Flow Imaging of Hot PVC Melt in a High Temperature Rheo-NMR System

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Introduction
The rheological properties of polymer melts play a crucial role for the processing of polymer materials. Therefore there is a significant interest in monitoring the flow behavior of polymers directly during the processing what is the focus in the parallel project 'inline-NMR for polymer processing' (presented on poster N-496). On the other hand there is a basic interest in a better understanding of the mixing and the melting of one component in the matrix of another. Pulsed field gradient nuclear magnetic resonance (PFG-NMR) provides simultaneous information about the chemical composition and flow properties and provides the option of spatial resolution. It is therefore predestined for rheological investigations, for studying mixing/demixing under shear as well as for melting/freezing processes and reactive processing. PFG-NMR was successfully applied for the study of flow in a room temperature rheo-NMR cell [1], e.g. for polymer solutions [2] or food materials [3]. It is desired to apply this method for polymer melts of technical relevant polymers as well, but then high temperatures in a very restricted volume are required. In a cylinder with an inner diameter of 30 mm as much as possible sample material is placed and heated but on the wall of this cylinder must be kept at room temperature. A high temperature rheo-NMR system permitting flow experiments up to 200 °C has been constructed [4] and applied for first flow experiments of a hot PVC melt.

Background
In NMR spectroscopy the permanent magnetic field is tuned as homogeneous as possible. Then the precession frequency of the spins does not depend on position but only on the local environment formed by other nuclei and electrons. Highly resolved spectra can be obtained containing information about the chemical composition and the mobility of the sample.

On the other hand in the pulsed field gradient NMR (PFG-NMR) the permanent homogeneous magnetic field is temporary superimposed by well-defined magnetic field gradients. Doing so the precession frequency depends on position, i.e. the position of the spins is encoded. This method provides spatial resolution encoded either in the phase or the frequency of the NMR signal. It is possible to encode the position of the spins at two times, providing the distance that the spin has moved in the time between, resulting in its velocity. The velocity information can be obtained spatially resolved, leading to complete flow fields. Moreover, chemical and mobility information can be retained (as well as temperature information). Hence, the flow fields can be separated for different components. The complete information would result in a multi-dimensional data field, which is uneasy to handle. Therefore the reduction of the number of dimensions based on symmetry arguments is advisable.

Such separated flow fields are very useful for studying the processes in polymer processing machines. But even the investigation of processes in model geometries, fitting in a wide- bore spectrometer might be helpful for understanding polymer motions better. A typical geometry for rheometers is the cylinder- cylinder geometry (Couette). This is also used for the first experiments in the high temperature cell. The velocity profile depends on the gap width between the two cylinders, the rotor velocity and the material properties. In classical rheometers the parameters are optimized to guaranty a linear velocity profile. The torque is measured integral over the whole

sample. The viscosity as well as some other material parameters are calculated from the known probe geometry assuming a linear profile. But, it is known that the viscosity of polymers depends on the shear rate and hence the profile becomes easily non linear. By means of the velocity profiles obtained by rheo-NMR the linearity can be proved. Moreover there is the possibility to study non-linear flow as well. In addition the information from the NMR spectrum (chemical shift, relaxation times) can be utilized to generate contrast for single components in a complex system.

Experimental
The flow measurements have been performed at a Bruker Avance 300 NMR spectrometer with a Larmor frequency of 300 MHz for protons. The spectrometer was equipped with a microimaging accessory permitting a maximum gradient strength of 1 T/m in three axes. A 30 mm birdcage resonator mounted on a microimaging probe micro2.5 has been used.

The construction of the high temperature rheo-NMR cell is based on the room temperature cell from P.T. Callaghan [1] will be described elsewhere [4]. It permits experiments at temperatures up to at least 200 °C so far. For the experiments described here it was heated by air up to about 170°C. The rotor ($\varnothing$ 5 mm) of the high temperature cell is driven by a stepper motor connected to a gear box 100:1 and controlled by the motor control unit from the room temperature cell. The inner diameter of the stator is 10 mm.

A soft, i.e. low melting PVC served as sample for the first flow measurements (Decelith® 80077 natur 0002, ECW-Eilenburger Compound Werk GmbH, Eilenburg, Germany). 1.3 g were molten offline in oven at 155 °C in the sample vessel of the cell. Air bubbles were removed and the rotor was placed in the middle of the cell in its final position. A second PVC sample was filled with 0.6 g glass spheres ($\varnothing$ = 300 - 400 µm).

The 3D flow imaging experiments have been performed with the standard Bruker pulse and automation programs including flow compensation [5]. A slice in z direction of 5 mm has been selected using a Gaussian shaped soft π pulse. The velocity in y direction in this slice was encoded. The spatial coordinates were encoded by frequency (x) and phase (y). 256 pixel in read and 16 pixel in phase direction determine a digital resolution of 0.06 mm x 1 mm (field of view 15 mm). The strength of the flow encoding gradient has been incremented in 16 steps from -0.61 T/m to 0.54 T/m, its duration δ was 1.18 ms, the evolution time Δ 49.26 ms, resulting in a field of flow of 0.5 cm/s.

The data obtained have been processed as follows: The phase dimension was zero filled to 128. After the Fourier transform of both spatial dimensions the equator slice was extracted (the 65th row in phase direction). In all voxels situated here only coherent motion in y-direction takes place and the encoding of flow in one direction, just in y, contains all necessary information about the velocity profile. It was zero filled to 64, apodized and Fourier transformed.

Results and Discussion
The results of the first flow experiment with PVC is shown in Fig. 1. 1a is the image of the cross section of the cell, i.e. this slice of the experiment in which the flow gradient equals zero. The intensity represents the material. Obviously it sticks at the rotor (inner cylinder) and at the stator (outer cylinder). In between there is gap. In the beginning of the experiment the gap between both cylinders was filled completely. Something caused the material during the experiments. This behavior is the result of the history of the sample. It was treated several hours at high temperatures (around 170 °C). PVC contains a lot of additives which become unstable at higher temperatures and

may effect the polymer as well. After removing the cell, some darkish sample material was found near the top of the cell, possibly deposited at the cooler parts.

The velocity profiles reflect the spatial distribution of the sample as well. Fig. 1b represents the profile at zero rotor speed. Consequently, the whole material is motionless. The gap between the polymer at the rotor and that on the stator is herein also visible. Fig. 1c shows the profile at ν_{rotor} = 0.075 Hz (corresponding to a velocity at its surface of 0.12 cm/s). The material sticking at the rotor rotates with exactly the velocity of the rotor. There is no transmission of the shearing force to the remaining material at the wall of the stator, it stays static. (Note: The intensity in the center is an artifact.)
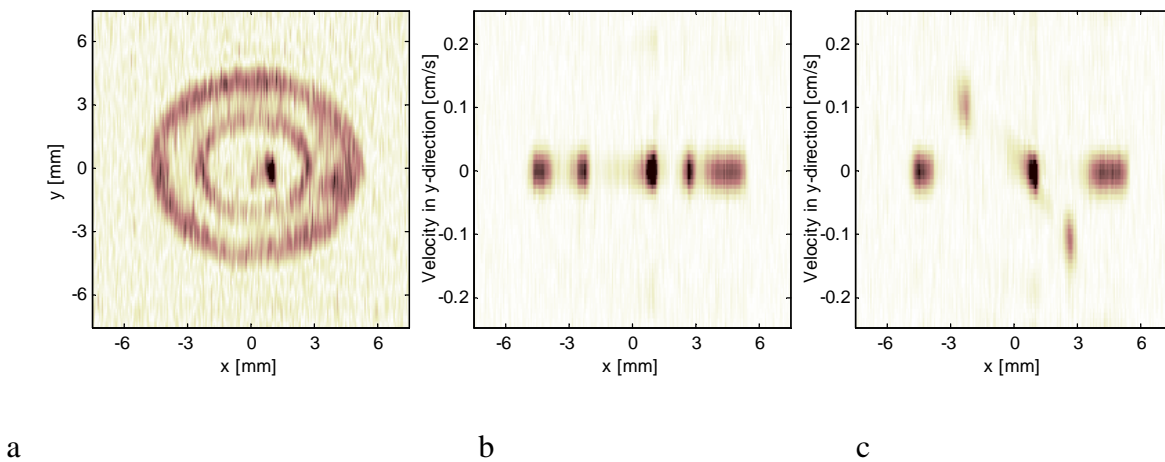
a   b   c

Fig. 1: First flow imaging experiment of PVC melt in the high temperature Rheo-NMR cell, left: 2D-image, middle: velocity profile at the equator at ν_{rotor} = 0 Hz, right: ν_{rotor} = 0.075 Hz (ν_{max} = 0.12 cm/s)

Next, the cell was filled with nascent PVC material. (It includes 0.6 g glass spheres this time, however this does not play any role for the results presented here, because the diameter of the spheres is below the spatial resolution employed here.) The sample was heated rapidly to the final temperature (170°C below the sample vessel) in order to obtain the required data before the decomposition.

The results are shown in Fig. 2. The image (Fig. 2a) makes obvious that the vessel is filled completely. Fig. 2b and c represent the velocity profiles at zero rotor speed and for ν_{rotor} = 0.04 Hz (corresponding to a velocity at its surface of 0.06 cm/s), respectively. The material at the rotor wall rotates with the maximum velocity, i.e. that of the rotor. The shearing force is transmitted through the material. The velocity decreases continuously with increasing distance from the rotor and reaches zero velocity at the wall of the stator. The profile is non linear. Surely due to the large gap width rather than to the velocity, which is very low.

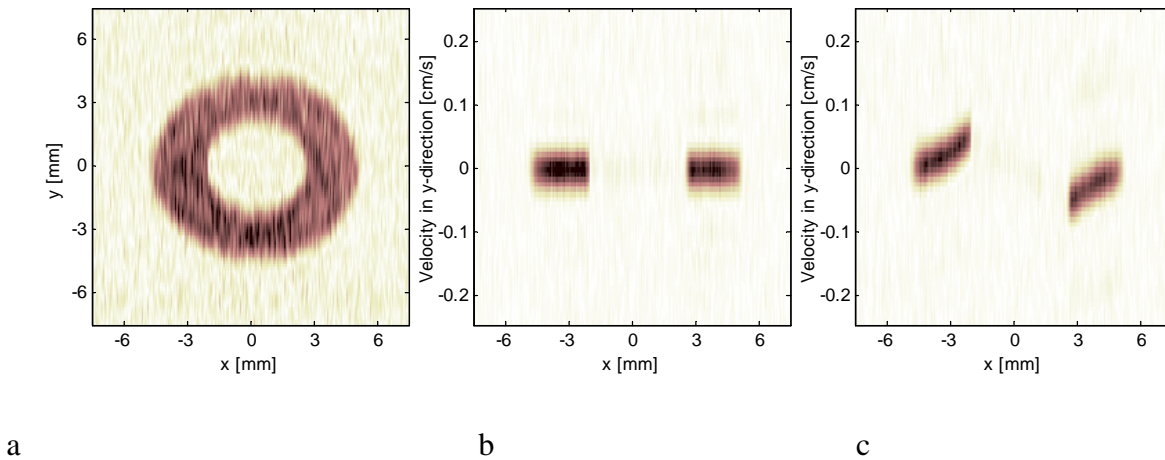a   b   c

Fig. 2: Second flow imaging experiment of PVC melt in the high temperature Rheo-NMR cell, left: 2D-image, middle: velocity profile at the equator at $v_{rotor} = 0$ Hz, right: $v_{rotor} = 0.04$ Hz ($v_{max} = 0.06$ cm/s)

Figure 3 is a photograph of the remaining PVC after the second experiment. Although it is not as much damaged as in the first experiment (see spectra and images) the dark color proves a starting decomposition. Before the experiment the material was transparent, colorless or slightly yellow. The white dots should be some of the glass spheres (∅ 300 - 400 µm). The hole in the middle is the place of the rotor.
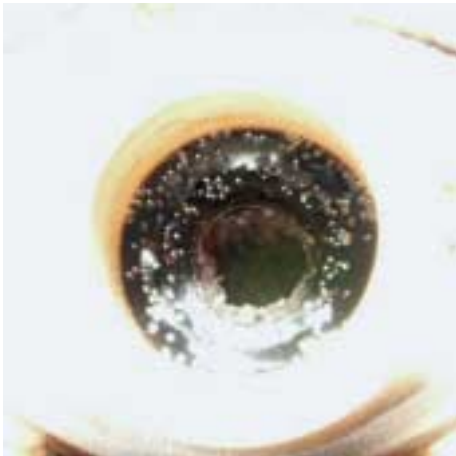

Fig. 4: Remaining PVC (dark mass) with some glass spheres (white dots) after the second experiment in the sample vessel. The hole in the middle is the place of the rotor (∅ ≈ 5 mm).

Summary/Outlook

A new high temperature Rheo-NMR system was constructed by modifying the commercially available Rheo-NMR system measurements at ambient temperature designed by Prof. P. Callaghan. The cell permits experiments at elevated temperatures of up to 200°C so far. First flow experiments with a technical relevant soft PVC have been performed. The method provides information about the spatial distribution of the material as well as its flow behavior. The loss of contact in the first

experiment is as visible as the non-linearity in the second experiment, proving the power of PFG-NMR being preserved for polymer melts in the high- temperature- rheo NMR system.

Near future developments will permit the use of the equipment up to 300 °C. Integrating a torque sensor in the equipment will yield to actual rheological data like viscosity. With this assembly the flow behavior of polymer melts, model systems as well as technical relevant polymers, especially filled polymers and polymer blends will be investigated.

Acknowledgement

References

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