

Apport de la spectroscopie à relaxation diélectrique sous pression pour investiguer la mobilité moléculaire dans les polymères thermoplastiques amorphes

Doctorant·e

TRUBERT Jules

Direction de thèse

DELBREILH LAURENT (Directeur·trice de thèse)

SAITER-FOURCIN ALLISSON (Co-directeur·trice de thèse)

Date de la soutenance

22/10/2024 à 09:30

Lieu de la soutenance

UFR ST - Batiment U1 - Salle 2.26, Avenue de l'université, 76801, Saint-Étienne-du-Rouvray cedex

Rapporteurs de la thèse

NAPOLITANO SIMONE Université Libre de Bruxelles

SERGHEI ANATOLI Université Claude Bernard - Lyon 1

Membres du jury

AFFOUARD FREDERIC, , UNIVERSITE LILLE 1 SCIENCES ET TECHNOLOGIE

ALBA-SIMIONESCO CHRISTIANE, , UNIVERSITE PARIS-SACLAY

DELBREILH LAURENT, , Université de Rouen Normandie (URN)

NAPOLITANO SIMONE, , Université Libre de Bruxelles

SAITER-FOURCIN ALLISSON, , Université de Rouen Normandie (URN)

SERGHEI ANATOLI, , Université Claude Bernard - Lyon 1

Abstract

The ambiguity surrounding the relationship between the glass transition temperature, isobaric fragility, and the characteristic size of the Cooperative Rearranging Regions (CRR) for glass-forming liquids has been resolved by considering the volumetric and thermal contributions of the structural relaxation. These contributions have traditionally been estimated by considering assumptions at atmospheric pressure, whereas they require pressure variations to be measured. The use of broadband dielectric spectroscopy under pressure offers a new perspective to experimentally determine the contributions of isobaric fragility. On the one hand, the measurement is performed for three amorphous thermoplastic polymers: Polylactic acid (PLA), polyethylene glycol terephthalate (PETg) and polyvinyl acetate (PVAc). These polymers show a strong correlation between the activation volume, which leads to the volumetric contribution of isobaric fragility, and the CRR volume. The thermal contribution is determined by two methods and evolves in an opposite manner to the volumetric contribution as function of pressure. The contributions explain the isobaric fragility behavior at atmospheric pressure. On the other hand, the poly(ethylene-co-vinyl acetate) (EVA) copolymer series, which presents a different ratio of polar side groups with an unchanged backbone chain, is analyzed in terms of intermolecular interactions from the dielectric relaxation shape. In this series, the polar side groups play a crucial role in the volumetric and thermal contributions of the isobaric fragility, which are also related to inter and intramolecular interactions. By combining these different results, a relationship between chemical structure and the influence of pressure/temperature on molecular mobility can be established. The effects of structural parameters, such as backbone and side group stiffness or packing efficiency, are highlighted and explain how isobaric fragility is affected.