Detailed Regulations of the RAL-GZ 896 Quality and Test Rules on the Homepage of the Quality Control Association PCM e.V.

1 Area of application

1.1 Definition of terms

PCMs and PCM Composites (PCM-V)
Further examples of PCM Composites:

(Note:
The examples presently included in the Quality and Test Rules, “PCM-graphite matrix, granulate, plaster, wood fibers, PCM foam matrix, PCM foil, PCM textiles (as material, not as finished garments, etc.), all dumpable materials,” are adequate, but will be added to as needed.)

2 Quality Regulations

2.1 Requirements on PCMs and PCM Composites

2.1.3 Cycle Stability (PCMs / PCM Composites)

Quality criteria to be inspected during Cycle Stability Test:

During the Cycle Stability Test, the following quality criteria are to be inspected in the case of PCMs and PCM Composites on heating up and on cooling down:

- Phase transition temperature
- Stored heat

2.2 Requirements on PCM-O

2.2.3 Reproducibility of the phase transition

Quality criteria to be inspected during Cycle Stability Test:

During the Cycle Stability Test, the following quality criteria are to be inspected in the case of PCM-O on heating up and on cooling down:

- Phase transition temperature
- Stored heat

3 Testing Regulations
Test Principles of the Quality Association PCM e.V. for External Monitoring

3.3 Adaptation of the tests to the state of technology

Newly approved measuring methods not included in the Quality and Test Regulations (issued September 2009) of the Quality Committee:

3.6 Special test regulations for PCMs und PCM compounds

3.6.1 Phase transition temperature and stored heat

3.6.1.2 Execution of the measurement

Specifications of the Quality Association PCM for execution of the measurements:

- *Number of samples and measurements*
  At least 3 samples per product must be investigated. At least one measurement must be carried out per sample (consisting of 3 cycles each (heating and cooling ramp) over the temperature range of the complete phase transition). The temperature range must be selected, taking the manufacturer's data into account, such that the sample is not damaged. All measurements on the same material must be made with the same device, to ensure comparability of the results.
  If one of the investigated samples is damaged, two further samples are investigated.
  The test of the product with regard to the tested quality criteria is considered as passed when no damage is ascertained after 3 measurements have been carried out, or a maximum of one case of damage after 5 measurements.

- *Process to ensure thermal balance*

  During measurement, the sample must be isothermal within the degree of precision of the measurement. The processes to ensure thermal balance within the sample vary depending on the method of measurement used:

  a) *Dynamic measurement with constant heating and cooling rate:*

  In the case of dynamic measurements with constant heating and cooling rate, e.g. in Hf-DSC or Calvet calorimeters, a sufficiently low heating and cooling rate must be used. This must be tested once in advance on one of the samples to be measured, by varying the heating and cooling rates. This means halving the heating rate and halving it again until one of the following criteria is fulfilled (meaningful heating rates must be chosen, depending on the device). First, the enthalpy of each heating and cooling ramp is shown in a graph over the temperature, as in Figures 3.6.1.2.A and 3.6.1.2.B. The turning points of the heating and cooling curves are taken into consideration. The maximum permitted heating rate has been reached when:

  i) The temperatures at the turning points of the heating measurements deviate from one another, and the temperatures at the turning points of the cooling measurements deviate from one another, by no more than 0.2 K

or

ii) The temperatures at the turning points of the heating and cooling curves at the same heating rate deviate from one another only up to a maximum of 0.5 K.

The slower of the two heating rates at which one of the criteria is met first, is used as the maximum heating rate for all further measurements on this sample material.

If several phase transitions occur while measuring the material, the criteria must be fulfilled for each phase transition singly.

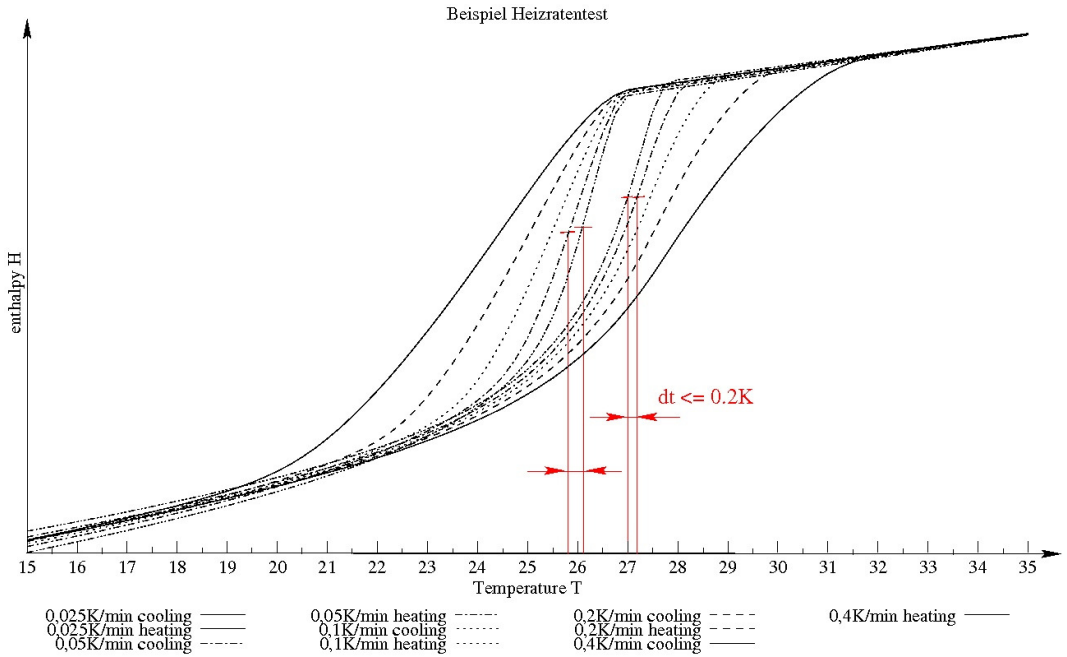

Fig. 3.6.1.2.A: Ensuring the thermal balance in the sample:
Version i): The turning points of the heating and cooling curves, respectively, change by less than 0.2K when the heating rate is halved.

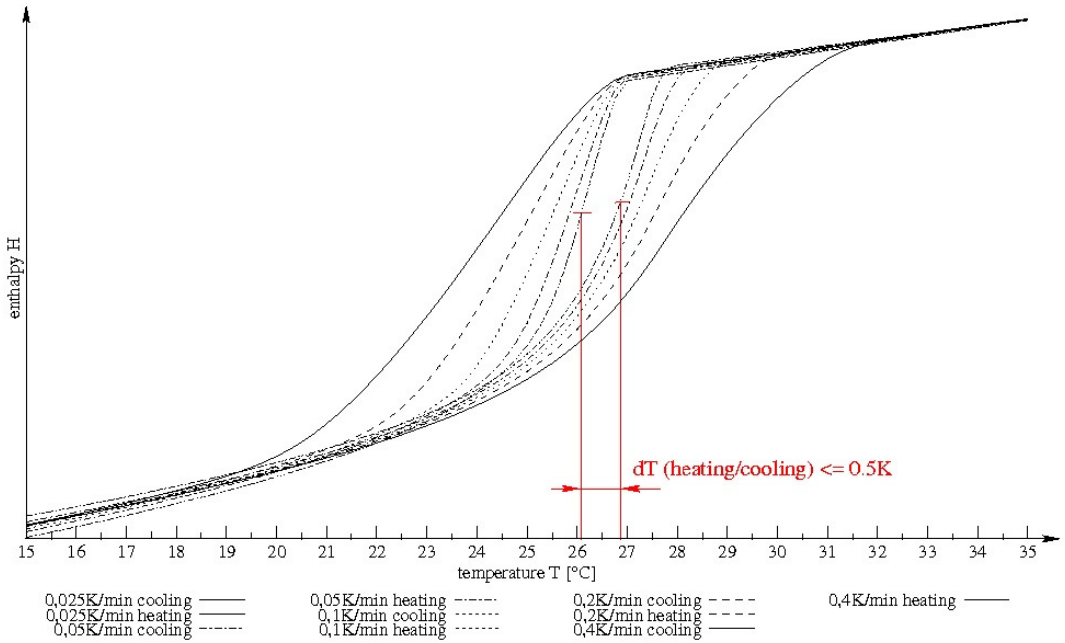

Fig. 3.6.1.2.B: Ensuring the thermal balance in the sample:
Version ii): The turning points of the heating and cooling curves for one heating rate are ≤ 0.5 K apart (not true in this case).

b) In the case of *dynamic measurements using the T-History method,* by analogy, a suitable final temperature for the measurement must be selected. This must be tested beforehand on one of the samples to be measured, by varying the final temperature. A suitable final temperature has been reached when:

i) The respective results of halving the temperature difference between the melting temperature (when heating) and the crystallization temperature (when cooling) and the final temperature change by less than 0.2 K. or

ii) There is a difference of less than 0.5 ° C between the results of heating and cooling measurements.

To check the precision of the temperature, a heating rate or a temperature jump can be selected, at which enthalpy evaluation is no longer possible.

c) In the case of *isothermal measurement (staged measurement) in DSC, or Calvet calorimeters*, a sufficiently long relaxation time must be chosen to allow the sample to attain thermal balance. This can be recognized by a lowering of the measurement signal to the base line.

3.6.1.3 Contents of the Test Results and Rest Report

Specifications of the Quality Association PCM regarding the content of the test results and the test report, over and above the Quality and Test Regulations:

- *Stored heat*

  The interval used must not exceed 1 K. Statements must be made for the temperature range of complete phase transition (heating and cooling) ± 5 K beyond Onset and Offset.
  The statements on the stored heat must always include the latent and sensible portions. This can, however, be emphasized in different ways. The mean values of at least 3 samples must be given, only the 3rd measurement cycle of each measurement being evaluated. The standard deviation of the measurements must be specified.

- *Degree of sub-cooling*

  The degree of sub-cooling is ascertained by determining the nucleation temperature, i.e. the temperature at which phase transition is triggered. For this purpose, if possible, three samples are cycled at least six times in the DSC. If a manufacturer wished to have a larger number of samples tested than is possible in the DSC, another suitable calorimeter may be used. Evaluation takes place from the 3rd sample on, ascertaining the minimum nucleation temperature at which phase transition was reliably triggered in all the cooling measurements. The nucleation temperature being to a certain degree dependent on the size of the sample, the smallest of the measured samples (volume and mass) must also be specified. These measurements may be carried out together with the measurements to determine the phase transition and the enthalpy temperature curve.

3.6.2 Cycle Stability

3.6.2.1 Testing the Quality Criteria

Quality criteria and threshold values to be observed, as defined by the Quality Association PCM:

- *Stored heat*
  It is a fault when there is a deviation of more than -10 % compared to the manufacturer's specifications.

- *Phase transition temperature*
  It is a fault when there is a deviation of more than ±1 K for Onset, peak and Offset temperature.

- *Tightness*
  It is a fault when a leak can be ascertained through purely visual inspection without technical aids.

- *Nucleation temperature*
  It is a fault when the value specified by the manufacturer is exceeded.

- Optionally: *Thermal conductivity* (only if desired by applicant / quality-seal user)
  It is a fault when deviation is more than ±10 %.

3.6.2.3 Making the measurement

Specifications of the Quality Association PCM for determining the temperature ramp:

- *Basis of measurement*

  First of all, the temperature ramp for the cycling must be defined. To do this, a detailed measurement of the overall enthalpy and of the enthalpy-temperature curve must be carried out, following the Quality and Test Regulations and the regulations on the making of measurements. The overall enthalpy is calculated according to the currently applicable specifications for dynamic difference calorimetry (based on DIN EN ISO 11 357). The integration boundaries defined on initial measurement must be retained for all subsequent measurements, so as to ensure comparability. In the further course of cycling, this measurement is used as the initial measurement (Cycle 0). The measuring results are used to determine the switch-over temperatures of the tempering. Any holding times, or minimum or maximum temperatures, must be taken from the manufacturer's data.
  Following initial measurement, cycling takes place until the respective check measurement. The number of cycles must be certified on the basis of temperatures measured in the sample.

- *Temperature boundaries*

  The PCMs are cycled through a specified sequence of heating and cooing periods, under certain circumstances with holding phases.
  To ensure the greatest possible comparability of the results, the sequence of heating and cooling periods must follow a defined course between temperature boundaries that are defined in dependence on the material. The decisive point is that the temperature of the sample at the point farthest from the heating/cooling element is far enough away from the melting point, in order to ensure a complete cycle.
  Two possible sequences of heating and cooling periods are defined below. Deviations in the limit values may be permitted by the Quality Association PCM e.V. in exceptional cases.

  a) Boundaries relative to the peak width

  When the point on the sample that is farthest from the heating surface reaches a temperature of *at least 2.5 times the peak width above the Offset temperature of the heating curve*, the heating cycle is regarded as complete (after any

holding time required by the manufacturer of the PCM). When the point on the sample that is farthest from the cooling surface reaches a temperature of *at least 2.5 times the peak width below the Offset temperature of the cooling curve*, the cooling cycle is regarded as complete (after any holding time required by the manufacturer of the PCM).

b) Absolute boundaries

In the case of materials with very wide melting peaks, or several superimposed melting peaks, the above definition can lead to unrealistically wide spreads of temperature. In these cases, the following applies: When the point on the sample that is farthest from the heating surface reaches a temperature of *at least 5K above the Offset temperature of the heating curve*, the heating cycle is regarded as complete (after any holding time required by the manufacturer of the PCM). When the point on the sample that is farthest from the cooling surface reaches a temperature of *at least 5K below the Offset temperature of the cooling curve*, the cooling cycle is regarded as complete (after any holding time required by the manufacturer of the PCM).

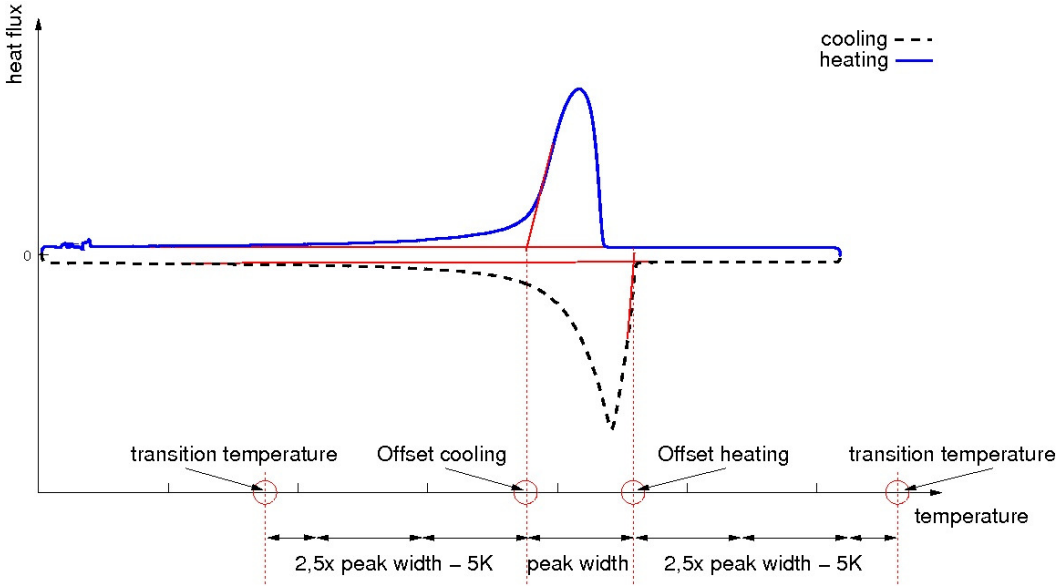

Figure 3.6.2.3.1: Definition of the peak width and resulting transition temperatures for the cycling, for relative definition.

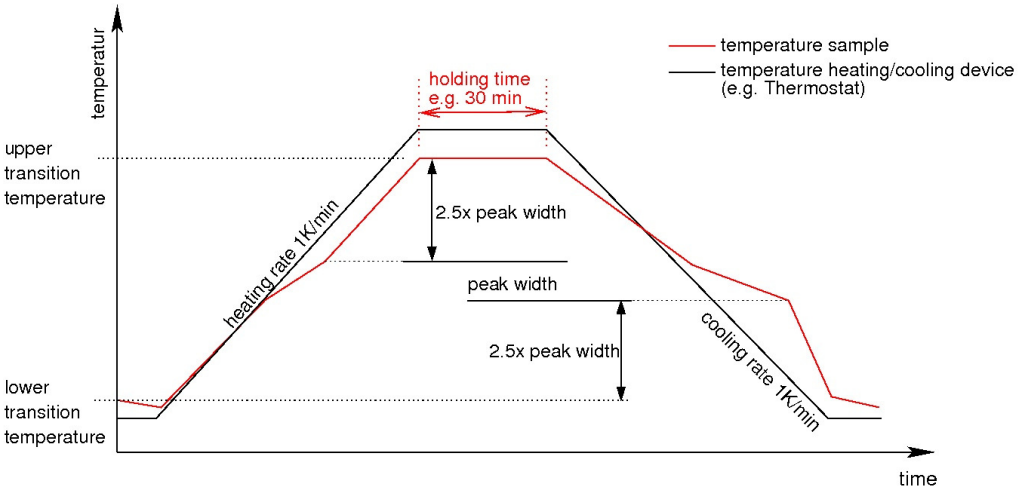

Figure 3.6.2.3.2: Example of a complete cycle with holding phases

- *Measuring the temperature of the sample*

  The temperature is measured at the greatest distance from the tempering surfaces. In the case of heating from at least two opposite heating surfaces, the temperature sensor is placed in the center of the sample; in the case of heating from one side, the sensor is on the surface of the sample opposite the heating surface.

- *Temperature program*

  The recommended heating rate is 1 K per min (± 0.1 K per min) at the metal contact or in the bath fluid. However, the heating rate within the sample is lower. Deviations in these values may be approved by the Quality Association PCM e.V., in particular for accelerated cycling. Furthermore, it may be necessary with some PCMs to observe holding times, in order to allow for thermal relaxation in the PCM. In this case, the manufacturer's specification must be taken into account. This must be noted in the log.

3.6.2.4 Content of the Test Result and Test Report

Specifications by the Quality Association PCM on the content of the test result and test report, over and above the Quality and Test Regulations:

The test report must, where applicable, contain the following information:

1. Reference to these “Test Principles of the Quality Association PCM e.V. for the Conduction of an Initial Test or External Monitoring”
2. All data necessary for the complete identification of the material investigated
3. Preparation of the sample for cycling
4. Method of cycling (air, fluid or metal contact)
5. Class achieved
6. Initial measurement and check measurements
    a. Number of cycles carried out hitherto
    b. Preparation of the samples
        i. Process for preparation of the samples
    c. Determination of the density of the sample
        i. Description of the measuring process
        ii. Result
    d. Determination of the stored heat as a function of the temperature
        i. Selection of the sample containers
            1. Material and
            2. Size
        ii. Selection of the measurement process
            1. Measurement method used
            2. Type of device used
        iii. Conduction of the measurements
            1. Temperature range
            2. Measurement program, parameters of the temperature program, including starting temperature, heating rate, final temperature, and cooling rate
            3. Result of the inspection for isothermal measurement
        iv. Result
            1. Number of samples, weight
            2. Measurement curves and result (Onset, peak, Offset) of the individual evaluation
               Total stored heat as a function of the temperature, in tabular form, for heating and cooling after forming the mean value of individual results, with reference to the mass of the samples in J per g
7. Cycling
    a. Parameters of the temperature program, including reversal temperatures, maximum and minimum temperatures of the tempering surfaces, holding times
    b. Documentation of cycles carried out (graphics or measurement data)
8. Date of the tests

3.6.3 Thermal Conductivity

3.6.3.3 Making the measurement

Specifications by the Quality Association PCM for the conduction of measurements:

- *Number of samples and measurements*
  At least 3 samples per product must be investigated. At least 1 measurement per sample must be carried out.
  If one of the investigated samples is damaged, two further samples are investigated.
  The test of the product with regard to the tested quality criteria is considered as passed when no damage is ascertained after 3 measurements have been carried out, or a maximum of one case of damage after 5 measurements.

3.7 Special test regulations for PCM-O

3.7.2 Phase transition temperature und stored heat

Specifications by the Quality Association PCM for the specification and measurement of the degree of sub-cooling:

The suitability of the method for measuring the degree of sub-cooling depends on the PCM-O. The suitability of the method must be clarified with the Quality Association PCM e.V. by the external monitoring institute.

3.7.3 Reproducibility of the phase transition

Specifications by the Quality Association PCM for the testing the encapsulation for tightness:

It is a fault when a leak can be ascertained through purely visual inspection without technical aids.

4 Monitoring

4.2 Initial test

In the initial test, the external monitoring institute must test the following quality criteria:

- Phase transition temperature
- Stored heat
- Cycle stability
- Further, optional, sample-dependent characteristics, according the wishes of the manufacturer or the specifications of the Quality Association RAL PCM (e.g. thermal conductivity)

4.3 External monitoring

The external inspection takes place at least every two years after the award of the seal of quality.

During the external inspection, the external inspector takes samples of the quality-assured products, and makes them available to the external monitoring institute for technical testing. At least 5 samples should be taken of each product that is to be lab-tested.

The lab test by the external monitoring institute should be conducted on 10% of the quality-assured products only, but on at least one product. The selection of products to be tested should vary from one external test to the next.

In the course of the external test, the external monitoring institute must test the following quality criteria:

- Phase transition temperature
- Stored heat
- Further, optional, sample-dependent characteristics, according the wishes of the manufacturer or the specifications of the Quality Association RAL PCM (e.g. thermal conductivity)