

RheoDSC: design and validation of a new hybrid measurement technique

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Abstract A newly developed hyphenated technique is presented that combines an existing rheometer and differential scanning calorimeter (DSC) into a single experimental setup. Through the development of a fixation accessory inside the cell of the calorimeter and the introduction of an add-on unit for the rheometer, the simultaneous calorimetric and rheological measurement inside the well-controlled thermal environment of a Tzero™ DSC cell opens new experimental possibilities. The evolution of thermal and flow properties of a material can be simultaneously monitored during steady or oscillatory shear flow and regular or modulated temperature DSC measurements. The technique offers interesting opportunities for the investigation of flow-induced transitions, such as crystallization or phase separation, and provides a possibility for high-throughput screening of materials. The signal quality of the novel technique in comparison to the stand-alone techniques is demonstrated by the evaluation of the calibration factors and by measurements on standard materials. Finally, combined rheological and calorimetric melting and crystallization experiments on polycaprolacton are performed.

Keywords DSC · Instrument design · Rheology

Introduction

To distinguish appropriate processing parameters of materials, knowledge about their flow behaviour and thermal properties is essential. The state-of-the-art approach for investigating these parameters requires the use of several analytical techniques, since a single technique does not supply sufficient understanding of the complex material behaviour. Transition temperatures are typically measured by a (modulated temperature) differential scanning calorimeter [(MT)DSC], whereas flow properties are commonly obtained in rheological tests. However, an accurate comparison of the quantities measured on individual instruments is not straightforward, since the measuring conditions such as sample size, sample morphology, sample history (thermal as mechanic), and temperature control, are always different. Especially for the investigation of (flow-induced) material transformations that are associated with changes in rheological and thermal properties, such as polymerization, melting and crystallization, or phase separation and remixing, an accurate comparison between these techniques is crucial. In literature, a few attempts for combining calorimetry and rheology can be found, where the interest of the authors is the added value of a hyphenated setup. The possibility to characterize material systems with complex behaviour and to study transformations, which are influenced by the flow conditions, would only be possible with a hyphenated technique.

Martins et al. [1] developed a shear differential thermal analyzer that allowed to apply controlled shear pulses during isothermal or non-isothermal solidification of polymers. Hereto, a capillary rheometer and a differential thermal analyzer were combined into a single device. The instrument has two capillaries, one for the investigated sample and one for a reference material, which are placed inside

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two separate identical ovens. The major disadvantages of this method are the large sample masses needed, resulting in large thermal lags during non-isothermal experiments, and the choice of a reference material, as it is difficult to match both the heat capacity and thermal conductivity. Nagatake et al. [2] and Rheometric Scientific [3–5] modified a commercial rheometer by adding two thermocouples on the base plate, which allowed the measurement of differences between sample and base plate temperatures. The major drawbacks are the positioning of the thermocouples, since only one axial temperature difference not necessarily represents the overall material response, and the thermal heat sink of the rheometer's upper plate, resulting in vertical temperature gradients. Calibration procedures were said to overcome this problem, but were not included in the patent.

In this work, the RheoDSC technique developed by Kiewiet et al. [6] is taken as a starting point. The previous instrument design showed some imperfections and measuring difficulties. The main drawbacks were related to the invasive change in the DSC oven, since holes were drilled into the DSC oven bottom to accommodate an insert for the fixation of the DSC crucibles. Another drawback was the, not so straightforward positioning of the cell with respect to the rheometer. To overcome these drawbacks, the design was changed significantly. In this paper, the design of a retractable insert and the general overview of the combined apparatus will be discussed. Subsequently, the potential of the technique is exemplarily highlighted with measurements on standard calibration materials. Finally, polycaprolacton (PCL) samples are studied to show actual advantages and applicability of the RheoDSC technique.

Design of the insert and construction of the combined instrument

A prototype RheoDSC instrument was constructed starting from two stand-alone commercial instruments: a Q2000 Tzero™ DSC (TA Instruments) and an AR-G2 rheometer (TA Instruments).

The Q2000 Tzero™ DSC uses the Tzero™ technology [7, 8], which is important for the correction of the thermal resistances and capacitances of the various heat flow paths in the cell caused by the modification of the calorimetric cell environment. The AR-G2 rheometer on the other hand, is a sensitive instrument, opening the range of ultra-low torques, which is of importance as the diameter of the measurement geometry is chosen to be of comparable dimension as the DSC sensor, namely 5 mm. Normal rheological geometry diameters are in the range from 10 mm up to 40 mm and have therefore much larger resulting torques during measurements.

The newly developed rheometer geometry has a permanent steel top section in which disposable geometries can be mounted. In the experiments shown, the lower disposable part is made out of a polyamide-imide engineering plastic with good thermal and mechanical properties up to 260 °C. Glass is one of the materials that can also be used. The thermal expansion of the rotor can be compensated by the rheometer, which allows for a linear temperature dependent gap compensation.

The general overview of the RheoDSC setup is given in Fig. 1. The rheometer add-on consists of several units. The smart swap magnetic coupling base for accurate positioning is united with a x - y -stage to position the DSC cell accurately (zone (a) in Fig. 1). The middle section (zone (b) in Fig. 1) is an extension platform where standard TA Instruments DSC cells can be plugged in. In this part, both the purge gas connections as well as the electrical signal connectors are a duplicate from the Q2000 DSC module, so that standard DSC application software can be utilized. Even though the principle is similar as described by Kiewiet et al. [6], the use of an extension platform allows for more flexibility, both in cell use and in positioning of the rheometer versus the calorimeter. The DSC cell is equipped with a standard refrigerated cooling system (TA Instruments), allowing for accurate cooling. This is actually one of the most important assets of this new equipment. In conventional rheometry, rheological measurements during a cooling step are difficult to perform because of the large thermal mass that is present in a rheometer oven. However, in a DSC, temperature control is much more accurate, which opens new possibilities for non-isothermal rheological experiments. On top of the cooling head, a combination of heat shields covers the DSC cell (zone (c) in Fig. 1). There are two silver lids for maintaining a uniform thermal profile inside the oven and a ceramic outer shield to erase any environmental influence. In the silver lids and the ceramic

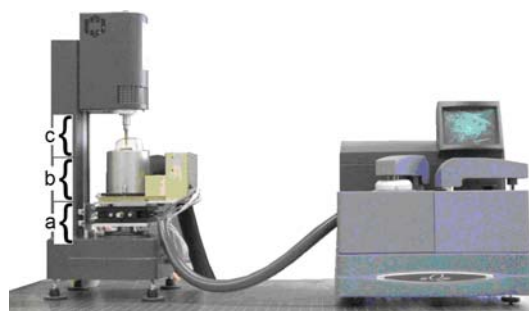


Fig. 1 Overview of the RheoDSC setup with three main parts: (a) smart swap coupling with x - y translation stage for precise positioning; (b) DSC extension plate with the electrical and gas connections and mounted DSC cell with RCS cooling head; (c) DSC cell thermal shields and the rheological geometry

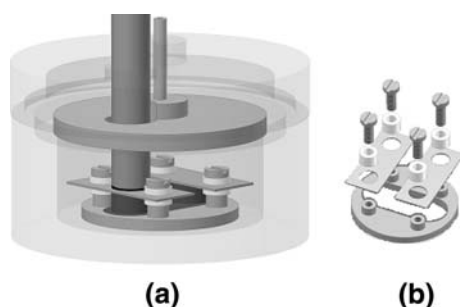


Fig. 2 Internal view of the RheoDSC setup (a). The insert with its components is surrounded by the DSC cell, sensor bottom plate (dark grey) and the polyamide-imide geometry (grey) on top of the sample (black). An exploded view of the insert (b) shows its composition

heat shield, holes are drilled, through which the rheometer geometry can be inserted. Care has been taken to design the holes as small as possible to preserve the shielding quality, an important requirement indicated by Kiewiet et al. [6].

A major modification with respect to the previous prototype is the use of a newly designed insert for the DSC oven. The insert serves as a rheological stator with reduced influence on the thermal environment. The main advantage with respect to the original design is that the aluminium insert surrounds the race track shaped sensor bottom plate precisely, providing a perfect fixation and eliminating the need for more invasive modifications of the cell. The insert can be readily removed and reinstalled. This gives an additional advantage since sample preparation and cleaning activities can be performed outside the DSC cell. An exploded view of the insert is shown in Fig. 2b. The insert has an aluminum bottom plate that fits around the racetrack shaped Tzero sensor plate. On this bottom plate, four extensions form the base of a pair wise fixation of sample and reference plate, using a polyamide-imide insulating ring.

Rheological calibration

In this section, the rheological parameters are investigated and the results will be compared with a standard rheometer to prove the experimental power and reliability of the newly developed prototype.

Three samples with a viscosity ranging from 50 up to 3×10^4 Pa s are used. The first sample is a PDMS (silly putty) material supplied by TA Instruments and is a commonly used evaluation material for their rheometers. At a temperature of 30 °C, the material has a cross-over of the storage modulus G' and the loss modulus G'' at $\omega = 5.46 \text{ rad s}^{-1} \pm 5\%$ with a storage modulus G' of $2.57 \times 10^5 \text{ Pa} \pm 8\%$. The second sample is a PDMS oil from Siliconas Hispánicas (Rhodorsil 47V1,000,000) with a zero shear viscosity of 1,000 Pa s at 25 °C. The last sample

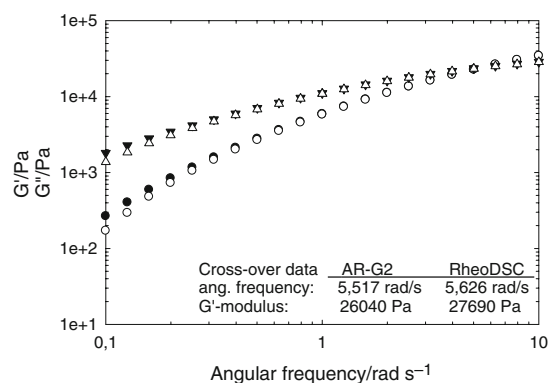


Fig. 3 Oscillatory rheological data for a PDMS silly putty material at 30 °C, measured on standard AR-G2 rheometer (filled circle G' and inverted filled triangle G'') versus the RheoDSC setup (open circle G' , open triangle G'') with a controlled oscillatory stress of 5,000 Pa. Both cross-over specifications are within supplier tolerance

is a viscosity calibration standard from Brookfield, with a steady zero shear viscosity of 59.20 Pa s at 25 °C.

Figures 3 and 4 show the comparison between the data obtained in the RheoDSC and measurements performed on a standard AR-G2 rheometer setup with a 40 mm steel parallel plate geometry and a Peltier temperature control element. In Fig. 3, the oscillatory data for the silly putty sample is shown. As can be seen in this figure, both the storage modulus G' and the loss modulus G'' modulus measured by RheoDSC agree well with the data obtained by a conventional rheometric experiment on the AR-G2. The calculated cross-over parameters are summarized on the curve, and are within the tolerance specifications of the supplier. A similar agreement between the measurement in the RheoDSC and in a conventional setup was found for the other two samples.

To point out the range of measurable viscosities that the RheoDSC can handle, the flow curves of the three samples under investigation are shown in Fig. 4. The results were obtained using a steady-state stepped stress ramp. The viscosity levels measured in the RheoDSC acceptably reproduce the levels measured in the conventional setup for all three samples. For the lower viscosity Brookfield oil, the resulting torque is well below 0.1 μNm at shear rates below 0.1 s⁻¹ and thus is approaching the minimal instrument torque limit of 0.01 μNm .

DSC calibration

The calorimetric part of the instrument is based on the Tzero DSC principle [7, 8]. Indeed, the Tzero DSC cell of the TA Instruments Q2000 DSC is designed for usage of an extended heat flux equation. This specific T4 calibration [7, 8] makes corrections in which the heat capacity and the

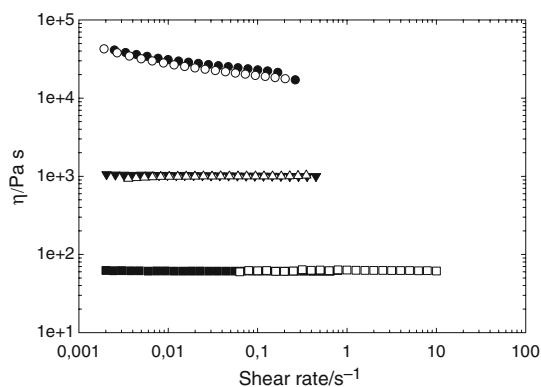


Fig. 4 Continuous flow curves for the three calibration samples; PDMS silly putty (*circles*), Rhodorsil 47 V (*triangles*) and a Brookfield oil (*squares*); comparison between the standard AR-G2 (*black*) and the RheoDSC setup (*white*). Imposed stepped shear stress ranged 5,000–0.05 Pa, depending on the viscosity of the sample

heat resistance of sample and reference side are calculated for all temperatures. To determine the thermal capacities and resistances required for this approach, a dedicated calibration procedure is followed.

Figure 5 shows the influence of the modifications on the heat flow signal: the DSC cell was calibrated without modifications (without insert, with normal lids) and subsequently a heat flow measurement was done with the RheoDSC set-up. This means that the experimental setup used in Fig. 5 consist of the DSC cell with the insert of Fig. 2 and in the presence of the rotor, which is not making contact with the sensor. The heating curves shown are heating ramps with heating rates of 5, 10, and 20 °C min⁻¹. The slight curvature of the baseline at higher temperatures results from the larger influences of the cell modification at temperatures above 100 °C. For subsequent heat-cool cycles, all heating curves are reproducible.

In Fig. 6, the heat flow signal for an indium temperature calibration and cell constant calibration is shown

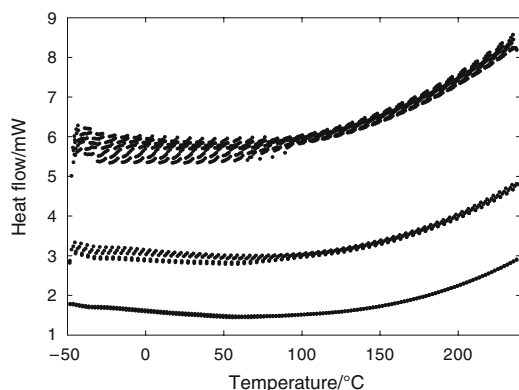


Fig. 5 Heat flow signal for heating ramps at 5, 10, and 20 °C min⁻¹ from -50 to 240 °C. All modification elements around the cell and no baseline correction performed

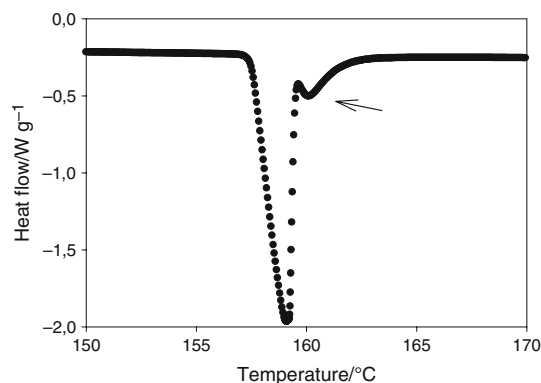


Fig. 6 DSC peak of Indium melting for calibration (all cell modifications present, rotor without contact). An anomaly possibly introduced by an imperfect T4 calibration in the RheoDSC set-up is indicated by an *arrow*

(experiment run in calibration mode). The cell constant is the ratio of the standard melting enthalpy of indium over the value derived from the calibration curve. A single point temperature correction is made by shifting the temperature over the difference between the standard melting temperature of indium and the melting temperature found from the calibration measurement. In the calibration experiment, a shoulder is observed at the high temperature side of the melting peak of the indium sample. This might indicate the importance of new heat flow paths in the RheoDSC setup not taken into account in the Tzero DSC approach. Nevertheless, the cell constant (1.58) and the temperature shift ($\Delta T = 0.9$ K) of the indium calibration in the RheoDSC setup do not significantly differ from the calibration parameters previously obtained for the same cell without modifications. This is due to the great care taken in the design modification.

RheoDSC measurement

To illustrate some capabilities of the new RheoDSC design, the crystallization of PCL will be discussed. The PCL used in this work was purchased from Aldrich and has a number averaged molar mass ranging from 70,000–90,000 g mol⁻¹. PCL melts at a temperature of ca. 60 °C and is stable in an inert environment up to 300 °C. The non-isothermal crystallization rate depends on the cooling rate and the corresponding crystallization temperature typically lies between 10 and 40 °C. The crystallization of PCL is frequently studied by rheology and calorimetry [9, 10], which makes it a good material to show the advantages of the technique.

Three experiments will be discussed. In a first experiment, a comparison between the RheoDSC technique and the stand-alone rheology and DSC is made. The other two examples contain rheological experiments during the DSC

measurement. First, a small amplitude oscillatory shear flow measurement is sensing the material's visco-elastic behaviour without noticeable influence on the crystallization behaviour. Second, continuous flow can be used to directly measure the viscosity. In this continuous flow step, a sufficiently high shear stress can accelerate the crystallization rate, which is known as stress-induced crystallization [11].

The experimental temperature profile is comparable to standard DSC profiles. It starts with an isothermal segment of 15 min at 100 °C to completely erase thermo-mechanical memory. Subsequently cooling and heating ramps are performed.

Rheology and calorimetry of PCL: comparison between RheoDSC and stand-alone techniques

The rheological oscillatory measurement is performed at a temperature of 100 °C and a stress amplitude of 2,000 Pa. The data of these experiments are given in Fig. 7. As could be expected from the calibration, a good agreement between the rheological results of the classical rheological approach and the RheoDSC measurement is obtained. Only at very high frequencies, the RheoDSC data starts to differ due to sample inertia. On this figure, two additional data points, obtained by the RheoDSC in steady shear mode are shown on the viscosity curve. As can be seen, the so-called Cox–Merz rule [12, 13] is obeyed and verified by the current setup.

Figure 8a shows the calorimetric data of the RheoDSC experiment for heating and cooling rates of 2.5 and 5 °C min⁻¹. Figure 8b shows a standard Q2000 DSC measurement for comparison. Good agreement for temperatures of the melting and crystallization peaks can be observed. The contact of the rotor on the sample causes a slower stabilization of the heat flow signals, as is clearly

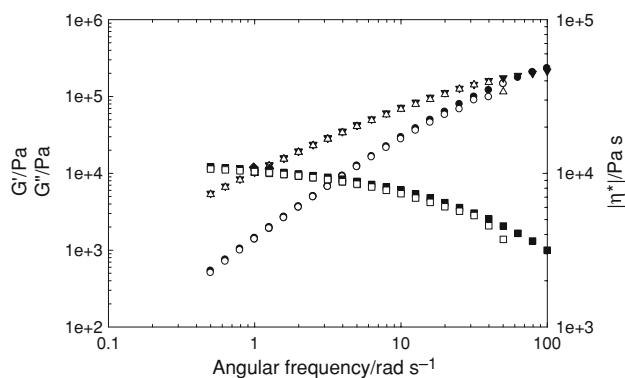


Fig. 7 Oscillatory flow of PCL at 100 °C. Black symbols represent the data from the AR-G2, the white symbols are from the RheoDSC. Two data points (black diamonds) from continuous shear at shear rates around 1 s⁻¹ are shown to prove applicability of the Cox–Merz rule

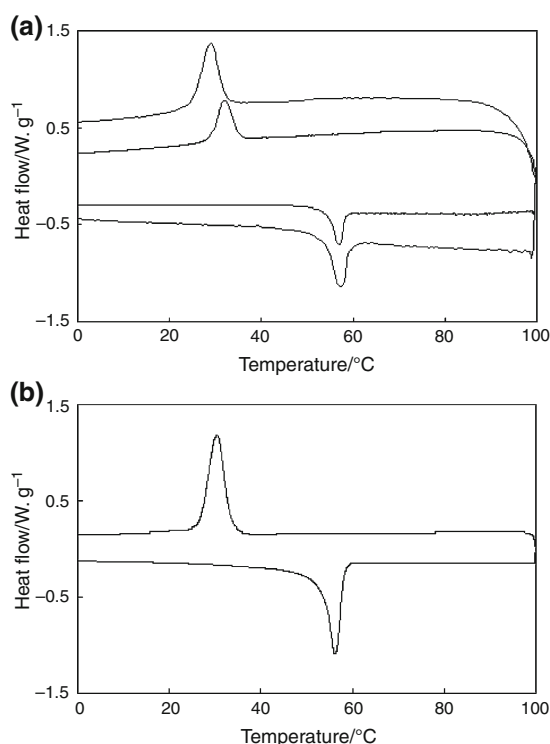


Fig. 8 Heat flow curves for polycaprolacton with ramps from 100 to –20–100 °C: **a** RheoDSC at heating and cooling rates of 5 and 2.5 °C min⁻¹; **b** standard DSC at 5 °C min⁻¹. To compare the results, the onset temperature values of the melting and crystallization peaks are summarized in Table 1. A fair agreement is obtained between a standard Q2000 DSC measurement (no flow) and the RheoDSC data without flow (no flow) and with oscillation or rotation. In the applied conditions, shear-induced crystallization is not playing an important role

observed at the start of the cooling segments (near 100 °C). At 2.5 and 5 °C min⁻¹, the stabilization takes 10 and 20 °C, respectively, indicating a relaxation time constant of the order of 4 min.

In order to improve the signal to noise ratio of the thermal signal by minimizing the effects of the cell modifications, larger sample masses are used as compared to classical DSC (masses ranging from 10 to 20 mg, rather than 1 to 10 mg). This, however, will also lead to a slower stabilization of the heat flow signal during non-isothermal measurements.

RheoDSC measurement in small amplitude oscillatory shear flow mode

One of the aims of the RheoDSC development is to measure viscosity data, or more generally rheological data, simultaneously with heat flow data for the same sample. To minimize the influence of the imposed flow on the transformation kinetics, small amplitude oscillatory shear flow is imposed.

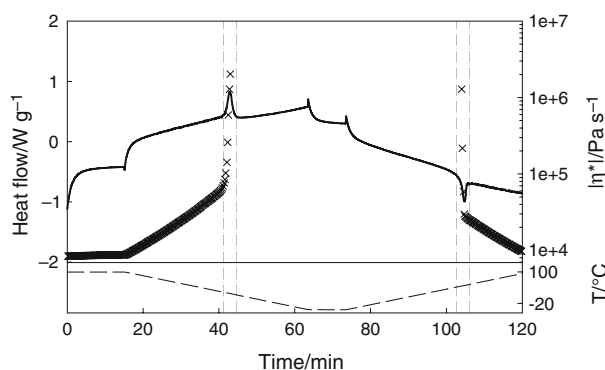


Fig. 9 RheoDSC measurement on polycaprolacton with cooling and heating ramp at 2.5 °C min^{-1} and oscillatory flow with $\omega = 1\text{ rad s}^{-1}$ and $\sigma = 2,000\text{ Pa}$ after a conditioning step at 100 °C for 15 min. Upper graph shows simultaneous measurement of heat flow (black line) with the modulus of the complex viscosity (crosses); temperature profile (dashed line) is shown in the bottom graph. Crystallization and melting are indicated with dash-dotted boundary lines

Table 1 DSC data for the heating and cooling of polycaprolacton, compared between standard Q2000 DSC (no flow) and RheoDSC (no flow, oscillation and continuous)

Heating rate/ °C min^{-1}	DSC			
	No flow	No flow	Oscillation	Rotation
2.5	54.8	54.6	54.6	54.4
5	54.5	53.4	53.9	53.6
-2.5	34.9	34.0	34.2	34.6
-5	32.1	30.5	31.0	31.3

The values are the peak onset temperature data in °C

The resulting signals of heat flow, viscosity and temperature are shown in Fig. 9. The crystallization and melting temperatures obtained from these experiments are in agreement with the values obtained during conditions without imposed flow (see Table 1, in which also the data for another cooling/heating rate is shown). As expected, the onset of the calorimetric crystallization exotherm coincides with the fast increase of the viscosity. Subsequently, the observed viscosity for the crystalline PCL is leveling off at 10^7 Pa s as a result of the contribution of the compliance of the instrument setup to the observed strain. Therefore, the corresponding data is excluded from Fig. 9. When the material melts, the viscosity decreases sharply.

RheoDSC measurement in steady shear flow

In the last measurement, a steady shear flow with an imposed stress of $2,000\text{ Pa}$ is exerted on the PCL sample that undergoes a temperature profile with heating/cooling rates of 2.5 and 5 °C min^{-1} . The RheoDSC curve is given in

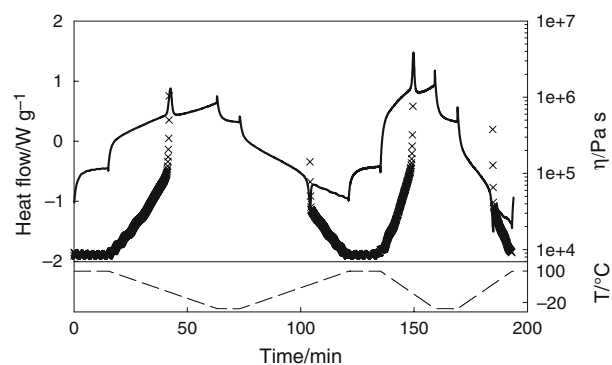


Fig. 10 RheoDSC measurement on polycaprolacton with heating and cooling ramps of 2.5 and 5 °C min^{-1} and continuous flow with $\sigma = 2,000\text{ Pa}$ after a conditioning step at 100 °C for 15 min. Upper graph shows simultaneous measurement of heat flow (black line) with the viscosity (crosses); temperature profile (dashed line) is shown in the bottom graph

Fig. 10. The resulting values of the melting and crystallization temperature are included in Table 1. Note that for all four peaks in the heat flow curve, the viscosity changes happen at the same time and hence at the same temperature. In the semi-crystalline state, no significant amount of flow can occur for the imposed stress of $2,000\text{ Pa}$, resulting in unreliable steady shear viscosity data. Therefore, all data between the rise above 10^6 Pa s during crystallization and the decrease below 10^6 Pa s were discarded.

At cooling rates of 2.5 and 5 °C min^{-1} , the crystallization occurred at nearly the same temperatures as found in the other experiments. This indicates that there is no stress-induced crystallization caused by the imposed continuous flow. Stress-induced crystallization is said to only take place when a minimum level of deformation is applied. The results indicate that an application of a steady shear stress of $2,000\text{ Pa}$ is not sufficient to induce stress-induced crystallization.

Conclusions

By relatively simple modifications, a commercial rheometer and calorimeter are coupled to form a RheoDSC setup. Compared to a previous design, significant improvements have been made that are not invasive for the DSC oven and that facilitate sample handling. The signals of this device were shown to be reliable and of good quality, even when compared with the performance of the two stand-alone techniques. By measuring simultaneously on a single sample undergoing an in situ imposed flow and temperature history, complementary and/or reliable information is obtained in a quantitative way. Measurements on a PCL sample showed the broad applicability of this technique.

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