

The faculty of Engineering of the Vrije Universiteit Brussel invites you to attend the public defense leading to the degree of

DOCTOR OF ENGINEERING SCIENCES

of **Hannelore Geeraert**

The public defense will take place on **Friday 9th October 2026 at 5pm** in room **I.2.03** (Building I, VUB Main Campus)

To join the digital defense, please click [here](#)

**STRUCTURE-PROPERTY RELATIONS AND CRYSTALLIZATION
BEHAVIOR OF POLY(3-HYDROXYBUTYRATE-CO-4
HYDROXYBUTYRATE) BIOPOLYMERS**

BOARD OF EXAMINERS

Prof. dr. ir. Ellen Roels

Prof. dr. Sebastiaan Eeltink

Prof. dr. ir. Jessica Mangialetto

Prof. dr. Bart Goderis

Prof. dr. Dario Cavallo

Prof. dr. ir. Antonella Esposito

PROMOTORS

Prof. dr. Niko Van den Brande

Prof. dr. ir. Eveline Peeters

Abstract of the PhD research

Polyhydroxyalkanoates (PHAs) are biodegradable and biocompatible polymers produced via microbial biosynthesis, potentially from renewable feedstocks. Owing to their broad structural diversity, PHAs exhibit a wide range of thermomechanical properties and are therefore considered promising alternatives to petrochemical-based polymers, including for biomedical applications. Among the members of the PHA family, poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)) is regarded as one of the most versatile, owing in part to its broad range of mechanical properties which can be tailored by its monomer composition. Despite its strong potential, fundamental insight into the structure-processing-property relations of P(3HB-co-4HB) remains limited. This is partly attributed to the biosynthetic origin and limited commercial availability of PHAs. To overcome the issue of limited sample availability, P(3HB-co-4HB) samples were produced through cultivation of *Cupriavidus* sp. USMAA2-4. The broad range of monomer compositions obtained enabled the thermomechanical properties of P(3HB-co-4HB) to be systematically studied. A key challenge for P(3HB-co-4HB) is its narrow temperature window between melting and the onset of thermal degradation, which complicates melt processing. To better understand the origin of this limitation, the influence of melt-processing temperature on the crystallization behaviour of P(3HB-co-4HB) was investigated. The results revealed that crystallization is strongly affected by both thermal degradation and melt-memory effects, highlighting the complex interplay between thermal history and crystallization kinetics. In the absence of melt memory effects, P(3HB-co-4HB) exhibits slow crystallization kinetics due to the inherently low density of heterogeneous nuclei associated with its biosynthetic origin. To address this limitation, biocompatible nucleating agents were identified and evaluated. Thymine was shown to act as a melt-soluble nucleating agent for biosynthesized P(3HB-co-4HB) with varying 4HB content, and its nucleation efficiency was assessed relative to the polymer's intrinsic self-nucleation potential. These insights were further translated into the development and validation of a numerical and physical crystallization model for P(3HB-co-4HB). By integrating established crystallization kinetics theory with experimentally determined physical parameters, the adapted model enables prediction of crystallization kinetics, particularly under self-nucleation conditions. Together, these results provide deeper insight into the structure-processing-property relations of P(3HB-co-4HB), with a specific focus on its crystallization behaviour. Such understanding is essential for improving its processability and enabling predictable and reliable performance in future applications.