	Experiment title: The morphology of expandable thermoplastic polyurethane during high temperature treatments under supercritical CO2	**Experiment number**: 26-02-873
Beamline: BM26B	**Date of experiment**: from: 26/11/2018 to: 30/11/2018	**Date of report**: 01/02/2019
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino (hermidam@esrf.fr)	*Received at ESRF:*

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Report:

The thermoplastic polyurethane (TPU) materials under investigation consisted of urethane-linked soft (polyTHF, Mw=1000 g/mole) and hard segments (4,4'-MDI chain extended with 1,4-butanediol), referred to as SS and HS. One TPU grade had a low (approx. 37%) the other a high (approx. 55%) HS content. Blends of these two grades at 20/80, 50/50 and 80/20 ratio were also studied. The experimental plan consisted of two parts (see experimental proposal).

Experiment 1: Studies of (TPU) samples loaded in the High Pressure (HP) sCO_2 cell.

Experiment 2: Heating TPU samples at 10°C/min from room temperature to above the final melting point (250°C) using a standard Linkam hot stage while collecting SAXS and WAXD data.

Experiment 1: We encountered multiple technical malfunctions with the high pressure set-up during this session. These malfunctions, including the breakdown of the HP pump and leaking of the cell at higher temperatures and pressures were solved during the beam time but this went at the expense of beam time by which not all planned experiments could be conducted.

In order to use the remaining beam time as efficiently as possible, an experimental protocol deviating from the original proposal was executed. SAXS and WAXD data collection was started at a certain temperature and pressure above the supercritical point of CO_2 (31.1 °C and 73.9 bar) and the temperature was ramped without further adding CO_2 which lead to an autogenic pressure increase. The theoretical and experimentally realized T-p evolutions are given in Figure 1. Clearly, the experimental T-p evolutions deviate from the theoretical path (red curve). This resulted from CO_2 leakage of the HP cell above a certain T-p condition. This leak was however reproducible, which allowed continuing the experiments (under non-ideal conditions).

Prior to the pressure-temperature ramps as indicated in Figure 1, SAXS and WAXD patterns of the TPUs at RT in the absence of $scCO_2$ were taken as a reference. In a second step the TPU material was brought to the starting T-p condition and left there for 20 min to reach the CO_2 absorption equilibrium. Once equilibrated the TPUs were subject to the Figure 1 pressure-temperature ramps. The three steps in each measurement are clearly visible in the acquired data, of which a typical WAXD data set in Figure 3 serves as an example. The data analysis is in progress.

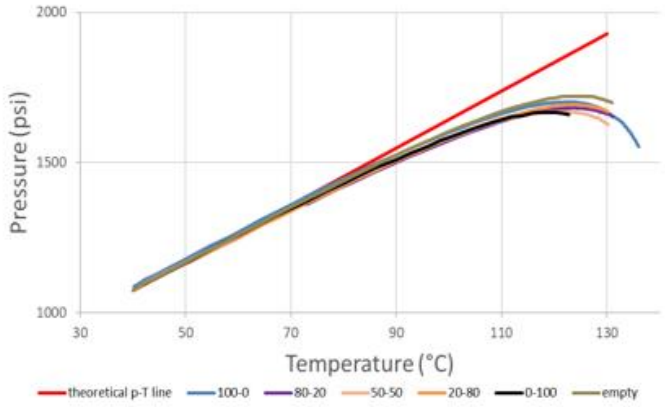

Figure 1: Theoretical (red) and experimental (other colors) T-p evolutions for the different samples in the presence of supercritical CO_2. The evolution of the cell without sample (empty) has been added as well.

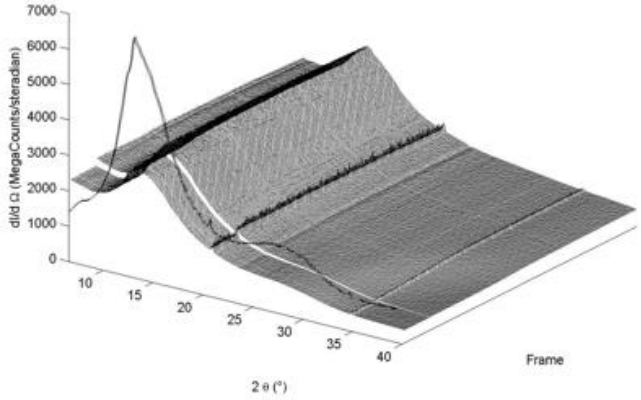

Figure 2: TPU S-H 0-100 WAXD data.

Experiment 2: Because of the experimental problems, also in this case the original experimental plan was modified. TPU samples were cooled at 10°C/min from above the melting point (250°C) to below the glass transition temperature (-70°C) and reheated at the same rate using a standard Linkam hot stage while collecting SAXS and WAXD data. Cooling induced HS phase separation and crystallization while during heating melting and remixing is observed in the time resolved SAXS and WAXD data. The SAXS data were interpreted in terms of irregular two phase structures (hard and soft phase) and making use of so-called clipped Gaussian random field model, Figure 3 [1]. The WAXD scattering patterns are a superposition of diffraction peaks originating from the crystalline HS and an amorphous halo from the SS. The WAXD data were analyzed by simultaneously fitting both contributions to the scattering pattern. From this information the crystal unit cell evolution and the crystallinity is extracted. Correlations between morphological features at SAXS and WAXD lengths scales are currently being made. It appears that only the pure sample with high HS content displays a sufficiently high crystallinity and crystalline perfection for an in depth, reliable analysis. Follow up experiments in the future, should therefore focus on this particular material.

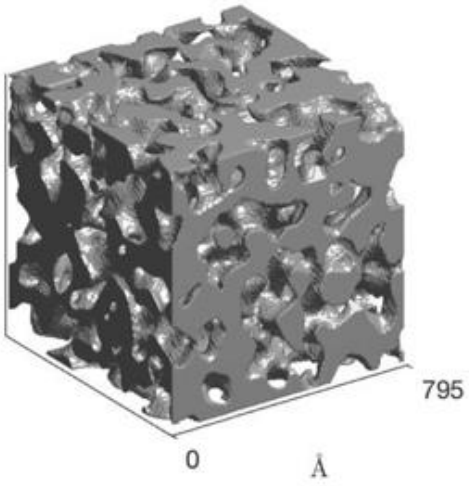

Figure 3: 3D representation of a TPU material containing 50 % HS (grey) at 30 °C as derived from SAXS data and using a clipped Gaussian random field model.

[1] C. J. Gommes, "Stochastic models of disordered mesoporous materials for small-angle scattering analysis and more," Microporous Mesoporous Mater., vol. 257, pp. 62–78, 2018