High pressure calorimetry as a tool for process optimization

GENERAL INTRODUCTION

The thermal behavior of materials submitted to high pressure processes during manufacturing or transformation may be misunderstood if their physicochemical properties are determined under normal pressure conditions. Although calorimetry has been extensively used to assess the subsequent effect of material exposure to high pressures, it can be noticed that high pressure calorimetry (or calorimetric experiments directly operated at high pressures) could be more widely employed.

Originally developed for the field of gas hydrate formation / dissociation, SETARAM Instrumentation High Pressure systems have now been adapted to a wider range of calorimeters and applications for the polymer, food, pharmaceutical, and energy industries.

Based on the 3D sensor technology DSC and calorimeters have been designed with vessels operating up to 1000 bar and temperatures between –130°C and 800°C. A dedicated high pressure panel (FLEXI HP 1000) is attached to the HP calorimeters to cover the pressure range either under controlled pressure scanning or isobaric conditions.

This approach, together with the Joule effect technology used to calibrate 3D sensor DSC and calorimeters, allows for the sensitivity of the instrument (i.e. the electrical signal / evolved sample heat effect ratio) to be pressure independent. It avoids repetitive and long standard melting calibration procedures at each tested pressures.
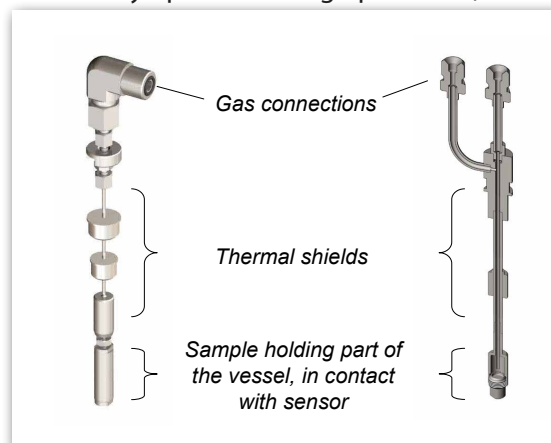

Figure 1 – Schematics of the high pressure vessel used with MICROCALVET (left, up to 400 or 1000 bar) and CALVET PRO (right, up to 400 bar)

1. T$_g$ evolution of an elastomer

INTRODUCTION

When an elastomer is cooled below its glass transition temperature (Tg), it loses its elasticity and becomes brittle. When used as O-rings to seal high pressure systems, their Tg may be shifted to higher temperatures. It is thus of a key interest to determine the limits of use of these elastomers.

EXPERIMENT

In the presented example, pieces of elastomer O-ring were cut, inserted in a HP vessel, and heated between -40°C and 20°C at a rate of 1K/min under isobaric conditions.

RESULTS AND CONCLUSION

As a first approach, the evolution of Tg was described by a linear equation on the tested range with a R^2 value of 1. More tests at different pressures helped at confirming this trend (not shown here).
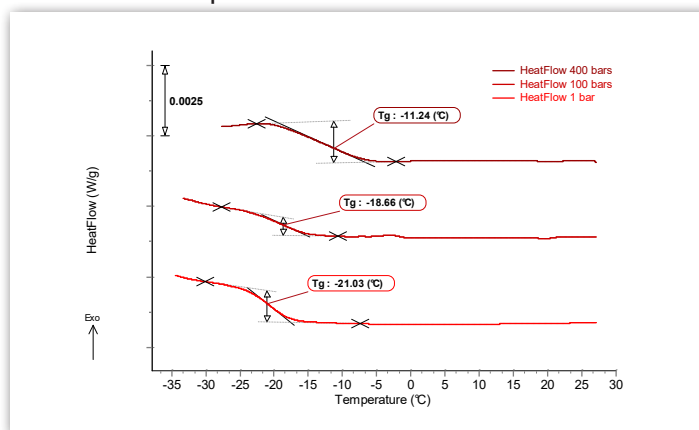

Figure 2 - Determination of elastomer glass transition temperature under 1, 100, and 400bar of nitrogen.
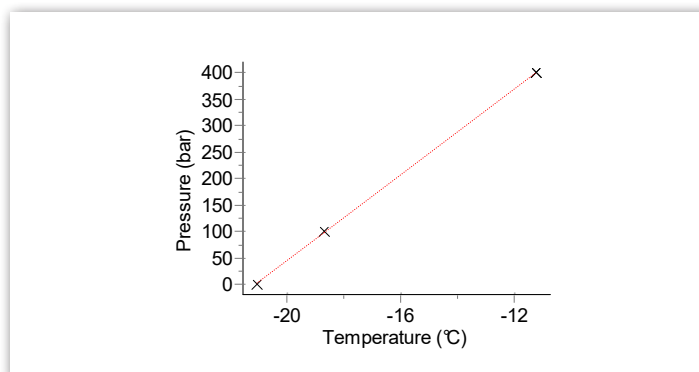

Figure 3 – Evolution of Tg with pressure.

2. Crystallization of margarine

EXPERIMENT

An industrial process of margarine crystallization was simulated by using DSC at a controlled cooling rate of 1 K/min under isobaric conditions.

RESULTS AND CONCLUSION

Experiment pressure has no influence on the enthalpy of crystallization of margarine (Table 1). The maxima of the two characteristic crystallization peaks were shifted to higher temperatures when pressure increased. The results show that the temperature shift becomes less significant when reaching pressures close to 400 bar. Mathematical calculation of the integral functions of heatflow data allows for plotting the crystallization progress vs. temperature.
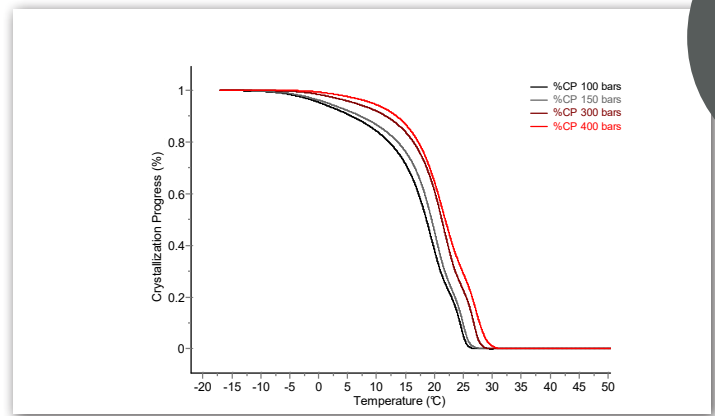

Figure 4 – Isobaric crystallization progress data as a function of temperature at pressures ranging from 100 to 400 bar

Test pressure (bar)	Enthalpy of crystallization (J/g)	Temperature at peak maximum (°C)	
		$T_{m,1}$	$T_{m,2}$
100	-41.81	19.44	24.49
150	-42.29	20.11	24.92
300	-42.03	21.63	26.79
400	-41.59	21.51	27.16

Table 1 - Results of margarine crystallization tests

3. C_P of a polymer used in injection molding

INTRODUCTION

Heat transfer simulation for high pressure manufacturing processes (ex: injection molding) require accurate heat capacity data.

EXPERIMENT

The continuous C_P determination method was applied at pressures from 1 to 350 bar to a polyamide 6 sample. Data were corrected from the heat capacity of the gas, which becomes significant when the test pressure increases.

Figure 5 – Nitrogen pressure dependence of the heat capacity of PA6 on the tested temperature range

RESULTS AND CONCLUSION

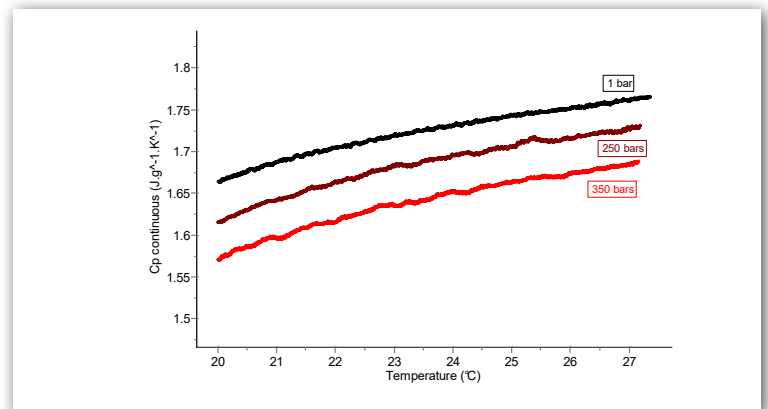At 25°C, the heat capacity drop equals -2.2% at 250 bar and -4.6% at 350 bar

4. Pressure induced phase transition

EXPERIMENT

A Calixarene based sample was tested in isothermal, pressure step mode with CO_2 as a pressurization gas. At a temperature of 0°C, its pressure was quickly raised from 1 bar to 30 bar . An immediate exothermic effect is recorded, corresponding to the heat of compression, followed by two lower intensity and slower kinetics effects.

RESULTS AND CONCLUSION

The first is a pressure induced phase transition, followed by a fast CO2 adsorption. Peak separation calculation allowed assessing the heat of each of these steps.
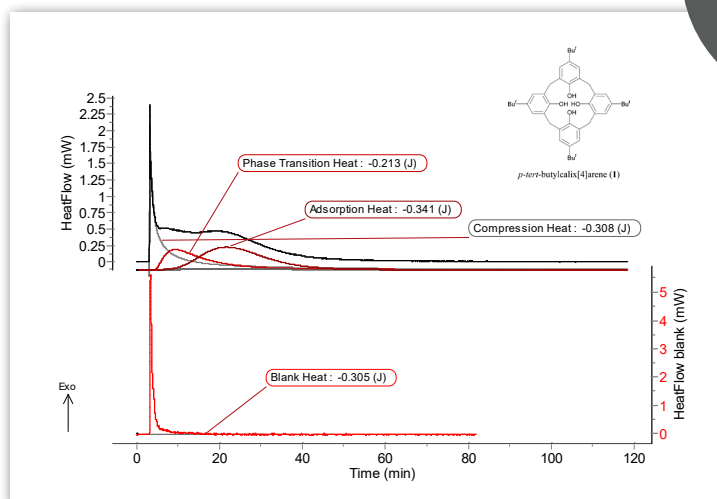
Figure 6 – Heatflow data vs. time during pressure step. Blank experiment allows checking the validity of the peak separation, with a difference of less than 1% between experimental and mathematical heat of compression

GENERAL CONCLUSION

The accurate characterisation of synthesis, transformation or purification processes is very important for industrial applications. Running experiments in conditions close to process ones is essential to avoid false calorimetry data scale up. We developed tools to simulate a large range of high pressure operations, and achieve accurate and reliable scale-up data.

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REIMAGINE MATERIAL CHARACTERIZATION

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