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Design, Specifications and application of a high pressure DSC cell

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Abstract

The construction of a high pressure DSC measuring head for the Perkin-Elmer DSC-7 is presented. The DSC cell is developed to work in a range of temperature from 290 to 570 K at a maximum pressure of 500 MPa using different silicon oils as pressure medium. This calorimeter works with the common heating rates from 0,1 K/min to 30 K/min. The noise of the base line is about 50-100 μW depending on the pressure in question. The repeatability of the base line amounts to 2-3 mW. The new high pressure cell is especially useful for DSC measurements in polymer science preliminary results are presented.

1. DESIGN

To come to an easy construction of the high pressure autoclave a cylinder symmetrical arrangement was chosen (Fig. 1). The autoclave was produced by Sitec AG (Switzerland). The cylinder is closed with two steel stoppers containing six electrical outlets each. The construction has the advantage of a high thermal symmetry for the sample and reference holders. This holders were made similar to the original device but built of aluminium instead of platinum because of the much better thermal conductivity.

The heating respectively measuring resistances employed are original ones from Perkin-Elmer measuring heads. They were insulated with glimmer against the aluminium and fixed with temperature resistant ceramics adhesive. The resistance thermometer is operated in four wire technique.

The thermal insulation of the sample holders against one another is executed by cylinders of glass-ceramics. The geometrical dimension of the glass-ceramics and silicon oil layers were optimised with aid of a finite element simulation programme. If the thickness of the glass-ceramics layer is to great relative to the oil layer, the heat loss is rather large because of the larger thermal conductivity of glass-ceramics. If, on the other hand, the film of silicon oil is to thick the convection produces a noisy heat flux signal.

Because of the buoyancy the sample and reference pans must

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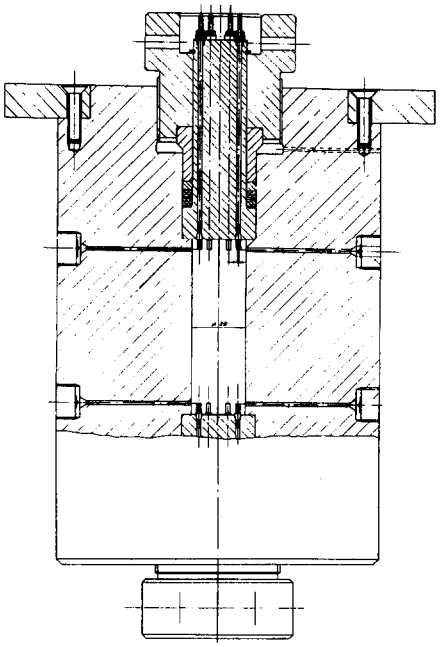

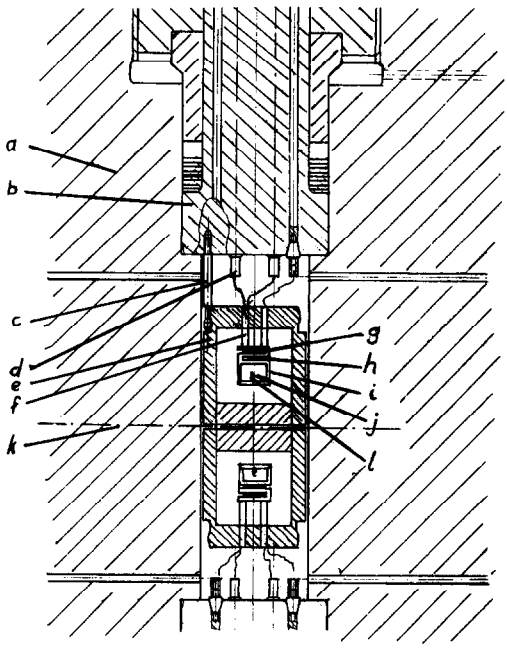

Figure 1. Autoclave. Figure 2. High pressure DSC cell. a autoclave, b stopper, c distance bolt, d electrical outlet, e glass-ceramics, f ceramic lead pipe, g resistance thermometer, h heater, i sample holder, j cavity for sample pan, k symmetry plain, l spring.

be held fast on the bottom of the heaters, this is done by a small spring fixed at the cover of the sample holders which for its part is fastened with a small bolt.

2. HANDLING

2.1 Experimental

One of the larger difficulties is the pressure tight preparation of samples into crucibles whereas cavities must be avoided to prevent deformations of the crucibles under pressure. Different possibilities of sample preparations have been applied successfully:

- pressed samples in Perkin-Elmer "sealed sample pans" and cold welded with a press but using two pans (one inside the other) instead of pan and lid as usual.
- as above, but with a ventilation hole in the upper pan. The ventilation hole was closed under vacuum with a proper adhesive.
- samples with larger volume change were sealed using aluminium foil as lid .

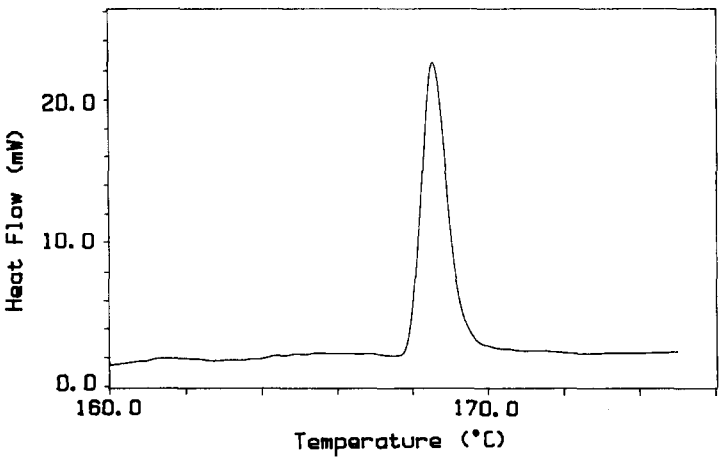

Figure 3. Melting peak of Indium at 400 Mpa, mass: 7.5 mg, heating rate: 10 K/min.

We used different silicon oils (type AK) from Wacker Chemie AG (Germany) as pressure medium. In principle the oil with the largest viscousity is best suited because of the lowest convection, but it tends to solidification at larger pressure. In practice we used AK-2000 for pressure until 250-300 MPa, AK-100 or AK-500 for pressure until 400 MPa and AK-10 for a pressure from 300 MPa to 500 MPa (the number behind AK means viscousity in mm/s^2).

The high pressure DSC must be calibrated due to temperature and heat. As usual we tried to do this with Indium (Fig. 3). Unfortunately neither the pressure dependence of the melting temperature nor that of the melting heat is well known.

Relative to the temperature calibration and its pressure dependence it must be stated, that it is not clear from literature [1,2] whether the authors use the extrapolated onset or the peak maximum as melting temperature, thus there is a lot of uncertainty in these values. On the other hand the temperature dependence of the platinum resistance thermometer is well known [3] and used for temperature correction in the DSC-7. As the pressure dependence of this resistance is important for temperature corrections, we measured it at 300 and 373 K with the aid of the same autoclave. The result is, that the resistance decreases with pressure and that this decrease depends on temperatur. From this an additional correction term is calculated and listed in Table 1. In Fig. 4 the resulting melting temperatures of Indium are plotted together with literature values.

Relative to the heat calibration the situation is rather unsatisfactory, because the pressure dependence of the enthalpy of common used reference materials is not well known. Fortunately the functionality of the power compensated DSC

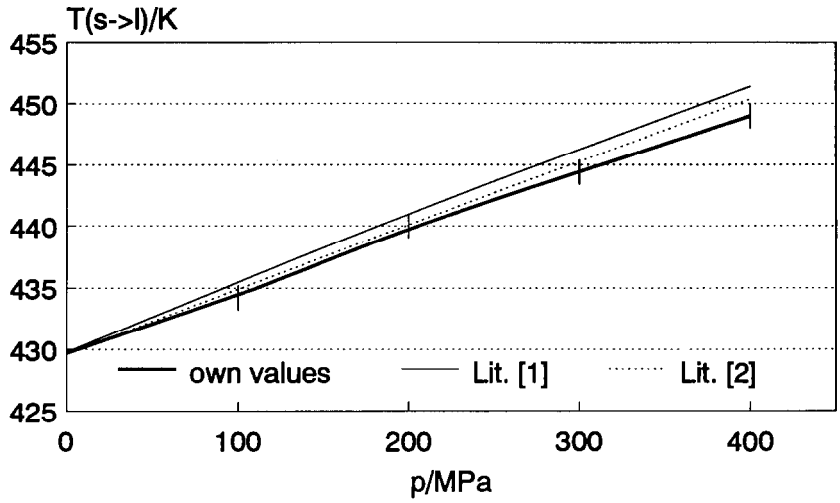

Figure 4. Dependence of melting temperature of Indium on pressure.

Table 1
Pressure dependence of Indium melting temperature

Pressure in MPa	Correction in K	Melting temperature of Indium in K		
		This paper	Lit.[1]	Lit.[2]
1	+0.0	429,7	429,7	429,8
100	+0.6	434,2	435,5	434,9
200	+1.1	440,0	441,0	440,1
300	+1.5	444,4	446,3	445,3
400	+1.9	449,0	451,4	450,4

allows to estimate the pressure dependent calibration factor from the pressure dependence of the heater resistance, leading to a correction factor of about 1.001 per 100 MPa according to the temperature.

Another method is to calculate the enthalpie of melting from high pressure dilatometric measurements using the Clausius-Clapeyron equation.

2.2 Results

As this calorimeter shall be used in polymer science, the first measurements were done with such materials. From Figures 5 to 8 the reader is able to judge the quality (resolution and noise) of the new DSC cell and the applicability to research problems in this field.

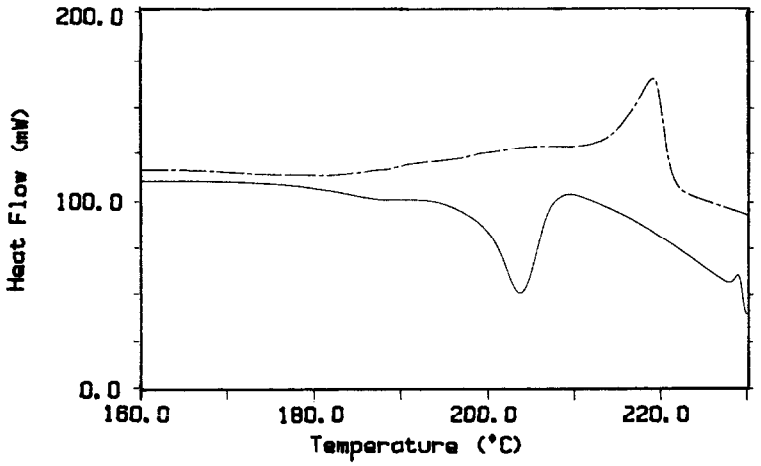

Figure 5. Melting and crystallisation of polyethylene wax at 400 MPa (mass: 16 mg, heating and cooling rate 10 K/min).

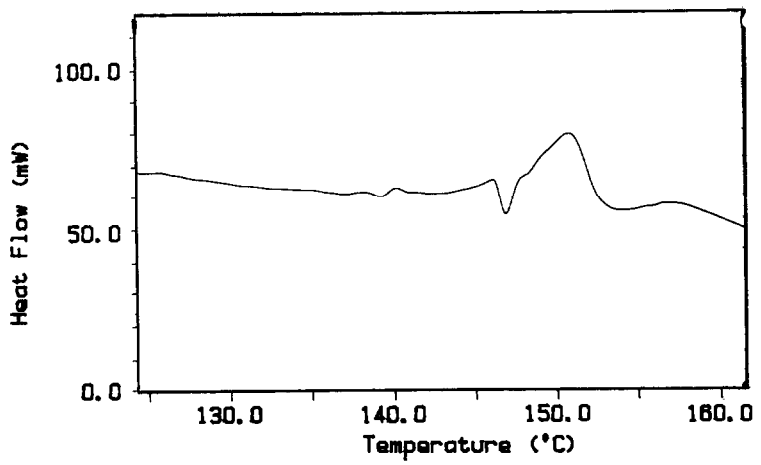

Figure 6. Melting run at 50 MPa of polyethylene wax crystallized at 400 MPa (run following those of Fig. 5) (mass: 16 mg, heating rate: 10 K/min).

3. Acknowledgements

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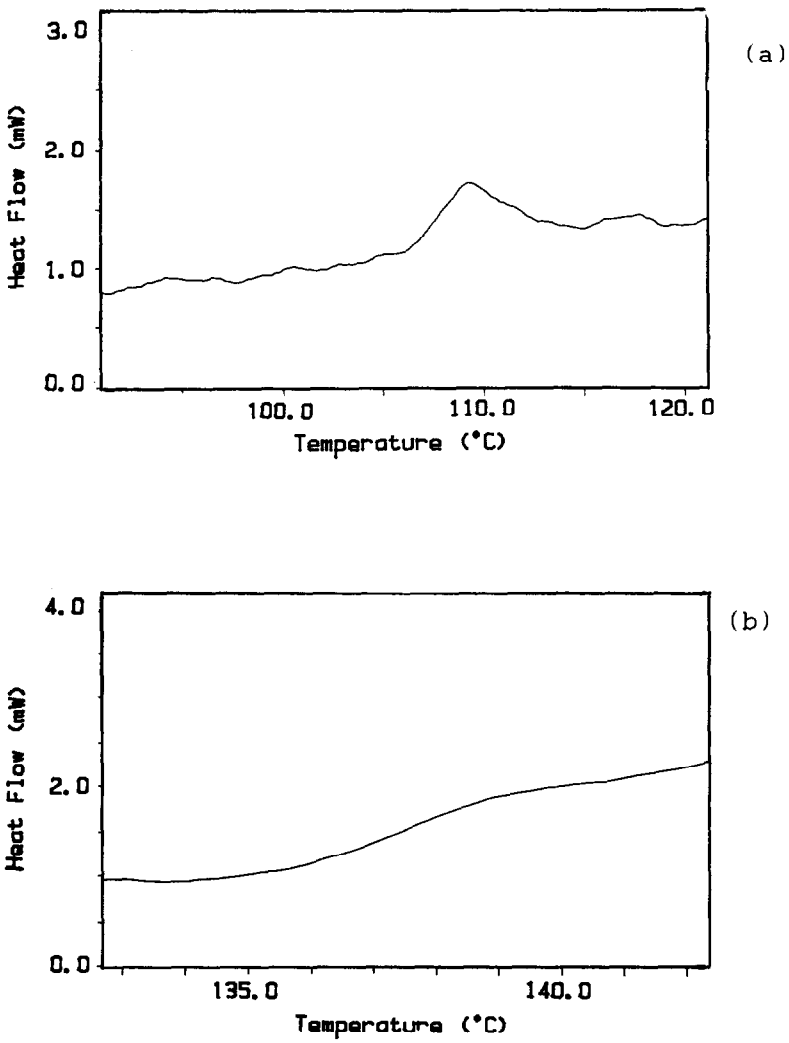

Figure 7. Glass transition of polystyrene at 0.7 MPa (a) and 100 MPa (b) (mass: 17.9 mg, heating rate: 10 K/min).

4. References

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