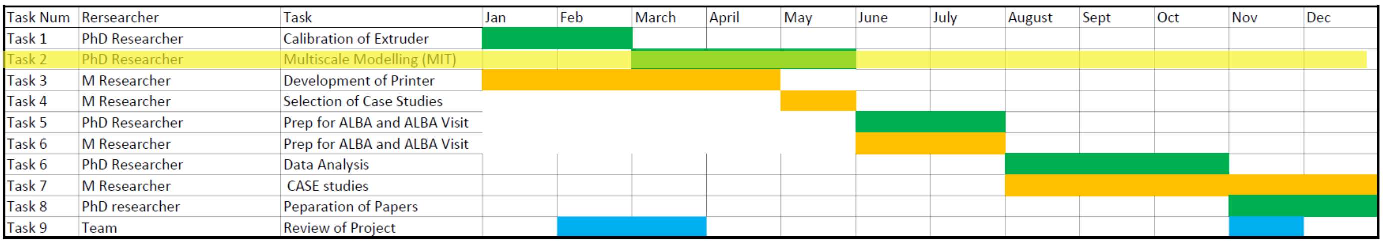

Figure 1 – 3DPMTP Project chronogram.

However, due to the complex onboarding process (mainly dependent on data and file validation) and the availability for the reception of visiting students, the mission at MIT was postponed to the fall season.

The effective dates were the following:

Start Date: 03/October/2022

End Date: 22/December/2022

Officially, clearance for lab and room access was granted until the end of the year (3 months in total, just as planned), but the last weeks of the present month correspond to an academic pause.

In the first meeting between the principal investigator and the research fellow of 3DPMTP and the supervisors from MIT, a broad visit plan was defined.

MIT Visit Plan:

- **Visit researcher:** Daniel P. da Silva; CDRSP Researcher with ORCID: 0000-0002-7431-3275.
- **Visit goal:** Gaining experience in polymer processing simulation, using the sliplink molecular dynamics (MD) model.
- **Specific skills to be learned:** Polymer Rheology – mainly Linear Viscoelasticity; Software packages (Jupyter, Mathplotlib and Scipy – python-based software packages for general data processing and analysis); Using the computation cluster to perform simulations.
- **Training materials:** Live hand-on sessions and pre-recorded lectures; reading manuals and tutorials; Attending classes.
- **Skills and competencies measurement/evaluation:**

  Application to case study of specific project.

  1. Parameterizing the model for a relevant 3D printing case study. Performing simulations of uniaxial time-varying flow.
  2. Extracting and analyzing information about molecular orientation as a function of flow parameters.
- **Supervision at MIT:**

  Prof. Gregory Rutledge, Professor of Chemical Engineering, principal investigator. 30 years in academic research, teaching and student supervision.

  Dr. Marat Andreev, Postdoctoral Research Associate, primary supervisor. 12 years in academic research, mentoring, teaching and student supervision.
- **Department and Office:** Chemical Engineering – Building E17 – Room 530 (Rutledge Research Group).

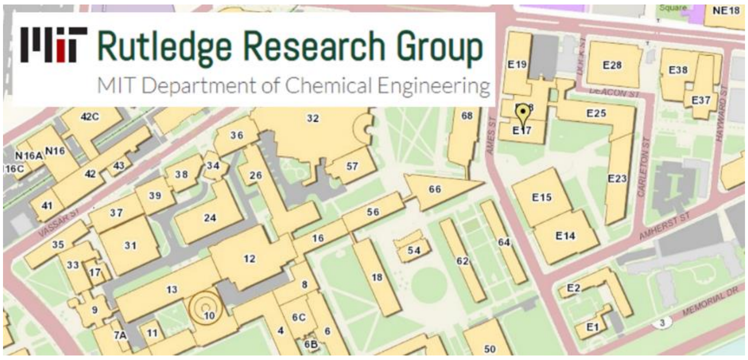

Figure 2 – Designation and location of the office in the MT Chemical Engineering department.

In practice, the visit was managed in accordance with the tasks/stages list below. (This strategy was defined in the context of a few meetings with the MIT supervisors: prof. Gregory Rutledge and Ph.D. Marat Andreev.)

Main Tasks/Stages List:

- Group integration
- Books studying
- Preliminary research
- Cluster Engaging
- Learning the Navigation on the System
- Lectures on Molecular Dynamics
- Tutorials Execution
- Application in 3D Printing

Work Description:

Following the list above, the visit started with the integration on the Rutledge lab team and a few discussions about the practical applications of the sliplink model in 3D printing. The application of the model requires the study of the fundamentals of polymer rheology, and this study was also part of the work scope of the visit.

The supervisors recommended specific literary references in order to reinforce the knowledge background prior to the lectures attended. Figure 3 represents the set of books used to understand some of the main concepts in polymer melt rheology.

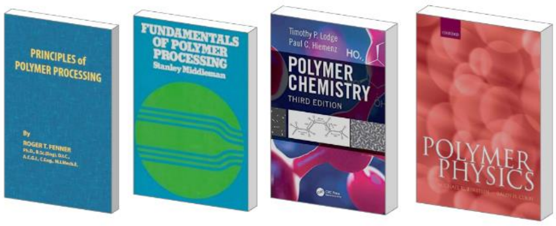

Figure 3 – Suggested books with relevant chapters for the visit work.

Focusing on extrusion, the visiting researcher got access to some relevant papers of previous studies of polymer rheology in extrusion-based 3D printing, mostly focusing on computational fluid dynamics (CFD). Although the macroscale is important for the understanding of polymer melt flow behavior during extrusion, the goal of the visit was to develop some skills in the micro and nano scales.

Fortunately, the application of the spliplink model is already used in the extrusion field, associated to other production technologies. First reads about its utilization were important to contextualize the notions presented in the tutorials. Also, with this first insights, it was concluded that there are new opportunities for research developments using the computational model instead of experimental data (obtained with rheometers, as an example).

As already said, MD Models require specific polymer rheology background. For the execution of the tutorials (pre-recorded practice sessions), the visiting researcher used the model almost exclusively as an end-user, although some understanding of the python scripts allowed him to adapt them to the 3D printing context. Further script and job understanding can be better developed during the execution of the doctoral program of the researcher.

In general, the project demanded the exploration and development of knowledge in several fields: Computation, Linux Interface and Commands, Python programming, Molecular dynamics, and Polymer Rheology, apart from extrusion-based 3D printing and polymer morphology analysis. The software environment for simulations was particular since it doesn't have a graphical user interface. It runs on Linux commands and the tutorials were a great asset to explore the cluster environment and the navigation in the Linux command prompt, along with the background software to perform job/python script edition, grant access to code libraries and manage simulation jobs. All the required software was installed in the first weeks of the visit, and the preliminary runs of the sliplink model were executed along the cluster engaging. One of the outputs of the project was a set of commands and a setup step list of all the required packages in the MIT computational cluster. Some adjustments are surely needed to engage other computational clusters, but this knowledge was important to understand the different tools necessary to run the simulations using CPU memory. GPU memory can be explored in future research projects.

Once again, with some additional searches, an important connection was established between the sliplink model and 3D printing (as it is possible to conclude in the case study project description – next section of the visit report). Successfully we infer from the effect of the flow properties in the nozzle on the final properties of the molten material, by the observation of the conformation tensor and the analysis of viscosity (significant to 3d printing and material property mapping with the process conditions).

<u>Case Study Project:</u>

Sliplink is a computational molecular dynamics (MD) model based on the consideration of polymer entanglements. Polymer chins typically have tens of thousands of bonds and assume extensions of a few microns. The fact behind this is that very elongated objects tend to entangle, just as in spaghetti or headphone wires. The effect in practice is viscoelasticity since there is some resistance while pulling the long chains apart, as a function of the number of entanglements and the time it takes for the polymer chains to relax. There are previous MD models, but sliplink considers the approximation of the entanglement point to links between vicinity chains and the main/analyzed chain, and the time for relaxation of a molecular chain is dependent on the overall internal energy of the polymer melt.
With this model, it is possible to analyze the elastic modulus of the polymer, infer from its viscosity, and obtain a specific conformation tensor related to the average extension/elongation of the longest chains in the polymer flow.

We focused on the last two parameters.

The experimental work reported by [1] consisted of assessing the printability of several polymers, using data from a rheometer. One of the fundamental characteristics analyzed was their flowability, given by the level of shear thinning. This property is mathematically defined by the parameter n in the Carreu Model for the definition of the complex viscosity.

Basically, the first work consisted of the replication of the reported study using simulation. In order to obtain the complex viscosity curve, it was necessary to calculate the flow curves for several shear rate values (corresponding to the definition of different processing parameters). From each flow curve, the approximate value of steady-state viscosity was extracted, according to the scheme in Figure 4.

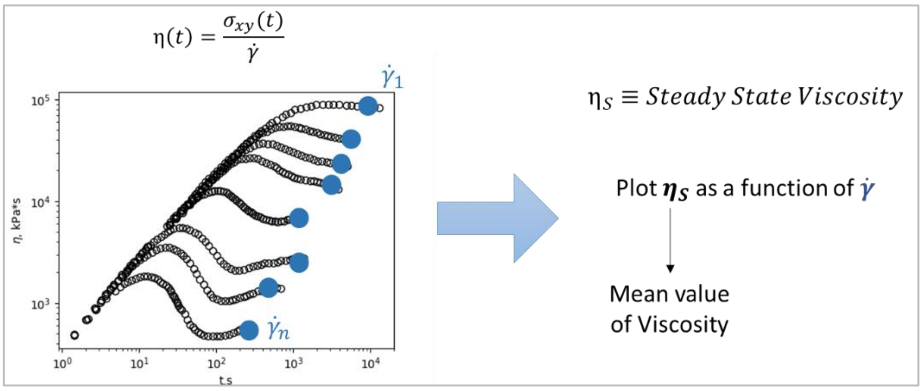

Figure 4 – Schematic of the experiment procedure.

To run the simulations, it was necessary to consider a typical value of the shear rate in the 3D printer nozzle. That value was found in accordance with [2], from which was possible to obtain a mathematical definition of the shear rate at the nozzle wall (as a function of the profile shape index, section, and the polymer melt flow), as it is observed in Figure 5.

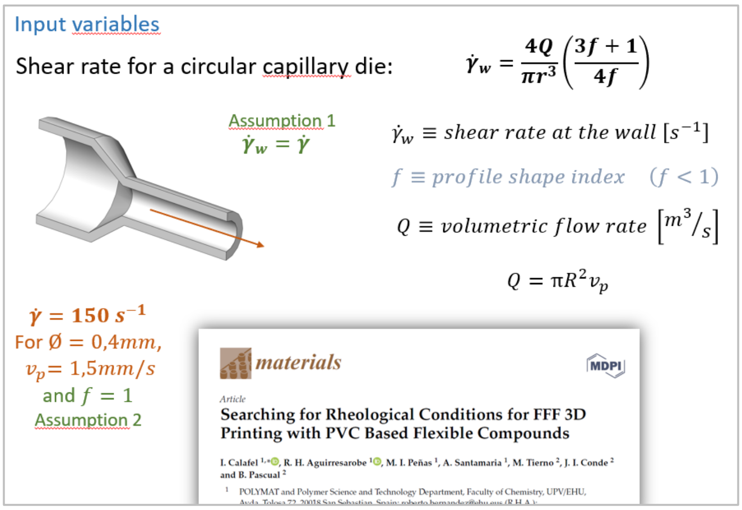

Figure 5 – 3D printing typical shear rate definition.

After assuming the nozzle section as perfectly circular, and a constant shear rate along the section, the typical value of the shear rate was found, and other values were assumed based on the orders of magnitude.

The following viscosity curve (in Figure 6) was obtained by plotting the values of steady-state viscosity with the respective sliplink shear rate values (simulation adimensional units). The definition of the melt temperature implied a step of time-temperature superposition.

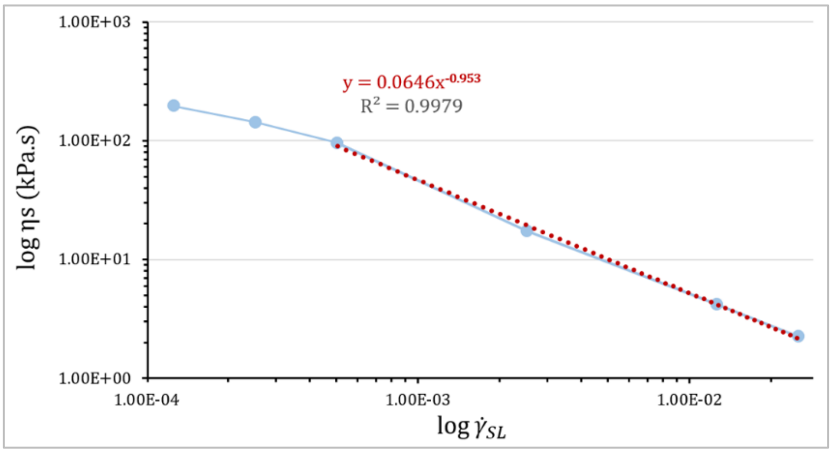

Figure 6 – Complex viscosity curve for the evaluation of shear thinning.

Once again, the slope of the power regression indicates the level of shear thining.

Transversally, the values of the conformation tensor (xy component) were obtained for the same process parameters (shear rates). An analogous procedure was followed: firstly, the flow curves for conformation were obtained (shown in Figure 7), and then the values of steady-state conformation were extracted.

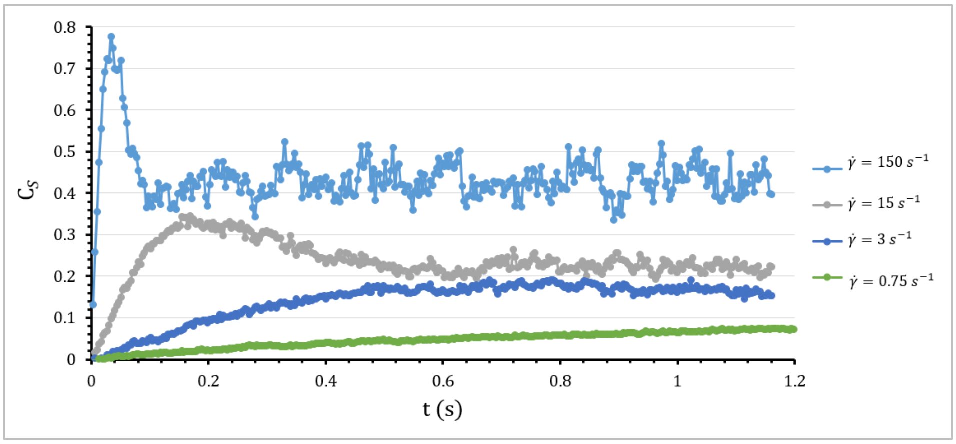

Figure 7 – Conformation tensor values as a function of deformation time.

The plot of the steady state conformation values as a function of the shear rate (in sliplink units) is represented in Figure 8.

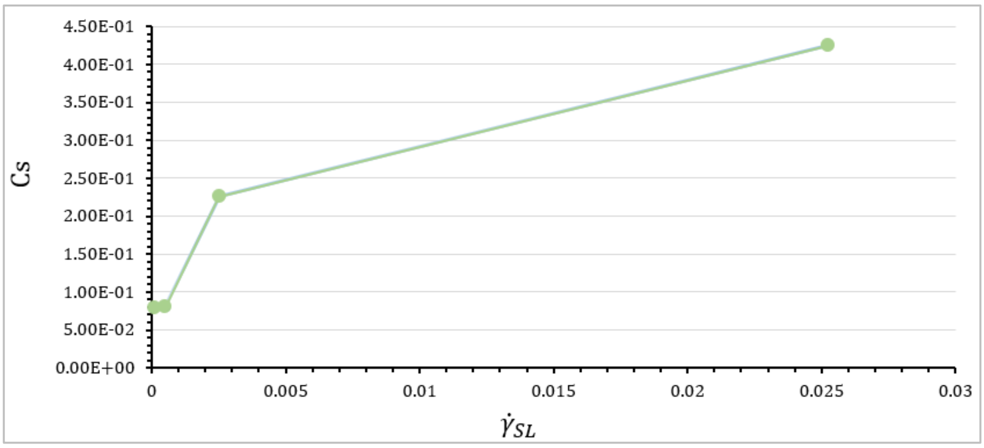

Figure 8 – Plot of the steady state conformation as a function of shear rate in sliplink units.

The conformation plot indicates expected an increase of the conformation tensor value (corresponding to a bigger elongation) with the shear rate. Thus, from a similar plot, it is possible to preview how the 3d printing process parameters affect the final material morphology, and, consequently, the final mechanical properties.

Conclusions:

At first, the longer onboarding process at MIT and the availability for the project supervision on-site implied its postponement to the fall season. Therefore, subsequent tasks were affected by this delay. However, besides that, it was possible to obtain some interesting outputs for the application of the multiscale methodology method to be applied in 3D printing, more specifically in the field of material properties definition during fabrication.

The work developed at MIT was, in practice, a set of intensive learning tasks on several subjects, such as polymer rheology, resources for computational cluster simulations, and python language for the interpretation of job scripts (simulation calculations programs).

It is fair to conclude that the acquired knowledge was essential to continue to perform evaluations of the orientation of the polymer chains in the melt polymer extrudate (as ultimately intended). Moreover, the analysis of the material in different sections of the extruder was also explored, by changing the python script codes and creating simulation jobs customized to our 3D printing context.

Additionally, a partnership was established with the Rutledge Lab team, in which some colleagues work with the Sliplink model on a daily basis.

Opportunities for future publications on the field were unraveled, namely by replicating polymer rheology experimental works (reported by other scientists) with MD simulations (providing insightful data of the material and their behavior in 3D printing in a very precise and agile way.

Future work includes the consideration of partially crystallized melts in the extruder nozzle, and that has a large potential for publication, presenting a breakthrough in the analysis of the materials' properties during processing. For the researcher's doctoral program studies, contact with a versatile simulation tool and highly recommendable literature was essential to the broad comprehension of the possibilities and practicality of the main idea behind the thesis work. Also, new skills have to be developed and enhanced in the fields of polymer chemistry and physics, as well as Python programming for model adaptation.

In a near future, the next step is to, in fact, apply this gained knowledge, *a priori*, in the printing trials, by means of the employment of a temperature-controlled nozzle.

References:

[1] Arrigo, R.; Frache, A. FDM Printability of PLA Based-Materials: The Key Role of the Rheological Behavior. Polymers 2022, 14, 1754. https://doi.org/10.3390/polym14091754

[2] Calafel, I.; Aguirresarobe, R.H.; Peñas, M.I.; Santamaria, A.; Tierno, M.; Conde, J.I.; Pascual, B. Searching for Rheological Conditions for FFF 3D Printing with PVC Based Flexible Compounds. *Materials* 2020, *13*, 178. https://doi.org/10.3390/ma13010178