**PhD thesis topic: Time-dependent properties of polymer glasses under pressure: from physical aging to microstructural complexity**

**Scientific supervision**

Supervisor: Prof. Laurent Delbreilh, University of Rouen Normandy, GPM UMR CNRS 6634
Co-supervisor: Dr. Nicolas Delpouve, University of Rouen Normandy, GPM UMR CNRS 6634

**Host laboratory**

Groupe de Physique des Matériaux (GPM), UMR CNRS 6634 – University of Rouen Normandy
Department / team: Disordered Systems and Polymers (SDP)

**Funding / start date**

PhD contract (University / French Ministry MESR funding, ~€2,300 gross/month) – start: October 2026

**Scientific background**

Many polymers are used under high-pressure conditions in demanding industrial environments (transport and production, gas/hydrogen networks, hydraulic systems, structures under high mechanical loads). In such situations, pressure directly affects density and molecular mobility, and therefore impacts time-dependent phenomena that control long-term performance: changes in mechanical properties, creep, damage sensitivity, and overall in-service stability.

Among these phenomena, physical aging plays a central role. It is a slow and reversible evolution of a glassy polymer kept below its glass transition temperature: the material progressively densifies and its properties change even at constant temperature. While physical aging is well documented at atmospheric pressure, its behavior under high pressure—and in particular the direct link between structural state and molecular dynamics during densification—remains insufficiently understood.

This PhD project proposes to use pressure as an experimental control variable to design rigorous protocols (in particular isothermal ones) and to quantitatively connect segmental dynamics, structural relaxation, and microstructural evolution. The studied material will be a widely used bio-based polymer, PLA (polylactic acid), investigated across a range of molecular weights and in states where the microstructure can become complex (amorphous / semi-crystalline).

**Scientific Goals**

The overall goal is to build a quantitative description of time-dependent properties of polymer glasses under pressure by combining in situ dynamic measurements with thermal/structural characterization. More specifically, the thesis aims to:

- Establish a reference at equilibrium under pressure: measure PLA segmental dynamics as a function of temperature and pressure, and quantify its sensitivity to density.
- Develop and analyze isothermal physical aging under pressure: apply pressure jumps and pressure holds below the glass transition, and monitor in real time how the dynamics evolves during aging.
- Address the complexity of aging: test whether the evolution can be described by a single internal time scale, or whether several mechanisms are required to interpret slow components.
- Link dynamics, molecular weight, and microstructure: understand how molecular weight and microstructured states (amorphous vs semi-crystalline, amorphous fractions with different mobility) affect the dynamics and aging kinetics, and how pressure influences the appearance/evolution of these microstructures between the glass transition and melting.

**Experimental program (approach and steps)**

The project relies on a combination of tools available at GPM:

- Broadband dielectric spectroscopy (BDS), including a hydrostatic high-pressure setup (direct monitoring of molecular dynamics).
- Calorimetry (DSC) and fast scanning calorimetry (FSC) to characterize structural states and quantify structural relaxation (enthalpic signature).
- Structural characterization adapted to semi-crystalline states (e.g., X-ray diffraction depending on needs and access).

From a scientific perspective, the project is structured around three main work packages:

**Work package A** — Segmental dynamics at equilibrium under pressure (reference)

- Map PLA dynamics under pressure over relevant temperature windows.
- Extract robust parameters describing the sensitivity of dynamics to pressure/density.
- Build the reference required to interpret out-of-equilibrium states (aging).

**Work package B** — Isothermal physical aging under pressure: real-time monitoring

- Implement "pressure jump + isothermal hold" protocols below the glass transition.
- Monitor relaxation time evolution using BDS under pressure (dynamic signature during densification).
- In parallel, characterize structural relaxation using DSC/FSC on selected states, with procedures designed to preserve the structural state when returning to ambient conditions.
- Compare the results with existing descriptions of physical aging (fictive variables, phenomenological models) and test recent hypotheses on kinetic complexity.

**Work package C** — Molecular weight and microstructural complexity under pressure

- Study a PLA series (from low to high molecular weight) to establish correlations between dynamic parameters, aging kinetics, and molecular weight.
- Design protocols between the glass transition and melting to explore the formation of semi-crystalline states and their effect on amorphous dynamics.
- Connect dynamic signatures (BDS) with thermal (DSC/FSC) and structural results, taking into account the coexistence of amorphous fractions with different mobility in some states.

**Outlook / scientific collaborations**

The project is part of a team-based research environment and can build on scientific exchanges with international academic partners working on aging and molecular dynamics.

**Candidate profile**

We are looking for a motivated candidate with:

- an MSc (Master 2) or engineering degree in physics, materials science, polymer science, or a related field;
- a strong interest in experimental work (careful measurements, progressive autonomy, good laboratory practice);
- an interest in glassy materials, molecular dynamics, physical aging and/or semi-crystalline polymers;
- the ability to analyze data and write scientific reports/papers (basic programming skills are a plus: Python/Matlab, etc.);
- good scientific English (reading and writing).

**Application / contact**

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