

Introduction

Transformations in polymers, such as polymerisation, melting/crystallization, and phase separation/remixing, are associated with changes in both rheological and thermal properties. To permit simultaneous calorimetric and rheometric measurements, the RheoDSC was developed. The RheoDSC combines two commercial instruments, a TA Instruments Q2000 DSC and a TA Instruments AR-G2 dynamic rheometer. A rheological measurement is performed on a sample sitting on a sample plate that is on top of the DSC sensor platform. This plate is fixed using insulated screws on an aluminium insert that sits around the base of the DSC sensor. The setup shown in Fig. 1.

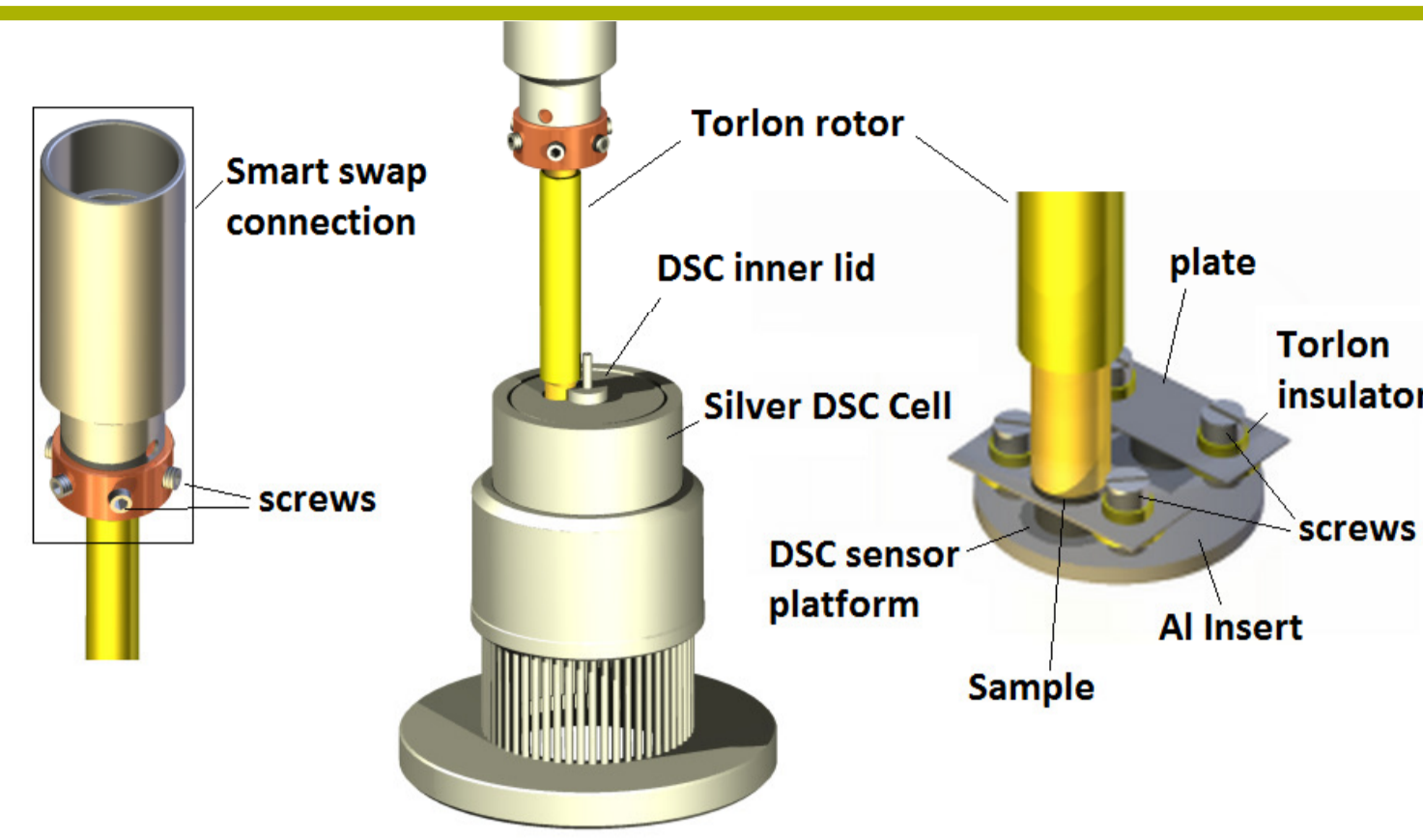


Fig. 1: RheoDSC setup: (left) rotor assembly with connection towards the rheometer permitting rotor alignment, (middle) DSC cell and rotor assembly showing the off-centered positioning of the DSC cell compared to the rotor, and (right) DSC sensor platform with stator assembly, sample, and rotor (right).

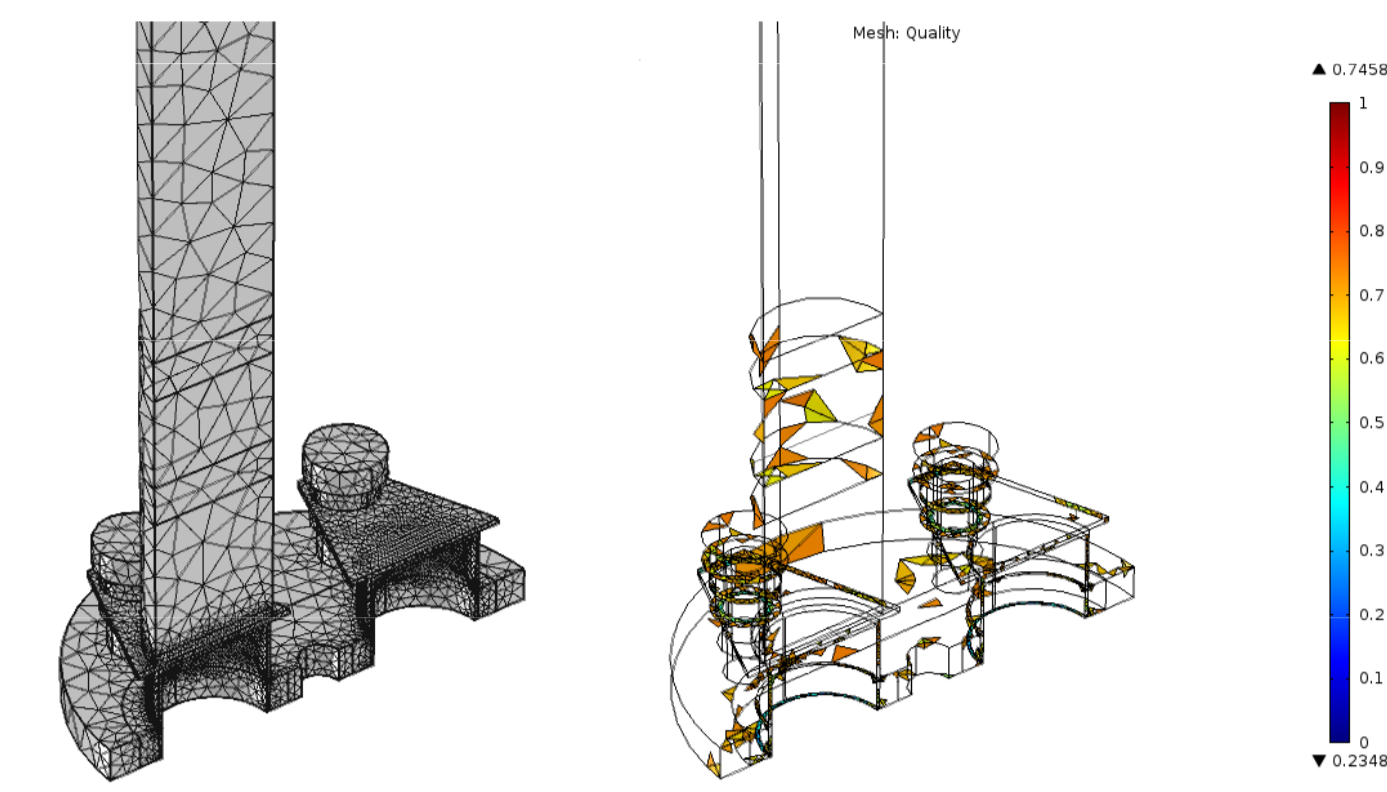


Fig. 2: (left) Meshed geometry with about 36000 elements, (right) Mesh quality depicted for the 5% worst elements.

Finite Element modelling

Through heat transfer modelling with COMSOL we successfully optimized the design and the material selection. All finite element simulations were performed using *Comsol Multiphysics v4.2* using the *Heat transfer module* and the *Chemical reaction engineering module*. The transient simulations were conducted with a direct PARDISO solver and backward differentiation formula (BDF) on a Windows XP 64 bit computer with an Intel® Core™ 2 Quad Q9550 @ 2.83 GHz processor and 16 GB RAM memory. The total assembly has approximately 36000 elements (Fig.2).

Comsol-aided design optimization

For the optimization of the instrument design, DSC experiments were simulated using Comsol. Simulations were made for reacting or crystallizing samples by including suitable models for the transformation kinetics. In this way, the simulated 'measured heat flux' can be compared to the heat release in the sample to evaluate thermal lag and peak distortions.

- Thermal lag simulations (Fig. 3):

In a heat flux type DSC, the heat flow rate to the sample is obtained by multiplying the temperature difference between the sample and reference sensors with a calibration factor. Thermal lag is observed when going from an isothermal to a heating segment. It is due to a different time constant for heat transfer on sample and reference side. The high heat capacity and low thermal conductivity of the rotor cause a slow equilibration and a considerable baseline shift upon heating. Both can be reduced by balancing sample and reference side by placing a PAI tower on it.

- Rotor material (Fig. 4)

Different rotor materials were evaluated for isothermal and nonisothermal conditions. For more conductive materials, more heat will flow into the rotor, leading to an important baseline in nonisothermal experiments. Subtracting the baseline shows that the reaction exotherm observed in ΔT_{SR} is only slightly deformed for PAI.

- Rotor design (Fig. 5)

To further reduce the heat conduction from the sample to the rotor, small holes were drilled in the lower section of the rotor. For crossed holes of 1.75 mm, the baseline offset is strongly reduced, as less rotor material is heated up.

- Validation (Fig. 6)

Experiments with the different rotor designs for the crystallization of an ethylene-vinyl acetate copolymer confirm the strong reduction of the baseline offset using the crossed holes rotor as well as the limited differences in peak distortion.

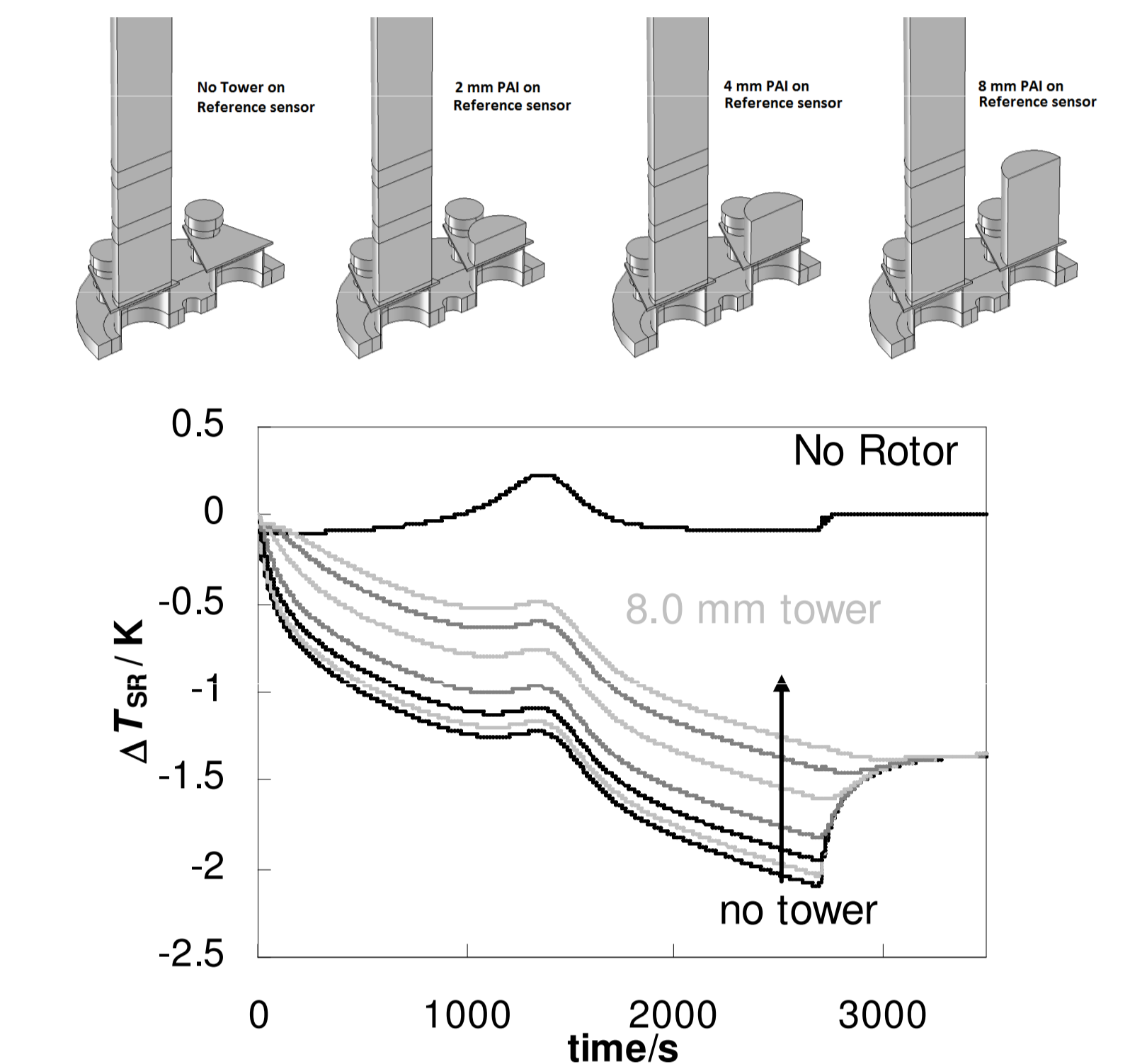
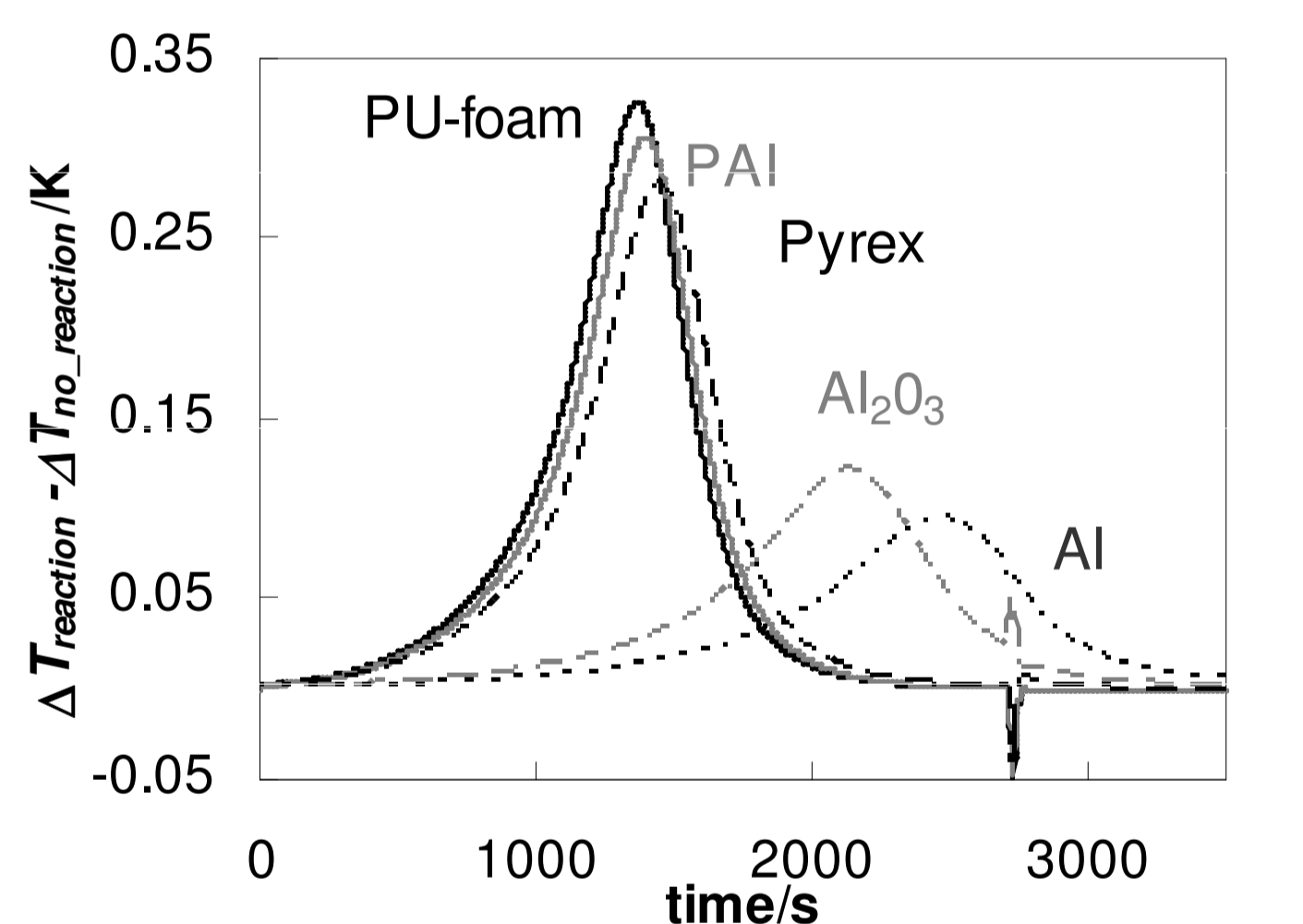
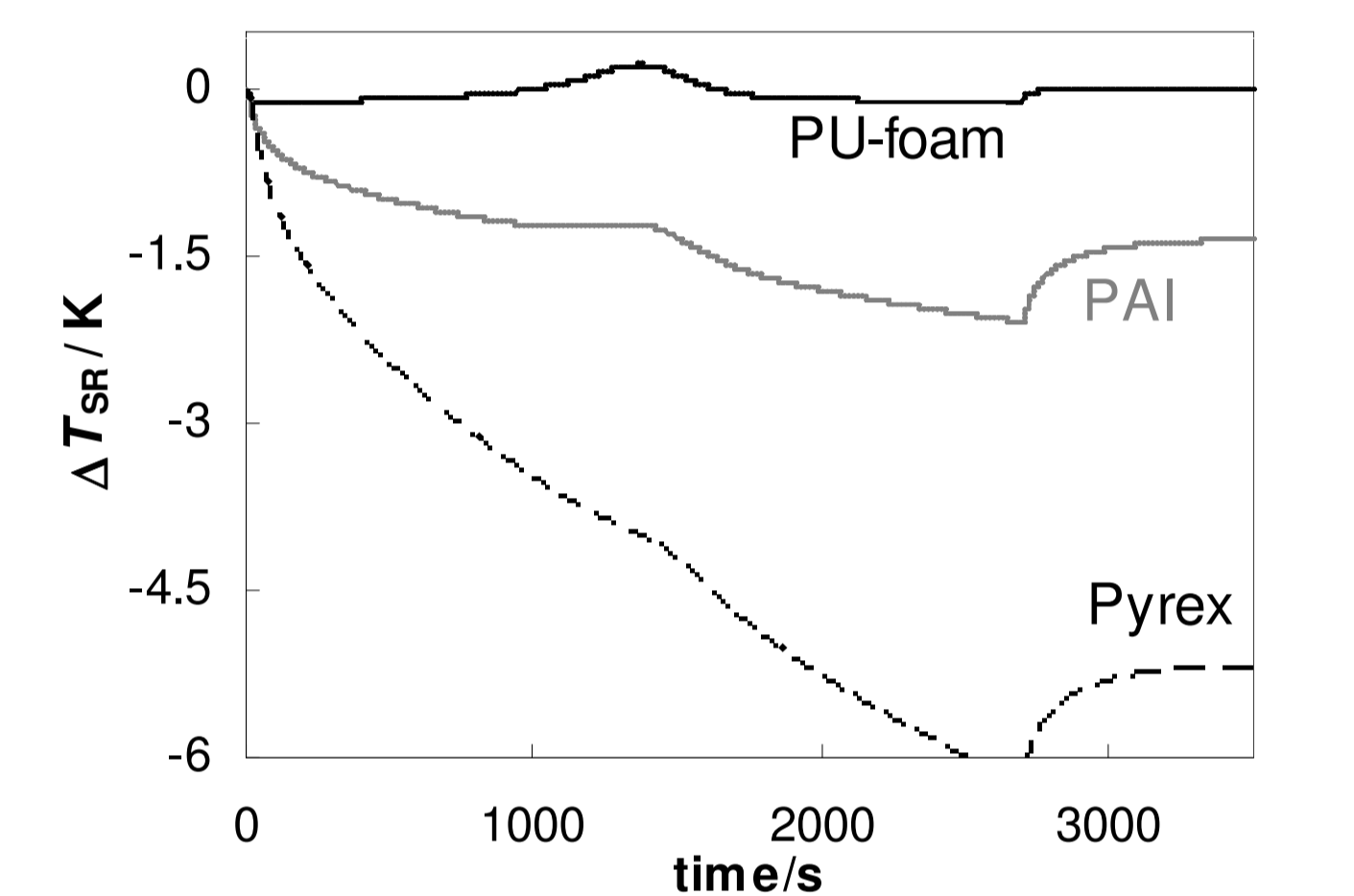
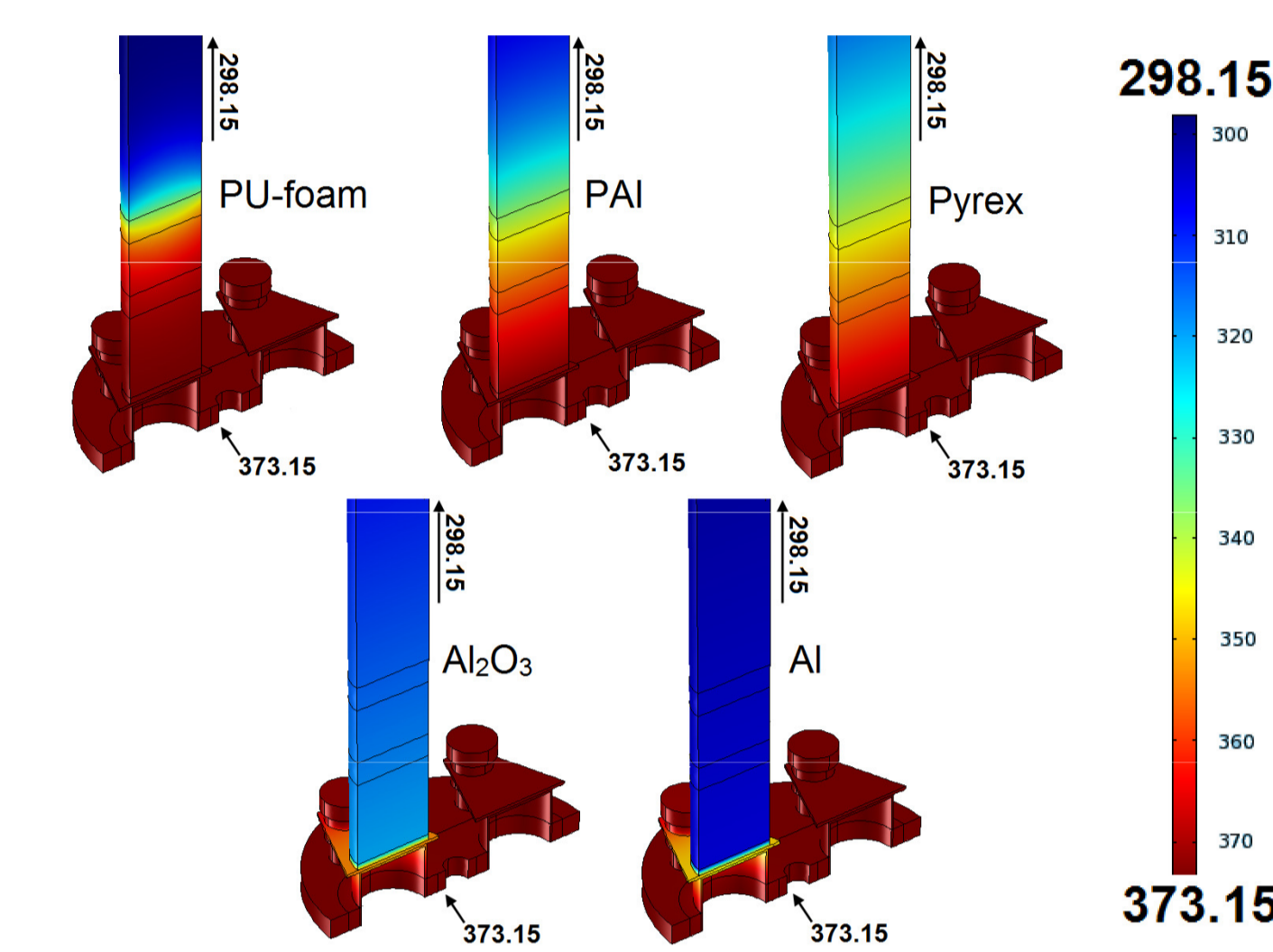


Fig. 3 Reduction of the thermal lag in RheoDSC by placing a cylinder in PAI, the rotor material, on the reference side to equilibrate the unbalance. (top) Geometrical model depicting PAI towers of different heights on the reference sensor. (bottom) Temperature difference between sample and reference sensor, ΔT_{SR} , for the cure of a thermosetting resin for different tower heights (no tower, 0.4 mm, 1 mm, 2 mm, 4 mm, 6 mm and 8 mm) of PAI towers on the reference sensor side and for comparison a setup with no rotor on the sample (heating from 25 °C to 250 °C at 5 K min⁻¹).

Fig. 4: Simulations for selecting the rotor material (top) Temperature distributions in the RheoDSC setup for different rotor materials for an isothermal at 100 °C. (mid) Temperature difference between sample and reference sensor, ΔT_{SR} , for different types of rotor materials. Simulation of non-isothermal cure experiments of a thermosetting epoxy amine (25 °C to 250 °C at 5 K min⁻¹). (bottom) Contribution of the reaction exotherm to ΔT_{SR} .

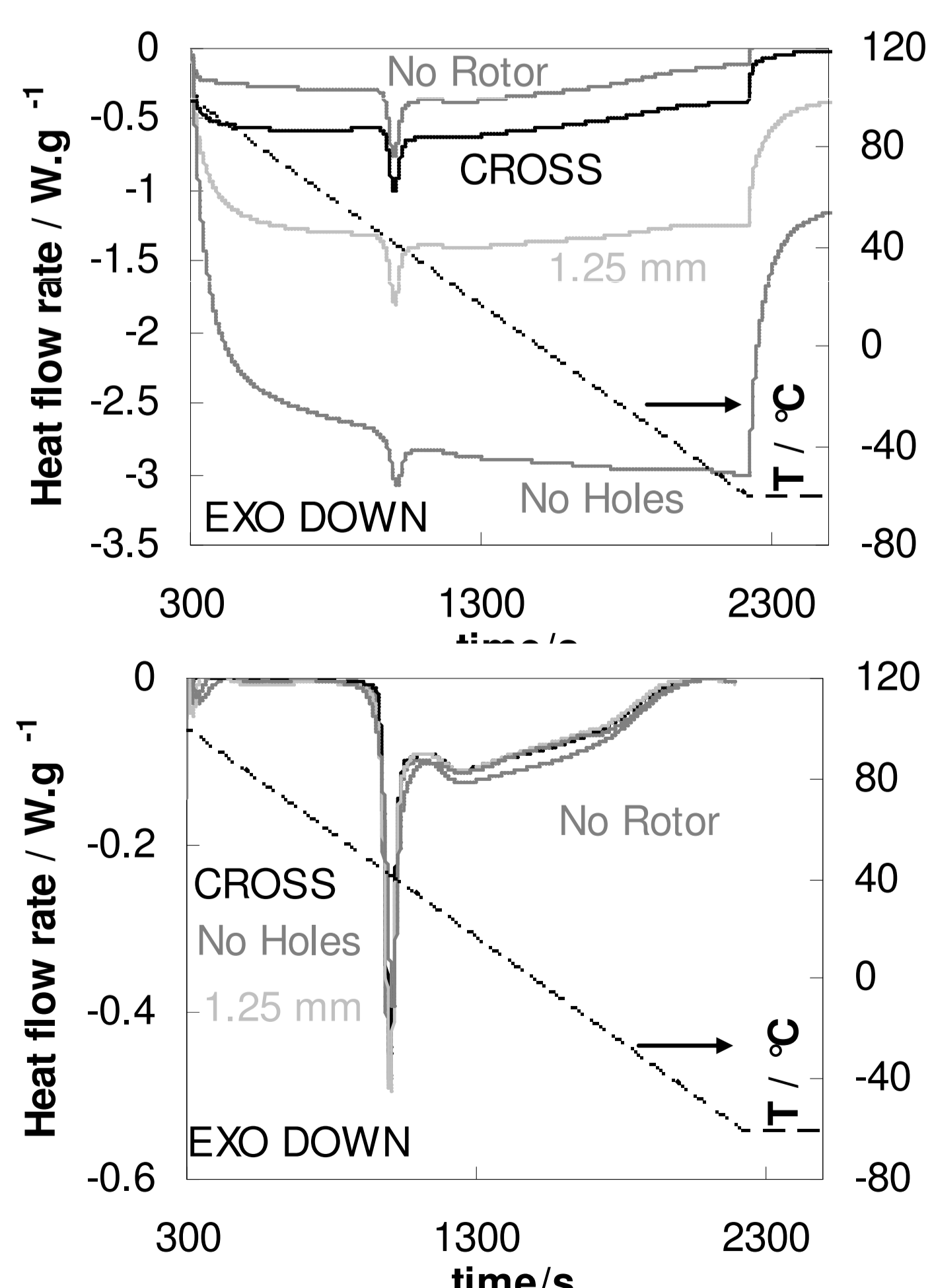


Fig. 6.: Heat flow rate signal for a cooling experiment of semi crystalline polymer (EVA 33) from 100 °C at 5 K.min⁻¹ towards -60 °C with the different rotor setups without (top) and with (bottom) subtracting a baseline.

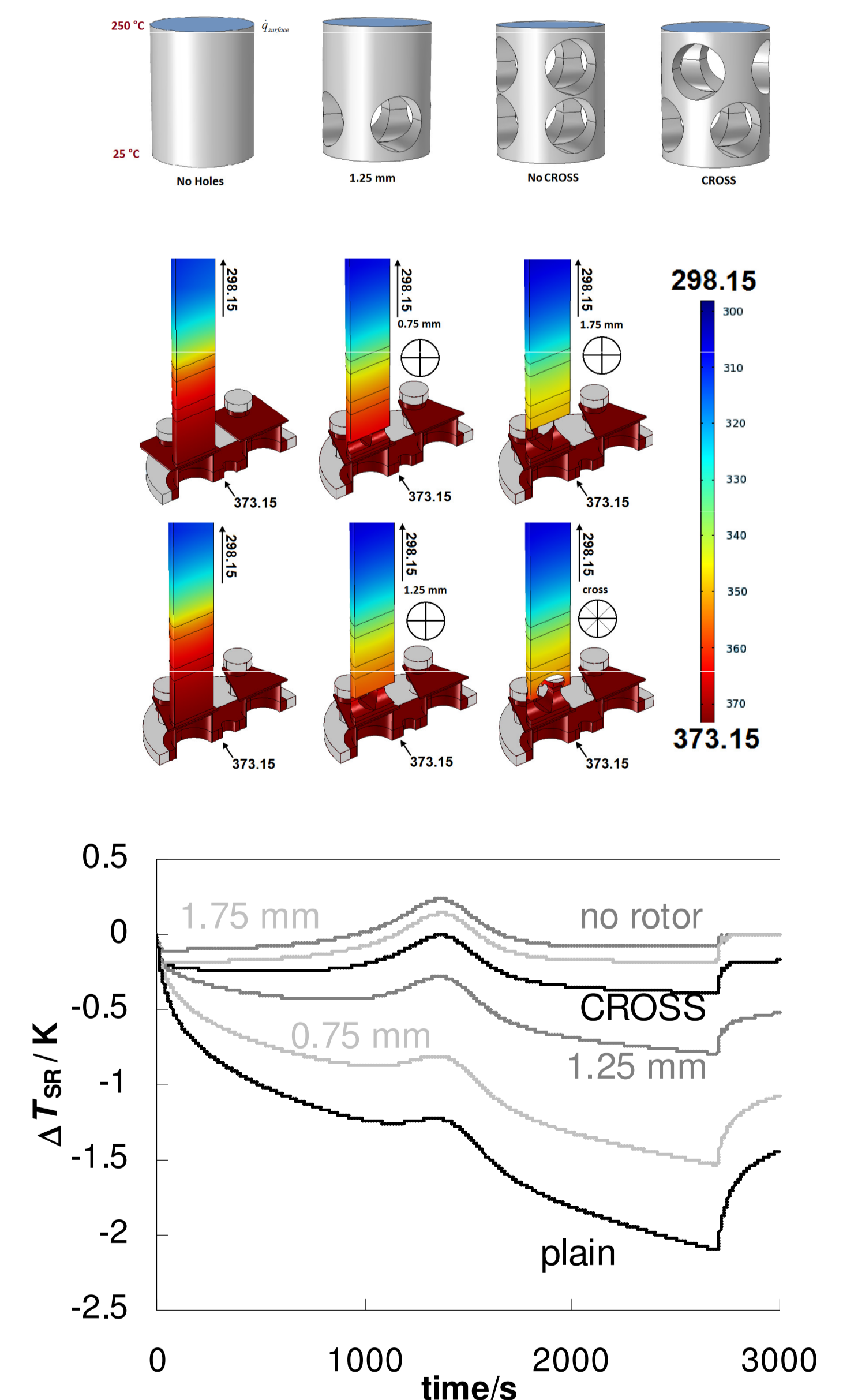


Fig. 5: Simulations for optimizing the rotor geometry. (top) Geometrical representation of modified PAI rotors. (mid) Simulated temperature distributions in the RheoDSC setup for a PAI rotor with two perpendicular holes with a radius of 0.75 mm, 1.25 mm, and 1.75 mm, and a rotor with two levels of holes in a cross pattern (cross) indicated with the pictogram, simulated for an isothermal at 100 °C. (bottom) Temperature difference ΔT_{SR} for the different rotor designs. Simulation of non-isothermal cure experiments of a thermosetting epoxy amine (25 °C to 250 °C at 5 K min⁻¹).