Sara Lindeblad Wingstrand

Phone: +45 4525 XXXX
E-mail: saliwi@kt.dtu.dk
Discipline: Polymer Materials

Supervisors: Ole Hassager
Peter Szabo

PhD Study
Started: September 2014
To be completed: September 2017

On the Correlation Between Young's Modulus and Melt Flow in Fiber Spinning Operations

Abstract
Polymers in extensional flow is encountered in a wide range of polymer processing techniques, among others fiber spinning. The purpose of this project is to investigate the correlation between extensional flow in fiber spinning operations and the final elastic properties of the quenched fibers. This has, until very recently, been impossible due to difficulties in obtaining a constant strain rate throughout the entire course of elongation. Consequently very little is known quantitatively about the relation between extensional rate and final strength of the polymer.

Introduction
Polymer fibers are known to have extraordinary strength. In fact, expressed in terms of strength-to-weight ratio, polymer fibers outperform steel [1]. Thus ultrahigh molar mass polyethylene (Dyneema by DSM) has a strength-to-weight ratio in the range 8-15 times that of steel.

The extraordinary properties are believed to be tied to molecular orientation in the solid fibers [2]. This, again, is believed to be due to the extensional flow in the processing operation for fiber spinning [3]. However to the best or our knowledge, there has never been a systematic investigation of the relation between extensional melt flow, cooling rate, frozen molecular orientation and ultimate fiber strength.

The strength of semi-crystalline polymers and their corresponding morphology are closely related. It has long been known, that molecular orientation, can be altered upon shearing of the molten polymer prior to quenching. This changes the morphology in terms of degree of crystallization, orientation of crystals and in some case even the type of crystal structure [4].

A vast body of work, connecting strength of polymers and shear-induced crystallization, exists. Despite the fact that extensional deformation is of just as great interest, the extent of research in the field is very limited. Results from one of the few exceptions are shown in Figure 2. Here it is seen that the morphology changes with the Hencky strain rate ($\dot{\varepsilon}$).

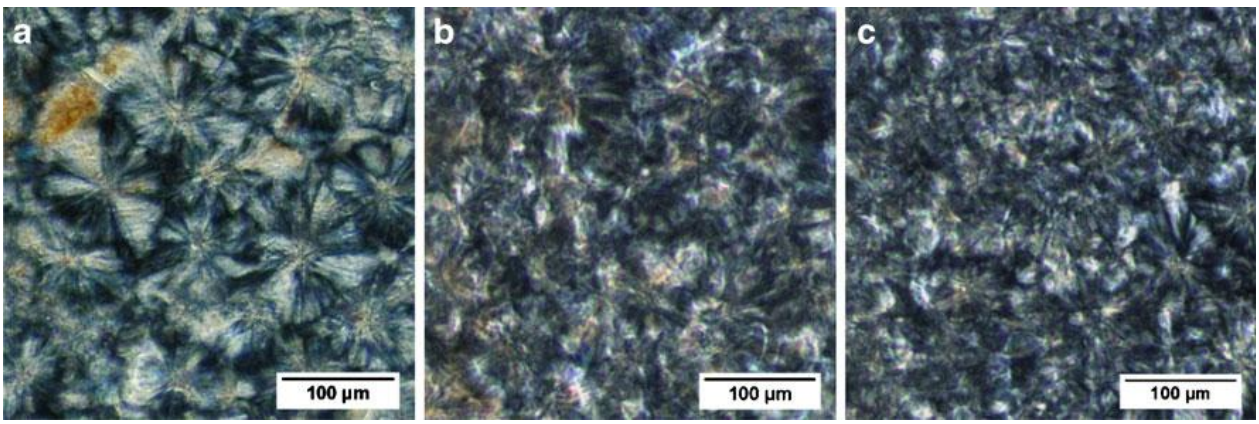

Figure 1: Polarized micrographs of final morphology in isotactic poly propylene (iPP) showing the size of spherulites in samples crystallized at $T_c = 146\,°C$, and (a) at quiescent conditions, (b) $\dot{\varepsilon} = 0.10\ s^{-1}$and (c) $\dot{\varepsilon} = 0.25\ s^{-1}$ [3].

The absence of literature is due to the great challenge in obtaining a constant Hencky strain rate ($\dot{\varepsilon}$) during the entire course of deformation [5]. In order to obtain a constant $\dot{\varepsilon}$, the diameter (D) needs to decay logarithmically in time sine the Hencky strain is given by:

$$\varepsilon(t) = -2\ln\left(\frac{D(t)}{D_0}\right) \qquad (1)$$

Recent advances in extensional rheometry have made it possible to maintain a controlled mid-filament diameter [6] using a filament stretching rheometer (FSR) (see Figure 1).

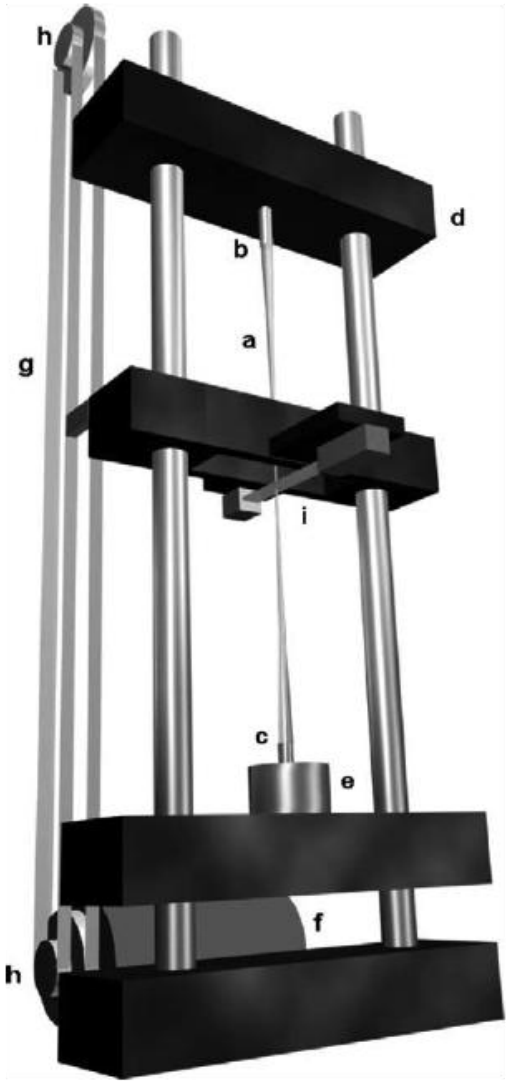

Figure 1: Sketch of the filament stretching rheometer at DPC. (a) filament, (b) top plate, (c) bottom plate, (d) movable support for top plate, (e) weighing cell (f) motor, (g) timing belts, (h) gearing and (i) laser. [7]

The FSR is capable of producing well-defined extensional kinematics and temperature up to 300 Centigrade. As depicted in Figure 2, the DTU-FSR consists of two parallel plates that can be separated in a controlled fashion. The polymer sample to be investigated is placed between the plates and allowed to reach the equilibrium temperature of the intended measurement. Once the sample has reached equilibrium, the plates are separated whereby a polymer filament is formed between the plates. The constant extensional rate is achieved by combination of a laser micrometer that monitors the filament diameter and a control loop that controls the plate separation as function of time. The up-graded DTU-FSR has the ability to quench polymer filaments by simply opening the oven in a fast manner.

Specific Objectives

The first part of the project will be devoted to the fabrication of a number of quenched polymer filaments that have been subjected to known stretch ratios at controlled stretch rates. Initially this will most likely be made with a polymer material for which experience with melt rheology is already available. These could be either polystyrene, polyethylene, polypropylene or poly(methyl methacrylate).

The second part of the project will concern the design and fabrication of sample holders to enable the measurement of Young's modulus and Poisson's ratio for quenched polymer filaments.

After the quenching technique and the solids characterization holders have been developed for a model polymer more systematic mapping of polymers subjected to large elongational deformations prior to quenching will take place. Combining characterization using the FSR to evaluate strength, with instrumentation able to reveal molecular orientation and crystal structure (e.g. electron microscopy, X-ray diffraction, and small angle neutron scattering), a systematic quantitative characterization of polymers in extension is possible.

References:

1. F. X. Kromm, T. Lorriot, B. Coutand, R. Harry, J. M. Quenisset, Polymer Testing 22 (4) (2003) 463–470.
2. B. Zhang, J. Chen, X. Zhang, C. Shen, Polymer 52(9) (2011) 2075–2084.
3. B. E. White, H.H. Winter, J. P. Rothstein, Rheologica Acta, 51(4) (2011), 303–314.
4. J.A. Kornfield, G. Kumaraswamy, A.M. Issaian, Industrial and Engineering Chemistry Research 41 (2002) 6383–6392.
5. R. Séguéla, Macromolecular Materials and Engineering 292 (3) (2007) 235–244.
6. J. M. Román Marín, J. K. b. Huusom, N. J. Alvarez, Q. Huang, H. K. Rasmussen, A. Bach, A. L. Skov, O. Hassager, Journal of Non-Newtonian Fluid Mechanics 194 (2013) 14–22.
7. A. Bach, H. Koblitz, P. Longin, and O. Hassager, Journal of Non-Newtonian Fluid Mechanics 108 (2002) 163–186.