Current projects within the DPI programme Polyolefins

Project #800: Quantitative Structure-Activity Relationships (QSAR) in Metallocene-Based Olefin Polymerization Catalysis (Revised Version) *(MET_QSAR_Rev)*
[a] University of Naples (IT), [b] University of Perugia (IT), [c] Lomonosov Moscow State University (RU)
September 2017 - March 2021

Project leaders:
[a] Roberta Cipullo, Peter Budzelaar
[b] Prof. Alexander Voskoboynikov, Dmitry Uborsky
[c] Alceo Macchioni, Cristiano Zuccaccia
Researchers:
[a] Dr. Christian Ehm (PostDoc)
[b] Leonardo Sian (PhD)
[c] Dr. Dmitry V. Uborsky (PostDoc)

This project aims to implement a rational predictive approach to metallocene olefin polymerization catalysis, with a combination of HTE, HTC and mechanistic investigations. Focus libraries of catalysts with different symmetries and wide structural diversity will be prepared at MSU with a novel parallel strategy. The polymerization behavior will be screened at UniNa using state-of-the-art HTE and HTC tools and methods. Structural characterization of catalytic precursors, activated species, ion pairs and further ionic aggregates will be studied by 1D and 2D multinuclear NMR at UniPg. The overall results will be assembled into structure-properties databases of unprecedented size, and utilized to compile a QSAR modeling instrument with predictive ability.

Project #801: Predictive modelling of mechanical anisotropy in oriented semi-crystalline polymers directly from morphological characteristics (OrientXpress)
Eindhoven University of Technology (NL)
December 2016 - August 2022

Project Leader: Dr. Hans van Dommelen
Researcher: Chavez Hernan Thieleman (PhD)

In this project, a quantitative structure–property relationship will be developed For flow---oriented semicrystalline polymers, in particular polypropylene (PP), in terms of the fully anisotropic yield kinetics and the underlying oriented macromolecular structure. This will involve (i) the incorporation of an oriented amorphous phase in a micromechanical model and (ii) the characterization of the slip kinetics for the individual slip systems of a semicrystalline polymer and their effect on macroscopically anisotropic yield kinetics. This way, a scale transition between the physical mechanisms of deformation and the micromechanical performance of oriented semicrystalline polymers is obtained.

Project #802: Structure determination at the nanoscale and atomic dynamics of MgCl2 primary particles in Ziegler-Natta catalysts (DisMgCl)
[a] University of Turin (IT), [b] Japan Advanced Institute of Science and Technology (JP)
October 2017 – October 2020

Project leaders:
[a] Prof. Elena Groppo
[b] Prof. Toshiaki Taniike
Researchers:
[a] Dr. Allesandro Piovano (PostDoc)
[b] Dr. Toru Wada (PostDoc)

Chemistry in Ziegler-Natta (ZN) catalysis is projected to the understanding of the ensemble structure and the interplay among TiCl4, donors, MgCl2 and the activator. Even though a certain progress has been made in recent years on the local active site chemistry relevant to TiCl4 and donors interacting with MgCl2 surfaces, our understanding on the identity of delta-MgCl2 stops at "rotationally disordered MgCl2", that had been one hypothesis to explain a broad XRD profile. In this study, JAIST and UNITO teams collaboratively revisit the structure at the nanoscale and the atomic dynamics of delta-MgCl2 as the primary particle of ZN catalysts by means of combined experimental and computational techniques, including machine-learning-aided and reverse Monte Carlo modeling, X-ray and neutron scattering, and traditional vibrational spectroscopies (Raman and Far-IR).

Project #803: HEat Management in Polymerization Reactors (HEMPR)
Eindhoven University of Technology (NL)
June 2017 – January 2022

Project leaders: Prof. Hans Kuipers, Prof. Martin Van Sint Annaland, Prof. Niels Deen, Dr. Ivo Roghair
Researchers: Dario Balice (PhD), Evan Milacic (PhD)

Gas phase polymerization processes are limited by the rate of heat removal, which is typically done by injecting and evaporating liquid droplets. This project experimentally and numerically investigates the implications of the droplets on the behaviour of the gas and solids phases, e.g. on the hydrodynamics, formation of agglomerates, heat transfer, and on the process operation as a whole. Multi-scale models, from fully-resolved particle-droplet interactions to meso-scale discrete particle simulations, will be developed and used to simulate and optimize the heat management in these reactors under industrially relevant conditions. Various optical/infra-red experimental techniques are used for model validation and verification.

Project #804: From homogeneous to "colloidal" olefin polymerization catalysts: effects of mass transport limitations on reaction kinetics and polymer microstructure (CollCats)
[a] University of Naples (IT), [b] University of Prague (CZ)
September 2017- December 2021

Project leaders:
[a] Prof. Vincenzo Busico
[b] Prof. Juraj Kosek
Researchers:
[a] Pavel Kupka (PhD), Geremia Schiano Moriello (T-Staf)
[b] Anna Zitková (PhD), Lenka Krajakova (PhD)

This project aims to explore, in the framework of a collaboration between chemists and chemical engineers and with a combination of experimental and theoretical tools and methods, the hypothesis that the entrapment of molecular olefin polymerization catalysts inside the produced polymer can limit

monomer transport to the active centres as soon as the system becomes "colloidal", i.e. earlier than polymer precipitation is clearly perceived. If this is proved true, conventional kinetics should be revised, and a number of puzzling observations could find simple explanations (just to mention a few: (a) the (much) higher chain propagation rates measured in Quenched Flow experiments compared with conventional ones; (b) the so-called "comonomer effect" in "solution"; or even (c) the broad or multimodal molar mass and/or comonomer sequence distributions obtained with certain single-centre catalysts).

Project #810 Online Polyolefin structuring during Cast Film Extrusion (OP_CaFE)
[a] University of Salerno (IT), [b] University of Groningen (NL)
June 2018 – May 2022

Project leaders:
[a] Prof. Roberto Pantani
[b] Guiseppe Portale
Researcher: [b] Federico Di Sacco (PhD)

The effect of processing conditions, polymer chain structure and additives on the final structure of polyolefin films will be studied to establish the structure/property relationships for cast film extrusion. Ex-situ microbeam and depth-resolved scattering techniques will be employed to analyse the film structure with high spatial resolution. Furthermore, a method to study in-situ the polymer structuring during cast film extrusion using synchrotron X-rays will be developed. Furthermore, the effect of different nucleating agents will be studied since it seems that a combination of optimal processing parameters and heterogeneous nucleation can lead to improved and stable optical properties.

Project #813 Multi-scale investigation of silica-supported ethylene polymerization catalysts during the early stages of the reaction (MULTIPOL)
[a] University of Turin (IT), [b] Utrecht University (NL)
May 2018 – May 2023

Project leaders:
[a] Prof. Elena Groppo
[b] Prof. Bert Weckhuysen
Researchers:
[b] Max Werny (PhD)
[a] Jelena Zarupski (PhD)

We aim to research Ziegler-Natta and metallocene-based polymerization catalysts in the early stages of the genesis of active sites and polymer formation by a multi-scale characterization approach under reaction conditions. Two PhD students will jointly work together on the same set of solid catalysts; one, based at Torino University, focusing on catalyst ensemble characterization, while the second, working at Utrecht University, will perform single catalyst particle characterization. Thereby we aim to link the macroscopic physical (e.g. mechanical strength and temperature gradients) and chemical (e.g. polymer composition, type and density) properties with nanoscopic chemical properties (e.g. oxidation state and coordination environment).

Project #814 Control of crystallisation, chain entanglement and rheology via process conditions (DisEntangled)
Ecole Supérieure de Chimie Physique Electronique de Lyon (Fr)
December 2018 – November 2022

Project leader: Dr. Timothy McKenna
Researcher: Roberta Lopes do Rosario (PhD)

Evidence shows that polyethylene (PE) chain (micro)structure (entanglement, MWD, nascent crystallinity) is influenced by the choice of the continuous phase; the degree of swelling appears to have a significant impact on these competing phenomena. We will focus on the use of supported catalysts, and study in situ swelling by different condensed and vaporised diluents on PE. DMA, thermal, mechanical, and spectroscopic testing will be used to characterise entanglements for high MW polymers, and proton NMR will be used for soluble PE1. The feasibility of a gas phase UHMWPE process will be explored.

Project #815 Augment the macroscopic PROperties of i-PP composites by controlling the microscopic Fiber-matrix Interactions via Transcrystallization (PROFIT)
[a] Eindhoven University of Technology (NL), [b] University of Genova (IT)
May 2018 – April 2022

Project leaders:
[a] Dr. Lambèrt van Breemen
[b] Dr. Dario Cavallo
Researcher: [a] Stan Looijmans (PhD)

Fiber-reinforced semi-crystalline polymer composites are largely employed for their improved strength with respect to the unfilled polymer matrix. The adhesion and mechanical interaction between the polymer and the fiber are known to play a key role in determining the mechanical behaviour of the final product. Heterogeneous nucleation on the surface of the solid fiber, together with stresses induced by matrix shrinkage upon cooling, is thought to positively affect the matrix/fiber interaction. In this project we aim to systematically relate the formation of transcrystalline layers at the fiber/matrix interface to its bulk mechanical properties via microscopic observations, both during processing and micromechanical testing.

Project #816 Correlation between process-induced crystallization and mechanical properties in injection molded isotactic polypropylene (iPP) (ProCrystal)
Leibniz-Institut für Polymerforschung Dresden (DE)
June 2018 – May 2021

Project leader: Dr. Ing. Ines Kühnert
Researcher: Yvonne Spoerer (PhD)

In injection-molded parts, the development of skin-core morphologies due to large gradients of cooling rates is well known. Additionally, specific layers occur due to the flow conditions. The interrelation between the locally different structure and global mechanical properties is one keypoint to obtain new application fields and therefore of high scientific and technological interest. This project focuses on the application of new experimental tools like fast scanning chip calorimetry to characterize crystallization/solidification at processing-relevant conditions in thin-walled molded parts, analysis of flow-induced crystallization and local structures of moldings by microscopy and X-ray scattering. These data will be used to optimize the injection-molding process such that solidification in the various zones of the molding occurs at pre-defined temperatures and strains, in order to tailor formation of specific local structures and with that of properties like the flexibility of film hinges. The link between

the experimentally determined crystallization kinetics and the injection-molding process is intended to be predicted by the application of simulation tools. Controlling the semi-crystalline morphology of injection moldings from new isotactic polypropylene (iPP)-based materials gives the opportunity to improve disadvantageous properties of the weakest region of moldings like flow hinges, serving as a sensitive measure of the success of the approach.

Project #817 An inter-disciplinary high-throughput approach to olefin block copolymers (HT-OBC)
University of Naples (IT)
September 2018 – December 2022

Project leaders:
Prof. Rosanna Pasquino, Prof. Nino Grizzuti
Researchers:
Dr. Daniele Tammaro (PostDoc), Gaia Urciuoli (T-Staf), Dr. Veronica Vanzanella (PostDoc), Dr. Antonio Vittoria (PostDoc)

Progress in polyolefins has always been the outcome of multi-disciplinary efforts; most success stories are characterized by fine control on all individual elements in the chain-of-knowledge, from catalysis to end-use properties. With growing complexity, though, the field calls for (more) holistic approaches with a higher throughput. Olefin Block Copolymers (OBCs) produced by 'chain shuttling' are an exemplary case; understanding these materials, which are innovating the LLDPE market, is virtually impossible without considering polymer chemistry and physics together. In this project, the intricate and still poorly defined OBC structure-properties relationships will be unraveled by means of an inter-disciplinary high-throughput approach with disambiguation loops encompassing adjacent elements of the chain-of-knowledge; this also includes an important tool implementation part. The proposed method can become a paradigm in future investigations of novel materials from complex catalytic routes.

Project #830: Electrostatic charging of polyolefin powders on the level of particles (ElstatCharge)
University of Prague (CZ)
January 2020 – December 2023

Project leader: Prof. Dr. Ing. Juraj Kosek
Researcher: Jana Sklenarova (PhD)

Triboelectric charging is a key phenomenon affecting particle agglomeration and wall sheeting. The project aims to quantitatively describe the charging of polyolefin particles caused by both particle-particle and particle-wall collisions. Experiments will focus on: E1) effects of material properties on charging – particle size distribution, surface roughness, temperature-dependent properties, excitation of surface electron states; E2) effects of interface on charging – humidity, antistatic agents, gas/liquid composition; E3) charge neutralization. The obtained knowledge will be simultaneously utilized in the development and validation of three levels of charging models and agglomeration models.

Project #831: Molecular modelling of stretch-induced crystallization in polyethylene and polypropylene layers (PO-Stretched)
[a] National Technical University of Athens (GR), [b] Eindhoven University of Technology (NL)
April 2020 – Aug 2024

Project leader: [b] Dr. Alexey Lyulin
Researchers:
[a] Stefanos Anogiannakis (PostDoc)
[b] Nikolaos Sigalas (PhD)

Flexible plastic packaging is the fastest growing segment of the packaging industry. Designing easily recyclable and energy efficient products is the challenge of the modern circular economy. Polyethylene (PE) and isotactic polypropylene (PP) are important plastics, but achieving a suitable combination of impact resistance, stiffness and toughness in all-PE multilayer packaging and filled PP has been a persistent challenge. In the PO-stretched project we will undertake multiscale simulations of semicrystalline morphology development upon high-strain mechanical deformation of polyethylene and polypropylene, to understand the mechanisms controlling crystallization, toughness, permeability, determine optimization design strategies and provide a molecular basis for finite-element simulations.

Project #832: Quality model for COntaminated Recycled Polyolefins (Q-CORP)
Ghent University (BE)
February 2020 – January 2022

Project leader: Dr. Karen van Kets
Researcher: Ruben Demets (PhD)

Q-CORP entails the development of a multi-factor quality model for the mechanical recycling of contaminated polyolefins. As contaminations we consider either (up to 20%) other polymers, introduced by multilayer packaging or imperfect sorting, or smaller amounts of components like inks, labels or barrier layers. The model is based in polymer science and will take aspects from miscibility, polyolefin chain architecture and deformation mechanisms to come to a predictive output that gives insight into potential applications for the recycled plastics. As such, it can be used for Design for Recycling (by product designers) as well as fitfor-use sorting (by sorters/recyclers).

Project #834: RHEOlogical determination of POLyolefin Architectures (RHEOPOLAR)
[a] ETH Zurich (CH), [b] University of Naples (IT)
January 2020 - December 2022

Project leaders:
[a] Prof. Theo Tervoort
[b] Prof. Giovanni Ianniruberto, Prof. Roberta Pasquino
Researcher: vacancy

Determining the molecular structure of polyolefin-based materials is a relevant scientific and technological challenge. Molecular weight, its distribution, and structural details are fundamental parameters for materials design and processing, but often difficult to ascertain. The main objective of RHEOPOLAR is to study the molecular details of specific polyolefin-based systems through an innovative rheological approach. Linear and non-linear rheology will be measured in concentrated, entangled solutions, instead of melts, thus overcoming some intrinsic experimental difficulties encountered in measuring the latter. Molecular models and constitutive equations for entangled solutions will be used to extract the quantitatively relevant microstructural information.

Project #835 Quantitative Structure-Activity Relationships (QSAR) in Post-Metallocene-Based Olefin Polymerizations Using Chemically Meaningful Computational Descriptors (POST_MET_QSCAR)
[a] University of Naples (IT), [b] MSU Lomonosov Moscow State University (RU)
January 2020 – December 2022

Project leaders:
[a] Prof. Roberta Cipullo, Prof. Alceo Macchioni, Prof. Cristiano Zuccaccia
[b] Prof. Alexander Voskoboynikov, Dr. Dmitry Uborsky
Researcher: vacancy

This project aims to develop predictive 'clear-box' QSAR models of selected post-metallocene olefin polymerization catalysts with octahedral transition metal centers. In a previous DPI project (#800) a research strategy integrating parallel precatalyst synthesis (MSU), high-throughput catalyst screening and QSAR modeling (UniNa) and focused mechanistic investigations of active species in solution by means of advanced NMR techniques (UniPg) was successfully applied to stereorigid C2-symmetric ansa-zirconocenes of 'Spaleck-type'. As a result, novel catalysts with improved performance were identified, notwithstanding the reputation of said catalyst class to have been fully optimized. The challenge here will be to demonstrate that the same approach can work also in the much more demanding case of catalytic species typically characterized by equilibria between several different isomers, some of which are dormant/inactive.

Project #836: Practical, High Throughput Quench Labeling Techniques for Information-Rich Analysis of Alkene Polymerization Catalysts (CAT_ChromQL)
[a] University of Naples (IT), [b] University of Wisconsin-Madison (USA)
January 2020 – December 2023

Project leaders :
[a] Prof. Roberta Cipullo
[b] Prof. Clark Landis
Researcher: vacancy

Accurate active site counts1 and kinetic models2 of catalytic alkene polymerization are essential to understanding modern processes. Sensitive, quantitative detection of distributions of live polymer chains, dormant chains, and dead chains with reaction time enables practical determination of these critical attributes. Chromophore quench-labeling (CQL) selectively and covalently tags live polymeryls with a strong UV absorber. Dual detection GPC reveals two MMDs: RI detection senses all polymeryls and UV detection selectively measures live polymeryls. This proposal extends the CQL technology to mixed NMR and UV analysis, high temperature GPC for analysis of polyethylene and polypropylene samples, and high throughput experimentation.