Workshop on Flow-Induced Crystallisation in Polymers

Monday 20 Jan

Jaap Den Doelder, Dow and TU/e, *Flow-induced crystallization: why industry should care.*

Progress in polymer melt rheology modeling has slowly but steadily penetrated the industry. Computational tools are actually being used for polymer development and for designing polymer processing equipment. Expansion of the theories, models, and toolboxes to include semi-crystalline structure development is intuitively the next step, but we need more than intuition. We need science and perseverance. Based on a few decades of progress, we are now at a point where the benefits can start to be reaped. In this contribution we aim to stimulate the overlap between the academic and industrial perspective on flow-induced crystallization in polymers.

Greg Rutledge, MIT, *Simulation of Flow-Induced Crystallization at Atomistic and Molecular Scales.*

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The structure and properties of most semicrystalline polymers depend sensitively on both the chemical physical nature of the polymer and the manner in which it has been processed. These phenomena in turn are operative on different, but inter-dependent, length and time scales. In this talk, we discuss first the use of nonequilibrium molecular dynamics (NEMD) simulations with atomistic resolution to characterize the nucleation of a new crystal phase from a melt of linear polyethylene-like chains under homogeneous flow conditions. A method based on mean first-passage times is used to characterize the kinetics and physics of nucleation enhanced by flow, in both simple shear and uniaxial extension. These results are used to assess several of the existing models in the literature for flow-enhanced nucleation, and several new models are proposed, based on physical insight into the nucleation phenomenon made possible by such simulations. In the second part, we present a variation of the discrete slip-link model (DSM) for the rheology of entangled polymer melts that accounts for partial crystallinity through blending of free chains with crosslinked chains that resemble the bridge and/or tail (“dangling”) segments between developing crystallites. This modified DSM simultaneously captures the evolution of viscosity and elasticity over the whole range of frequencies in the linear regime for a number of different polyolefins. Kinetic modeling at the two scales is coupled through the dependence of nucleation kinetics on molecular conformation, as predicted by the modified DSM, and through the dependence of rheology on the nucleation and growth of crystallites predicted by atomistic NEMD.

Phil Coates, University of Bradford, *In-situ studies of structure development in micromoulding and solid phase orientation processing of polymers.*

P D Coates, B R Whiteside, P Caton-Rose

Polymer IRC, University of Bradford, UK

Y Men, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, China

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in-situ microbeam, time-resolved (33ms) x-ray studies for both solid phase orientation and most recently micromoulding have been undertaken for the first time by our team (including our Joint International Laboratories in China), using two purpose-built processing rigs designed and built in Bradford, and used in the Shanghai high precision beam line. Time resolution for the initial micromoulding in-situ experiments is 33ms. The results show the evolution of organised features prior to the formation of full shish-kebabs. We compare initial results with studies on samples from our ultraprecision micromoulding and solid phase forming facilities in Bradford. The ultra-high strain rate and ultra-high thermal gradient micromoulding process leads to rather different polymer structures than conventional injection moulding processes. Also, solid phase orientation by die drawing is shown to lead to different crystal domain effects than free drawing, forming what appears to be a more stable structure.

Gerrit Peters, TU/e, *Flow-Induced Crystallization in Polypropylene: how processing dominates structure development.*

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Depending on the conditions, Isotactic Polypropylene (iPP) can form different crystalline phases and different crystalline morphologies, as it can be clearly seen in injection moulding samples by applying X-ray scattering methods. Over the sample thickness, a distribution of four different crystal phases (?, ?, ?, meso) and multiple crystalline morphologies (spherulites and shish-kebabs) is found that depends on the local thermo-mechanical history. A prototype industrial flow device (piston driven slit flow) combined with in situ wide angle X-ray diffraction and small angle X-ray scattering was used to measure the evolution of these (oriented) crystalline structures and phases for different flow conditions. On the basis of the experimental results, an accurate model was developed, able to describe flow-induced crystallization of isotactic polypropylene at high pressures and shear rates. In the present work, the model is implemented in a two-dimensional finite element solver and fully coupled with nonlinear viscoelasticity, compressibility and non- isothermal flow equations. The build-up and relaxation of the pressure difference and the development of the different structures and phases during and after flow are accounted for. Simulations are run for a wide range of imposed pressures and piston speeds and the model is tuned to represent the interaction between the crystallization process, the thermo-mechanical conditions and the rheological properties of the polymer. Quantitative agreement with experiments is obtained. This experimentally validated model forms the bases for (commercial) more application directed software codes and for characterization methods.

Daniela Mileva, Borealis, *Cast-film processing effects of isotactic polypropylene homo- and copolymers based on different catalysts.*

Mostly transparent cast films represent one of the most relevant applications of isotactic polypropylene (iPP) homopolymers and random copolymers with ethylene in terms of volume. The production of these films having a thickness in the range of 30-250 µm involves rapid cooling resp. quenching from the melt in combination with limited stretching in the melt state, making an alignment between material properties and processing conditions very important. Both the primary properties of the film, stiffness and transparency, and the stability of the same over time in storage and sterilization are critically dependent on crystallinity and crystal modification. Quenching at high cooling rates will normally generate high fractions of the mesomorphic phase of iPP, but earlier studies have shown that the chain structure as well as the molecular weight will critically affect its development. In an ongoing project, different iPP homo- and copolymers based on novel single-site catalysts (SSC) and conventional Ziegler-Natta catalysts (ZNC) are studied regarding their crystallization behaviour as well as the resulting effect on film structure and properties. First results from four different polymers tested under different processing conditions on 50 µm cast films and analysed regarding crystallinity, mechanics and optics will be presented. Chill roll temperature is confirmed as main influence factor on film crystallinity, as it predominantly controls the average cooling rate, giving higher crystallinity for higher temperatures. A reasonable set of correlations can be achieved between film modulus and α-phase crystallinity for all polymers and processing variation.

Ron Larson, University of Michigan, *Role of Nematic Order and Chain Tension in Nucleation and Growth of Polyethylene Crystals.*

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We use both all-atom and united-atom molecular dynamics (MD) simulations to quantify the role of nematic orderin both linear and short-chain-branched polyethylene (PE) nucleation when chains are at equilibrium and when stretched. We combine atomistic MD simulation and mean-field theory to determine the nematic coupling parameter by imposing a tension on a fraction of the chains, and measuring induced nematic order on the other. This effect can lead to phase separation of stretched chains. We also mix stretched periodic PE chains with free PE chains of length o500 and 1000 backbone carbons (C500 and C1000). By simulating isothermal nucleation and performing mean-first- passage time analysis for the growth of the largest nucleus in our simulations, we show that the nucleation rate of PE increases exponentially with increasing average nematic order of monomers and is strongly slowed by short-chain side branches. We also validate the predicted quiescent nucleation rates by computing the crystallization half-time at various temperatures using the crystal growth velocity, sampled from simulations of isothermal crystallization of free chains near crystalline slabs, and the Avrami equation. The predicted crystallization half-times are in agreement with experiments, suggesting our predicted nucleation rates are reasonable. The results provide information that can be used towards developing a quantitative theory of flow-enhanced crystallization of polyethylene.

Charley Schaefer, University of York, Silk: *A natural example of a sticky entangled polymer*.

C Schaefer (1), P Laity (2) , C Holland (2), T McLeish (1)

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Silk is one of the most intriguing examples of biomolecular self-assembly, yet little is understood of molecular mechanisms behind the flow behavior generating these complex high-performance fibers. This work applies the polymer physics of entangled solution rheology to present a first microphysical understanding of silk in the linear viscoelastic regime. We show that silk solutions can be quantitatively modelled as reptating polymers with 'sticky' calcium bridges whose strength can be controlled through electrostatic screening. This approach provides a new window into critical microstructural parameters, in particular identifying the mechanism by which potassium ions are recruited as a powerful viscosity control in silk. Our model constitutes a viable starting point to understand not only the 'flow-induced self-assembly' of silk fibers, but also a broader range of phenomena in the emergent field of materials-focused synthetic biology.

Oleksandr Mykhaylyk, University of Sheffield, *Mechano-Optical Rheology of Polymers and Soft-Matter Materials* .

There is a continuously growing interest in a combination of rotational rheology with other techniques such as small-angle scattering and spectroscopy for structural characterization of soft-matter materials. However, a significant progress has also been made in the well-established field of mechano-optical rheology where a number of new technical solutions for rheo-optical microscopy and rheo-birefringence techniques have been proposed. In particular, recently developed shear-induced polarized light imaging (SIPLI) [1, 2] provides a relatively simple tool to deep insight of structural transformations in soft-matter materials. The technique is combinatorial and allows properties of materials to be tested in a wide range of shear rates in a single measurement. This gives a unique opportunity for in-situ studies of shear-induced phenomena such as stress, orientation and morphological transitions taking place in gels, polymers, copolymers, liquid crystals and colloids. Simultaneous rheo-optical studies using mechanical rheology coupled with SIPLI visualization and/or quantitative birefringence measurements will be demonstrated for various materials including flow-induced crystallisation of semicrystalline polymers, silk protein fibre formation under flows, morphological transformations of self-assembled copolymer nanoparticles and orientation of liquid crystals. The results are compared with small-angle x-ray scattering (SAXS) measurements. In addition, applications of the SIPLI technique for routine operations such as sample loading and monitor during rheological measurements using plate-plate and cone-and-plate geometry will be demonstrated.

Mykhaylyk O. O.; Warren, N. J.; Parnell, A. J.; Pfeifer G., Laeuger J., Applications of shear-induced polarized light imaging (SIPLI) technique for mechano-optical rheology of polymers and soft matter materials. Journal of Polymer Science Part B-Polymer Physics 2016, 54, 2151-2170.

Mykhaylyk, O. O., Time-resolved polarized light imaging of sheared materials: application to polymer crystallization. Soft Matter 2010, 6, 4430-4440.

Tuesday 21 Jan

Location: Maths Level 8, MALL 1 & 2, School of Mathematics, Univ. Leeds

Richard Graham, University of Nottingham, *Multiscale modelling of flow-induced crystallisation in polymers.*

Simulating and modelling flow-induced crystallisation in polymers is notoriously difficult, due to the very wide spread of length and timescales. We will present results from an ongoing multi-scale modelling project. This project combines novel modelling that addresses several of the key issues affecting flow-induced crystallisation. This includes a detailed model of the non-linear flow of polydisperse linear polymers, molecular dynamics simulations of nucleation under flow from well-entangled chains and a coarse-grained model of nucleation that accounts for the wide spread of chain deformation that occurs in industrial melts under flow. We have developed these new techniques into a continuum model of polymer FIC that inherits monomer-level detail from molecular dynamics simulations but is sufficiently cheap for use in computational fluid dynamics. We will present results from this model, including a comparison with FIC data from industrial melts.

Alicyn Rhoades, Penn State Behrend, *Flow-Induced Crystallization in PEEK: Molecular Weight Effects and Accelerated Kinetics at Low Temperatures.*

The flow induced crystallization behavior of Poly (ether ether keytone) has been established as a function of molecular weight and shear history. Using both rotational rheology and fast scanning calorimetry, enhanced flow-induced crystallization kinetics are observed even at very low crystallization temperatures - a very different behavior than has been established for more flexible polymers such as polyamide 6,6 and iPP. In addition, A flow-induced nucleation model has been developed that incorporates the idea of a critical nucleus volume that is similar in size to the volume of 3 - 4 Kuhn monomers.

Miguel Cordova, Sabic, *Is shear-induced crystallization driving morphology in impact polypropylene?*

Miguel Cordova[a], Winke Van den fonteyne[a], Bo Chen[b], Julie Kornfield[b]
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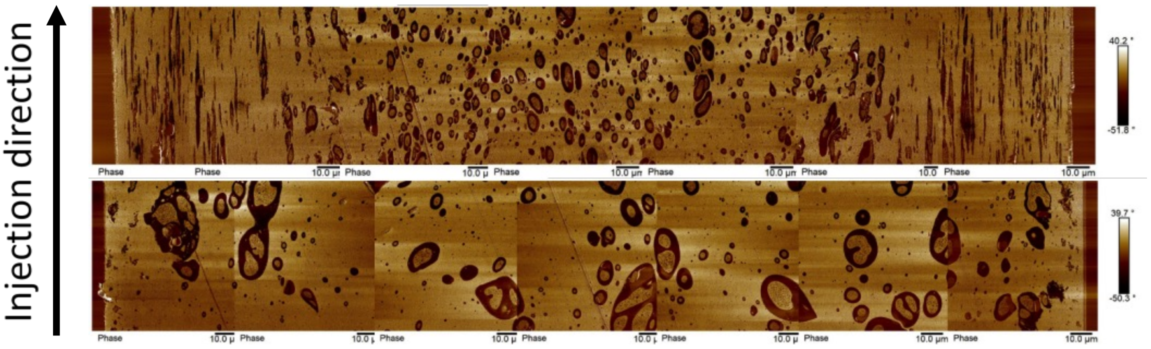

Figure 1 Phase angle atomic force microscopy images of a cross section of an impact polypropylene injection moulded at 600 kPa for two different temperatures; (top) 160°C and (bottom) 180°C

In-reactor blends of polypropylene and propylene-ethylene random copolymers are commonly used for applications that require high stiffness, combined with high impact toughness, such as car bumpers. The impact/stiffness balance depends on the chemical composition of the dispersed copolymer phase and the morphology of the material as present in the application. Automotive parts are most often injection moulded, subjecting the material to high shear stresses and rates. Understanding the interplay between chemical structure, shear dependency of the viscosities of the matrix and the dispersed phase and their influence on each other is vital for predicting the morphology and hence the mechanical performance of the finished part. In this work, in-reactor blends were subjected to shear rates of the same order of magnitude as in an industrial injection moulding process, while in-situ birefringence measurements were conducted. Crystallization of the matrix phase and stretching and relaxation of the dispersed phase were observed in this way. It was shown that the viscosity drop caused by temperature alone could not result in the obtained morphology. Therefore, we theorize that shear induced crystallization occurs at temperatures as high as 160°C. This crystallization triggers a viscosity drop in the matrix phase, resulting in viscosity ratios at which deformation of the rubber phase takes place.

Scott Milner, Penn State *Experimental and Theoretical Nucleation Barriers for Polyolefins*

Classic experiments on homogeneous nucleation in polyethylene (PE) and polypropylene (PP) using the emulsion-drop technique provide values for the nucleation barrier. Nucleation theory predicts the barrier, in terms of the bulk free energy difference between undercooled melt and ordered phase, and the interfacial tensions of the ordered phase with adjacent melt. Nuclei for polymers are roughly cylindrical, with distinct side-face and end-face tensions. End-face tensions can be inferred from melting point suppression; recent simulations predict the side-face tensions. In addition, evidence suggests nucleation in PE and PP proceeds via mesophase, rather than directly to the crystal. End-face tensions for the mesophase can be inferred from the crystallization line, while recent simulations can predict side-face tensions of mesophases, as well as their bulk free energy difference from the undercooled melt. Thus all ingredients are in place to compare experiments to theory, for nucleation via crystal and via mesophase. We predict at experimental undercoolings that nucleation via mesophase indeed has a lower barrier, consistent with experiment. However, the predicted barrier for PE is about 3 times too big, suggesting tensions for nanoscale nuclei are smaller by about 30 percent than inferred from experiments on fully developed lamellae and simulations with periodic boundary conditions.

Qiyun Tang, Institute of Theoretical Physics, Georg-August Universität Göttingen, *Fast evaporation enables 2D polymer single crystals.*

Solvent evaporation is a diffusion process where volatile solvents continuously evaporate from a solution into air or vacuum across a free surface, and it has been employed for guiding the self-assembly of ordered nanostructures and nano-crystals. Once the recede rate of the free surface caused by evaporation is faster than the diffusive current of the solutes (such as polymers), there is a non-uniform skin layer emerged on top of the polymer solution. This skin layer is usually a quasi-2D region of increased density, which might be suitable for the fabrication of 2D polymer crystals.

Recently, we demonstrate by molecular simulations that the Ostwald ripening of crystalline polymer nuclei within the fast-evaporation-induced 2D skin layer is retarded at suitable temperatures and evaporation rates [1]. Such an anomalous ripening can be attributed to the interplay between the thermodynamically-driven diffusion of non-crystalline fragments towards the growing nuclei and the diffusive current away from the free surface caused by the densification in the non-equilibrium skin layer. The growth orientation of the nuclei inside the skin plane can be adjusted during this anomalous ripening process, which is beneficial for fabricating 2D polymer crystals. We foresee that these findings might facilitate further experimental and theoretical studies of the polymer crystallization during fast evaporation, and also stimulate new explorations of the Ostwald ripening in other non-equilibrium conditions, such as shear and elongational flow.

[1] Q. Tang, M. Mueller, C.Y. Li, and W. Hu, Anomalous Ostwald ripening enables 2D polymer crystal via fast evaporation, Phys. Rev. Lett., accepted (2019).