Rheology and Crystallization of Polypropylene

Exploring the Processing Conditions

This article gives a brief overview on the theoretical background of the rheology as well as crystallization of polymers with dissolved gas. As an example, a long-chain branched polypropylene is examined with a pressure cell. The understanding of the rheology and crystallization under processing conditions, such as high pressure and dissolved gas, is crucial in foaming.

Introduction
Foams are one means to address the issues of energy consumption and emissions. Based on foams as insulation in houses, energy for heating (or cooling) can be saved. When used for the weight-reduction of cars, their fuel consumption is reduced.

A good understanding of the fundamental material’s properties is essential for foaming, especially since the rheological properties of the gas-filled polymer determine the morphology of the foamed product. Thereby the foams’ properties such as elastic modulus, strength, impact behaviour and thermal conductivity are affected [2].

During foaming, process conditions such as temperature, pressure and blowing agent affect the flow behaviour as well as the crystallization of the melt and thereby the product properties.

After the cellular structure is formed, it must be stabilized to keep its morphology and to prevent the collapse of the structure. Crystallization is the main mechanism for stabilization for semi-crystalline polymers. Therefore, it is crucial to understand the effect of processing conditions on crystallization to obtain a desired foam morphology.
Rheology
Flow-curves of polymers at different conditions of temperature T, pressure p, and gas concentration c exhibit self-similarity. Using a general shift factor a, the viscosity functions at different conditions can be shifted along lines of constant stress to a master-curve:

\[ \eta(\dot{\gamma}) = a \eta \left( \frac{\dot{\gamma}}{a}, T_{Ref}, P_{Ref}, c_{Ref} \right) \]

Ref denotes the reference state. \( \dot{\gamma} \) stands for the shear rate and \( \eta \) for the shear viscosity. The general shift factor is a product of the shift factors of temperature \( a_T \), pressure \( a_p \) and gas-concentration \( a_c \):

\[ a = a_T a_p a_c \]

\( a_T \) for semi-crystalline polymers is usually described by the Arrhenius equation:

\[ \ln(a_T) = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{Ref}} \right) \]

with an activation energy \( E_a \) and the universal gas constant \( R \).

In contrast to temperature, higher pressure leads to an increase of viscosity.

Like temperature and pressure, dissolved gas has a distinct effect on polymer processing. Viscosity is reduced by dissolved gas.
A common method to measure the rheological properties of polymers under gas-loading is in-line rheometry. The setup consists of an extruder, a system for gas-delivery and a slit or capillary die (Fig. 1). A back-pressure assembly is required to keep the pressure above the critical solubility pressure. A melt pump in front of the die ensures a constant flow rate.

The measurement of the flow properties of gas-loaded polymers is also possible in a pressure cell for a rotational rheometer, which will be explained later on.

**Crystallization**

The crystallization kinetics and crystalline morphology of common semi-crystalline polymers are well known due to their importance in the manufacturing of polymer products, e.g. by fibre-spinning, blow moulding and injection moulding. In case of foams, it is well known that crystallization phenomena play a major role.

Depending on the limiting mechanism for crystallization, the effect of dissolved gas on crystallization rate can be positive or negative. If the motion of polymer chains to the crystal-surface is limiting, dissolved gas leads to a faster crystallization due to increased molecular mobility. However, if crystallization is nucleation-controlled, the crystallization rate is decreased by dissolved gas due to its negative effect on crystal nucleation.

A common method to study crystallization with dissolved gases is high-pressure Differential Scanning Calorimetry (HPDSC) [1]. Its advantage is the ability to closely monitor the crystallization process. However, the apparatus is unable to create flow fields, which are present during foaming. The most important drawback is significant gas-diffusion during non-isothermal measurements.

Another solution is the use of a pressure cell for a conventional rheometer. Some exemplary results from this device will be shown in this article. The applied cell is an accessory for the MCR 301 Rheometer (Anton Paar). The pressure cell is a gas-tight measurement cell. Inside the cell, the upper plate is supported by ball bearings. Torque is transferred magnetically to the rheometer’s measuring head (Fig. 2).

For gas-saturation measurements, the sample is subjected to a constant shear-rate (related to the outer rim of the coaxial plate-plate system) and gas-pressure is applied. The equilibrium concentration is calculated from Henry’s law (S=kHp, S: solubility, kH: Henry constant). After saturation is reached, the flow curve of the melt is measured. The crystallization is studied by cooling the cell at a constant shear-rate. When crystallization takes place, the viscosity of the sample increases until a peak is reached, where the solidified sample loses adhesion to the plates.
The onset-temperature of crystallization is chosen as the temperature, where torque rises more than 10% above its average baseline before the peak.

**Results**

The section shows rheological results from pressure-cell experiments of a long-chain branched Polypropylene (LCB-PP, WB 140 HMS, Borealis, Austria) and CO₂.

**Rheology**

The viscosity functions of fully saturated PP are plotted in figure 4a for various CO₂-concentrations at 180°C. The viscosity reduction by dissolved CO₂ is eminent. A viscosity reduction by one order of magnitude at a constant shear-rate at a saturation pressure of 400 bar compared to the gas-free sample is observed. The gas-concentration shift factor (Fig. 4b) is obtained by shifting the respective viscosity functions to a master-curve. An exponential decrease of αc with gas-concentration independent of temperature is observed. The results were also compared to in-line-results with dissolved gas. The curves of both methods agree well (Fig. 5: see crossmedia bar).

**Crystallization**

Torque-temperature curves at different saturation pressures are plotted in figure 6a. The distinct increase of the torque at a characteristic temperature shows the onset of crystallization. Crystallization is delayed, when CO₂ is dissolved. The crystallization temperature TC is plotted as a function of CO₂-concentration (fig. 6b). TC distinctly decreases with the CO₂-concentration, which is probably due to higher chain mobility. At high concentration, the slope of the curve levels off due to an increased effect of pressure. Since crystallization is affected by the mobility of the polymer chains, the rheological properties were correlated to the crystallization behaviour. The combined shift factor for p and c correlates well with the crystallization temperature (Fig. 7).

The dependence of the shift factor αₚ,c on the crystallization temperature obeys an Arrhenius-law:

\[
\ln(\alpha_{p,c}) = \frac{E_{a,c}}{R} \left( \frac{1}{T_C(p,c)} - \frac{1}{T_{C,0}} \right)
\]

with the crystallization temperature without CO₂ and pressure TC,0, the crystallization temperature at gas saturation at a given pressure TC(p,c) and the activation energy Ea,c, which yields 142 kJ/mol. Interestingly, this is two times the activation energy for αT, which signifies the coupling of rheological and
crystallization properties in the investigated parameter-range.

The shown results emphasize the great potential of the applied rheological method for measurements of crystallization phenomena.

Summary
A novel method to characterize the crystallization properties under high pressure and gas-loading as well as the rheology under those conditions was applied for a high melt strength polypropylene.

The viscosity was significantly reduced by dissolved CO₂. The gas-concentration shift factor was exponentially dependent on gas-concentration. The crystallization temperature was distinctly decreased due to increased chain mobility. This reduction was related to the shift factor for pressure and gas-concentration according to the Arrhenius equation.

Summarized, the pressure cell proves to be an effective method to measure both rheology and crystallization of a polymer saturated with a blowing agent. More research will be conducted in the future to explore the capabilities and limitation of this method.

Acknowledgement
The financial support of the German Research Foundation (DFG) in the frame of the research project number Al 474/18-1 is highly acknowledged. PP was provided by Borealis AG, Austria.

Authors
D. Raps¹, S. A. Sanchez Vazquez¹, L. Heymann² and V. Altstädt¹
¹ Department of Polymer Engineering, University of Bayreuth, Germany
² Department of Applied Mechanics and Fluid Dynamics, University of Bayreuth, Germany

Contact
Daniel Raps
Department of Polymer Engineering
University of Bayreuth
Bayreuth, Germany
daniel.raps@uni-bayreuth.de

References

More articles on Rheology: http://www.laboratory-journal.com/search/gitsearch/Rheology

References and Figures: http://www.laboratory-journal.com/science/material-science/

Video on polymer crystalization:
https://www.youtube.com/watch?v=s9en3n8no08