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Plastics — Temperature modulated DSC —

Part 1: General principles

Plastiques — DSC à température modulée —

Partie 1: Principes généraux

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Foreword

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

A list of all parts in the ISO 19935 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The ISO 19935 series specifies temperature modulated differential scanning calorimetry (DSC) methods for the thermal analysis of polymers such as thermoplastics, thermosets and elastomers.

It is designed for observing and quantifying various phenomena or properties of the abovementioned materials such as

— physical transitions (glass transition, phase transitions like melting, crystallization, and cold crystallization, etc.);

— chemical reactions (cross-linking and curing of elastomers and thermosets, etc.);

— heat capacity;

— separation of overlapping thermal transitions.

This document describes the realization of several standardized thermoanalytical test methods which can be used for the determination of comparable data needed for data sheets or databases as well as for research purposes, but it can also be applied to quality assurance or to routine checks of raw materials and finished products, if desired. The procedures mentioned in this document apply as long as special product standards or standards describing special atmospheres for conditioning of samples do not require alternate provisions.

For scientific investigations or resolution of special analytical problems, all technical capabilities of the instruments beyond the provisions of this document may be used.

Plastics — Temperature modulated DSC —

Part 1: General principles

1 Scope

This document establishes general principles of temperature modulated differential scanning calorimetry (DSC) such as description of the principle and the apparatus, sampling, calibration and general aspects of the procedure and test report common to all parts of the ISO 19335 series.

NOTE Details on performing specific methods are intended to be given in the future parts of the ISO 19335 series.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 11357-1, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 80000-5, *Quantities and units — Part 5: Thermodynamics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472, ISO 11357-1 and ISO 80000-5 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Calculation of heat flow rate and heat capacity

4.1 Temperature modulation, *T(t)*

A periodic temperature profile superimposed to a linear temperature change or constant temperature, is given by Formula (1):

$$T(t) = T_0 + \beta_0 \cdot t + T_A \cdot f(t) \tag{1}$$

where

t is the time;

T_0 is a start temperature;

β_0 is the underlying heating or cooling rate;

T_A is the amplitude of sample temperature profile;

$f(t)$ is the periodic function of the temperature profile.

The periodic temperature profile can have any waveform. Multi-frequency temperature modulation can be used in one and the same measurement.

4.2 Heating rate

The heating rate is not constant as in the case of conventional differential scanning calorimetry (DSC), which follows from Formula (1):

$$\frac{dT(t)}{dt} = \beta_0 + T_A \cdot \frac{df(t)}{dt} \tag{2}$$

If the temperature profile is a sinusoidal function with angular frequency, ω [see Formula (3)]:

$$f(t) = sin(\omega t) \tag{3}$$

Formula (2) is derived as shown in Formula (4):

$$\frac{dT(t)}{dt} = \beta_0 + T_A \cdot \omega \cdot \cos(\omega t) \tag{4}$$

4.3 Heat flow rate Φ(t) and heat capacity

4.3.1 General

For a temperature perturbation that consists of an underlying part $\Phi_{underlying}$, a periodic part $\Phi_{periodic}$, and an additional endothermic or exothermic excess heat exchange part $\Phi_{ex.}$, the heat flow rate $\Phi(T, t)$ can be expressed as Formula (5):

$$\Phi(T,t) = \Phi_{underlying} + \Phi_{periodic} + \Phi_{ex.} \tag{5}$$

assuming the pure thermodynamic heat capacity is as shown in Formula (6):

$$\Phi(T,t) = C_p(T) \cdot \frac{dT(t)}{dt} + \Phi_{ex.} \tag{6}$$

$$= C_p \beta_0 + C_p \cdot \frac{T_A}{K(\omega)} \cdot \frac{df(t)}{dt} + \Phi_{ex.}$$

where

C_p is the heat capacity;

$K(\omega)$ is the frequency-dependent calibration function of the heat capacity (see 7.1).

The different cases are distinguished in 4.3.2 to 4.3.4.

Formulae (5) and (6) are enabled only for slow modulation with $\omega\tau << 1$, where τ is the time constant of the instrument. For higher frequencies, the calibration factor $K(\omega)$ [see 7.1, Formula (26)] has to be used.

4.3.2 Heat capacity with no processes

In this case, Formula (6) applies with $\Phi_{ex.} = 0$, if the temperature profile is a sinusoidal function, then Formula (4) yields:

$$\Phi(T,t) = C_p \beta_0 + C_p \cdot \frac{T_A}{K(\omega)} \cdot \omega \cdot \cos(\omega t) \tag{7}$$

Formula (7) means that the measured heat flow rate is the sum of two components, the first term is referred to as the underlying, $\Phi_{underlying}$, and the second one is the periodic, $\Phi_{periodic}$. The average within one period by integration derives $\Phi_{underlying}$ as Formula (8):

$$\Phi_{underlying} = \int_{t-t_p/2}^{t+t_p/2} \Phi(T,t)\,dt = C_p \cdot \beta_0 \tag{8}$$

If the underlying part is subtracted from the measured heat flow rate, the periodic part is given as:

$$\widetilde{\Phi}(T,t) = \Phi(T,t) - \Phi_{underlying}(T,t) = C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) = \Phi \cdot \cos(\omega t) \tag{9}$$

From the amplitude of the periodic part, Φ_A, the heat capacity of the sample is:

$$C_p = \frac{\Phi_A}{T_A \cdot \omega} \tag{10}$$

The specific heat capacity, c_p:

$$c_p = \frac{C_p}{m} = \frac{\Phi_A}{m \cdot T_A \cdot \omega} \tag{11}$$

where m is the mass of the sample, called “specific heat capacity”.

NOTE True C_p can be found either by calibration procedure using the calibration factor $K(\omega)$ [see 7.1, Formula (26)].

$$C_p = \frac{\Phi_A}{T_A \cdot \omega} \cdot K(\omega) \tag{12}$$

$$c_p = \frac{\Phi_A}{m \cdot T_A \cdot \omega} \cdot K(\omega)$$

or calculated following the manufacturer’s instructions.

Formulae (7) to (11) are valid for a sinusoidal temperature modulation. There are different types of temperature modulation functions and evaluation procedures:

a) stepwise temperature changes with isothermal segments;

b) single frequency modulations;

c) use of non-sinusoidal modulation waveforms, such as square, triangle, etc.;

d) multi-frequency modulation.

The procedure in Formulae (7) to (11) is categorized under type b). Similar formulae can be derived for other waveforms, too. The generalized theory of temperature modulated DSC is described in Annex A and in the related References [1] to [7].

4.3.3 Heat capacity with additional processes

In this case, additional processes with endothermic or exothermic latent heat exchange are taking place, Formula (7) is extended with the excess heat flow rate shown in Formula (13):

$$\Phi(T,t) = C_p \cdot \beta_0 + C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) + \Phi_{ex.}(T,t) \tag{13}$$

Subtracting the underlying part from the total signal yields the periodic part:

$$\Phi(T,t) = C_p \cdot T_A \cdot \omega \cdot \cos(\omega t) + \frac{\partial \Phi_{ex.}(T_u,t)}{\partial T} \cdot T_A \cdot \sin(\omega t) \tag{14}$$

where $T_u = T_0 + \beta_0 t$ and $\Phi_{ex.}$ can be substituted by the first approximation of the Taylor series. Formula (14) can be written as Formula (15):

$$\Phi(T,t) = \Phi_A \cdot \cos(\omega t + \delta) \tag{15}$$

where

$$\Phi_A = \sqrt{\left(C_p(T) \cdot T_A \cdot \omega\right)^2 + \left(T_A \frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)\right)^2};$$

$$\delta = tan^{-1} \frac{\frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)}{C_p(T) \cdot \omega}.$$

From the amplitude, an "apparent" heat capacity $C_p^{app.}$ can be calculated in a similar manner as in Formula (10):

$$C_p^{app.} = \sqrt{\left[C_p(T)\right]^2 + \left(\frac{1}{\omega} \frac{\partial \Phi_{ex.}}{\partial T}(T_u,t)\right)^2} \tag{16}$$

Formula (16) is understood as the absolute value of a complex heat capacity which is given either as real and imaginary parts or as magnitude and phase angle in the following relations (see Formulae (17) and (18):

$$C_p^* = C_p' + iC_p'' = \left|C_p^*\right| \cdot e^{i\delta} = \left|C_p^*\right| \cdot cos\delta + i \cdot \left|C_p^*\right| \cdot sin\delta \tag{17}$$

$$\left|C_{\mathrm{p}}^{*}\right| = \sqrt{C_{\mathrm{p}}^{'2} + C_{\mathrm{p}}^{''2}}\text{, and } \tan\delta = \frac{C_{\mathrm{p}}^{''}}{C_{\mathrm{p}}^{'}} \tag{18}$$

In the case with additional endothermic or exothermic latent heat exchange, the real and imaginary parts of the complex heat capacity are as shown in Formula (19):

$$C_{\mathrm{p}}^{'} = C_{\mathrm{p}} \text{ and } C_{\mathrm{p}}^{''} = \frac{1}{\omega}\frac{\partial \Phi_{\mathrm{ex.}}}{\partial T}\left(T_{\mathrm{u}}, t\right) \tag{19}$$

4.3.4 Time dependent heat capacity

In this case, the relaxation processes like vitrification or devitrification are considered. Time dependent heat capacity means a non-equilibrium state of a system of the sample. Formula (6) is not valid anymore and is replaced by the convolution product of the time dependent heat capacity and the heating rate given by Formula (20):

$$\Phi\left(T,t\right) = \frac{d}{dt}\int_{-\infty}^{\infty}\left(C_{\mathrm{p}}\left(T, t-t'\right)\cdot\frac{\partial T\left(t'\right)}{\partial t}\right)dt' \tag{20}$$

The convolution product in time domain is transformed into a common product in the frequency domain via Fourier transform, $\tilde{F}$, [see Formula (21)]:

$$\tilde{F}\left[\Phi\left(t\right)\right] = \tilde{F}\left[C_{\mathrm{p}}\left(T,t\right)\right]\cdot\tilde{F}\left[\dot{T}\left(t\right)\right] \tag{21}$$

which is equivalent to a product of two complex function in Fourier space as shown in Formula (22):

$$\Phi^{*}\left(\omega\right) = C_{\mathrm{p}}^{*}\left(\omega\right)\cdot\dot{T}^{*}\left(\omega\right) \tag{22}$$

5 Principles

5.1 General

The difference between the heat flow rate into a specimen and that into a reference is measured as a function of temperature and/or time while the specimen and the reference are subjected to the same controlled temperature modulation under a specified atmosphere.

Depending on the design of instrumentation, the calibration procedures of the modulated part of the apparent heat capacity are required.

5.2 Mode of temperature modulation

5.2.1 Variable heating rate of periodic modulation

The simplest modulation type is a fixed frequency periodic temperature change. This can be done in sinusoidal waveform [see 4.2, Formula (3)] or alternative waveforms such as square, triangle, etc. Different modes of temperature modulation are distinguished depending on the magnitude of β_0, T_{A}, and ω as shown in Figure 1.