INTERNATIONAL STANDARD

ISO 18373-2

First edition
2008-02-15

Rigid PVC pipes — Differential scanning calorimetry (DSC) method —

Part 2: Measurement of the enthalpy of fusion of crystallites

Tubes rigides en PVC — Méthode utilisant la calorimétrie différentielle à balayage —
Partie 2: Mesurage de l'enthalpie de fusion des cristallites

Reference number
ISO 18373-2:2008(E)

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Published in Switzerland

Contents

Page

Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 18373-2 was prepared by Technical Committee ISO/TC 138, *Plastics pipes, fittings and valves for the transport of fluids*, Subcommittee SC 5, *General properties of pipes, fittings and valves of plastic materials and their accessories — Test methods and basic specifications*.

ISO 18373 consists of the following parts, under the general title *Rigid PVC pipes — Differential scanning calorimetry (DSC) method*:

— *Part 1: Measurement of the processing temperature*

— *Part 2: Measurement of the enthalpy of fusion of crystallites*

Introduction

Studies have been undertaken at the international level to determine a method of measuring the enthalpy of fusion of crystallites produced during the processing of rigid pipes. These studies have demonstrated that a test using differential scanning calorimetry (DSC) fulfils these requirements.

The method involves taking small samples from the pipe wall and heating these in a differential scanning calorimeter. Small endotherms are used to detect the thermal history of the samples and the enthalpy of fusion of crystallites is derived from these data.

The technique requires a good understanding of DSC instruments and techniques, particularly in relation to PVC. It is important that newcomers to the technique familiarize themselves with both the instrumentation and method prior to undertaking reportable tests.

This method is given as a guide and no specific requirement is given in this part of ISO 18373 for the enthalpy of fusion.

The method can also be suitable for other types of extruded rigid PVC products, but different sampling protocols might be required.

Rigid PVC pipes — Differential scanning calorimetry (DSC) method —

Part 2: Measurement of the enthalpy of fusion of crystallites

1 Scope

This part of ISO 18373 specifies a method for the determination of the enthalpy of fusion of crystallites in rigid PVC pipe samples. The method is based on the measurement of the thermal history using differential scanning calorimetry (DSC) and is suitable for all types of rigid PVC pipes.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
curve magnification
magnification of the DSC curve around A-onset and B-onset temperature (“zooming”)

2.2
A-onset
⟨enthalpy of fusion measurement⟩ first indication of “secondary” crystallite melting

2.3
B-onset
T_p
indication of maximum processing temperature

2.4
enthalpy of fusion
A-endotherm
ΔH_A
fusion enthalpy of the secondary crystallites in the pipe

NOTE Enthalpy of fusion is expressed in joules per gram.

2.5
instrumental baseline
measurement with empty sample pan, i.e. background subtraction

2.6
position of sample
location in the product from where the sample was taken

2.7
purge gas
gas used to ensure an inert environment

2.8
repeat samples
samples from the same position

3 Symbols and abbreviated terms

DSC differential scanning calorimetry

T_p maximum temperature reached by the melt during processing

ΔH_A enthalpy of fusion

4 Principle

DSC is a well-established method for testing the enthalpy of fusion, ΔH_A, or A-endotherm, in PVC products (see References [1] and [2]). The enthalpy of fusion depends upon processing conditions used to make the pipe and an optimum value reflects a well-processed pipe which will have optimum mechanical properties.

The benefits of this test are that an accurate assessment can be made of the enthalpy of fusion, as well as the possibility of finding variations in local areas of the product, due to the fact that only a small size of sample is required for the test. This enables the operator to cut samples from different locations around the pipe circumference. Thus, variations in the enthalpy of fusion in the pipe wall may be examined.

The characteristic A-endotherm occurs because secondary crystallites produced during the cooling phase after extrusion of the pipe will melt as the sample is heated, absorbing the latent heat of fusion of these crystallites as they do so.

5 Apparatus

5.1 DSC instrument, and associated software, calibrated.

NOTE Calibration should be carried out using at least two different metals. An instrumental baseline must be obtained with an empty sample pan and reference pan in place, and with temperature settings and purge gas identical to the settings to be used for the sample analysis.

5.2 Aluminium sample pans.

5.3 Inert purge gas (e.g. nitrogen, argon), of at least industrial quality.

5.4 Analytical balance, with an accuracy to within 0,01 mg.

5.5 Slow speed saw (see Reference [3]), **knife**, or any other device introducing neither heat nor stress into the sample as it is cut.

6 Preparation of the test pieces

6.1 Take at least four samples at the 0°, 90°, 180°, and 270° positions, respectively, around the pipe circumference, with all the samples being taken from the centre of the pipe wall.

NOTE The samples are taken from the centre of the pipe wall because the processing temperature at the centre of the pipe wall is often lower than that close to the inner and outer surfaces, where additional shear occurs.

CAUTION — Taking samples from the locus of a spider line can lead to an increase in the spread of results.

6.2 Prepare the test pieces having a mass of (20 ± 10) mg in a way that maximizes the contact surface between the pan and the test piece.

NOTE Maximizing the contact surface between the pan and the test piece reduces the resistance to heat flow through the DSC temperature sensors and results in maximum peak sharpness and resolution.

6.3 The best test piece shapes for optimum performance are thin disks placed on the bottom of the pan. Test pieces may be conveniently prepared by cutting out sections with a slow speed diamond saw, or with a razor or knife (5.5). A hole punch or cork borer may be used if the sample is very thin.

7 Procedure

7.1 Ensure that the scanning device is calibrated.

7.2 Encapsulate the test piece in an aluminium pan with cover (5.2).

7.3 The test piece shall not move in the pan during the measurement. The most common method of test piece immobilization is to crimp the pan cover in place with a crimper. This yields a tightly, but not hermetically, sealed pan without movement of the test piece in the pan during the measurement. Other methods of pan closure that immobilize the test piece can be used.

7.4 Using the following test parameters, perform and register the scan:

a) start temperature: $(35 \pm 15)\ ^{\circ}C$;

b) end temperature: 225 °C;

c) heating rate: $(20 \pm 1)\ ^{\circ}C/min$;

d) purge gas (5.3): (20 ± 5) °ml/min.

8 Expression of results

If necessary, magnify the relevant part of the curve using the zooming feature of the DSC instrument (5.1). Figure 1 depicts a typical curve. The A-onset temperature should lie somewhere between 100 °C and 120 °C; if it does not, it is most likely that there is interference in the DSC curve due to the presence of some additive(s) and these must be allowed for. If it is not possible to allow for these interferences, it may not be possible to determine the enthalpy of fusion for the sample.

The enthalpy of fusion, ΔH_A, is the net area under the curve lying between the A-onset and B-onset temperatures, after subtracting any area under the curve due to additive peaks. This area is normally calculated using the computer software built into the DSC apparatus. A straight line should be drawn between the A-onset and B-onset temperatures. Since the value of ΔH_A derives *only* from the secondary crystallites of the PVC and not from other components present in the pipe, such as fillers, pigments and stabilizers, the value of ΔH_A should be normalized to account for the PVC content of the pipe. For example, if the PVC content is 99 % by mass, the value of ΔH_A should be divided by 0,99. If it is 85 % by mass, then divide by 0,85.

NOTE 1 A typical curve consists of two endotherms between approximately 100 °C and approximately 200 °C where the A-onset temperature corresponds to the melting of the first “secondary” crystallites and the B-onset corresponds very closely to the maximum processing temperature, T_p. The enthalpy of fusion is derived from the first (lower temperature) endotherm. The change in energy levels is usually quite small. See Figure 2 for an example.

NOTE 2 Peaks due to additives are generally reproducible.

If the standard deviation of the results from three consecutive tests on samples taken from the same location (i.e. the same angular location) within a pipe is greater than 1 J/g, then the furthest outlying result shall be discarded and another single test carried out. If this does not bring the standard deviation of the results to less than 1 J/g, then the instrument may need recalibrating.

Uneven or irregular scan data shall be discarded. See Figure 3 for an example.

NOTE 3 The appearance of DSC curves can differ depending upon whether the instrument displays the results via an “exo up” curve (see Figures 1 and 2) or an “exo down” curve. The latter type produces inverted curves compared with Figures 1 and 2. Examples of the different types of presentation are shown in Annex A.