REVERSIBLE MELTING OF SEMI-CRYSTALLINE POLYMERS

Frequency dependence of the reversible melting enthalpy

F. Cser*, F. Rasoul† and E. Kosior†

CRC for Polymere Pty. Ltd., 32 Burinac Park Dr., Notting Hill VIC 3168, Australia

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Abstract

Modulated DSC (MDSC) has been used to study the heat flow during melting and crystallisation of some semi-crystalline polymers i.e. different grades of polyethylene (LDPE, LLDPE and HDPE), and polypropylene (PP).

The heat capacities measured by MDSC are compared with the hypothetical complex heat capacities of Schawe and it is shown that numerically they are equivalent; nevertheless, the concept of the complex heat capacity is problematic on a thermodynamic basis.

A reversing heat flow (proportional to the experimental heat capacity of the material) was present at all conditions used for the study. In the melting zone of the polymers it depends on the modulation frequency and on the amplitude. Higher amplitude and frequency of modulation reduce the ratio of the reversing heat flow to the total heat flow, the latter is nearly independent on these parameters.

The reversible component of the melting enthalpy of polymers depends on the modulation frequency, the modulation amplitude and the type of the polymer. It increases by increasing the branching in polyethylene.

The existence of the reversible heat flow during the crystallisation and melting is contrary to the current hypotheses and theories of polymer crystallisation.

Keywords: crystallisation, heat capacity, MDSC, melting, polymers

Introduction

Basics of MDSC

Modulated DSC (MDSC), developed by Reading et al. [1, 2] and produced by TA Instruments, combines the linear change of the temperature in a DSC cell.
with a sinusoidal modulation. The equipment records the actual (modulated) temperature, the actual (modulated) heat flow and the phase angle of these two harmonic functions. If the change of the temperature is within the harmonic range (which depends on the parameters of the modulation, the actual temperature and the overall heating rate), then the Fourier analyses of the response to the temperature function results in two functions: the heat capacity \( C_p \), which is determined mainly by the amplitude of the responses) and the total heat flow (which is the average of the heat flow) [1–4].

Reading et al. gave two differential equations as approximations for the total heat flow (Eqs (1a) and (1b)) and after their solution the results can be broken in two parts, i.e. into a reversing (reversible) and a kinetic (or non reversible) heat flows [1, 2]:

\[
\Phi(t) = \left( \frac{dQ}{dt} \right)_{total} = C_p(T) \frac{dT}{dt} + f(t, T) \tag{1a}
\]

\[
\Phi(t) = \left[ C_p(T) + f(t, T) \right] \frac{dT}{dt} + f(t, T) \tag{1b}
\]

\[
\Phi(t) = \Phi_{rev} + \Phi_{kin} \tag{1c}
\]

where the reversing heat flow is defined by Eq. (2):

\[
\Phi_{rev}(t) = \left( \frac{dQ}{dt} \right)_{rev} = -C_p(T) \beta \tag{2}
\]

i.e. the heat capacity multiplied by the overall rate of temperature change (β). The kinetic heat flow is an unknown function that can be defined according to Eq. (3) using Eq. (1a):

\[
\Phi_{kin} = f(T, t) \tag{3}
\]

and its slope is

\[
a_T = \frac{df(T, t)}{dt} \tag{4}
\]

The heat capacity function \( (C_p(T)) \) is the target of our next investigations. The heat capacity function is produced by the MDSC after deconvolution of the modulated heat flow using Eq. (5):

\[
C_p(T)_{rev} = \kappa_{C_p} \text{smoothed}[A_{HP}(t_3)] \frac{1}{\text{smoothed}[A_T(t_3)]} \omega \tag{5}
\]