Heat of fusion of polymer crystals by fast scanning calorimetry

Peggy Cebe [a, *], David Thomas [a], John Merfeld [a], Benjamin P. Partlow [b], David L. Kaplan [b], Rufina G. Alamo [c], Andreas Wurm [d], Evgeny Zhuravlev [d], Christoph Schick [d]

[a] Department of Physics and Astronomy, Center for Nanoscopic Physics, Tufts University, Medford, MA 02155, USA
[b] Department of Biomedical Engineering, Tufts University, Medford, MA 02155, USA
[c] Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310, USA
[d] Institute for Physics and Competence Center Calorimetry of Interdisciplinary Faculty, University of Rostock, Rostock, Germany

ARTICLE INFO

ABSTRACT

Knowledge of the specific equilibrium heat of fusion of polymer crystals, Δh_f^0 [J/g], is an essential thermal property of polymers which permits the degree of crystallinity to be obtained from thermal measurements. We describe an approach to evaluate $\Delta h_f^0(T_m)$ and implement this method using fast scanning calorimetry (FSC). Our method uses the measured enthalpy of melting plotted against the product of the sample mass times its crystallinity for samples with variable masses and/or crystallinities. Then, Δh_f^0 is obtained from the slope of the entire data set, reducing errors in the measurement. To demonstrate the method and give proof of principle, we measure $\Delta h_f^0(T_m)$ of samples of a narrow fraction of linear polyethylene (PE) with a weight average molecular weight of 60,700 g/mol, whose thermal properties are already known in the literature. For PE, we obtain $\Delta h_f^0(\text{PE}) = (281 \pm 6)$ J/g at $T_m = 136$ °C, in close agreement with literature values. Then, we apply the method to determine $\Delta h_f^0(T_m)$ of silk fibroin, a fibrous protein, yielding a first estimate of the heat of fusion of silk crystals, $\Delta h_f^0(\text{Silk}) \sim (137 \pm 7)$ J/g. Advantages include: reduction of error, applicability to all types of polymers, copolymers, and blends regardless of degree of crystallinity, and applicability to biomaterials which may require fast scanning rates of FSC to prevent degradation.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The specific heat of fusion of polymer crystals, $\Delta h_f^0(T)$ [J/g], is the energy needed to convert one gram of 100% crystalline solid into molten liquid at a temperature T. Commonly $\Delta h_f^0(T_f^0)$ is provided for the equilibrium melting temperature T_f^0. The crystals to which Δh_f^0 applies are crystals close to thermodynamic equilibrium in which the surface properties can be ignored compared to the bulk properties. For polymeric materials, examples of crystals to which the heat of fusion could approximately apply include solution grown single lamellae and extended chain crystals. But it is more generally the case that polymers crystallized from the melt do not form such perfect structures. Melt crystallized polymers typically form multi-crystalline aggregates (such as spherulites, axialites, or dendrites) whose fractional degree of crystallinity, ϕ_c, is less than unity. For such types of semicrystalline polymer structures, the measured

heat of fusion, Δh_f^{meas}, provides a means by which the degree of crystallinity can be assessed using calorimetric measurements, such as differential scanning calorimetry (DSC). A heating scan of semicrystalline polymer often yields a nearly symmetric melting endotherm with peak at T_m whose measured heat of fusion, Δh_f^{meas} [J/g], is related to Δh_f^0 to a good approximation [1,2] through the simple relationship:

$$\phi_c = \Delta h_f^{\text{meas}}(T_m) \Big/ \Delta h_f^0(T_m) \tag{1}$$

Thus, knowledge of $\Delta h_f^0(T_m)$ is an essential thermal property of polymers which permits the degree of crystallinity to be obtained from thermal measurements.

Such measurements of Δh_f^0 have been made for many polymers using extrapolative methods based on equation (1) [3–17] including: polypropylene [3–5], poly(ethylene terephthalate) [6], poly(trimethylene terephthalate) [7], poly(lactic acid) [8,15], poly(phenylene sulfide) [10], and nylons [11,12], inter alia. A series of samples is made in which the crystalline fraction is controllably varied, and a heating scan conducted to give different values for

* Corresponding author. Department of Physics and Astronomy, 574 Boston Avenue, Room 412J, Medford 02155, MA, USA.
E-mail address: peggy.cebe@tufts.edu (P. Cebe).

Δh_f^{meas}. Then, a physical property known to scale linearly with the crystallinity is measured for each sample. The results of two such measurements are shown in Fig. 1a,b for data on poly(phenylene sulfide) [10] and poly(lactic acid) [8], respectively. Through the data points, a line of best fit is drawn and extrapolated to the point where $\phi_c = 1$. However, some polymers, like polyamide 11, crystallize to limited extent (meaning ϕ_c is small), and the range of extrapolation is therefore large [12]. In the case of using X-ray scattering (as in Fig. 1a), the crystallinity is determined from the ratio of the area under the crystalline diffraction peaks to the total area of the scattering curve. This measurement can have a large uncertainly, especially if the sample scatters weakly or gives indistinct crystalline peaks. Use of specific volume measurements, as suggested by Fig. 1b, relies on knowledge of the polymer's amorphous and crystalline densities [6,10]. Some polymers, like polyethylene and polytetrafluoroethylene, however, are not readily obtainable in the 100% amorphous state for this type of measurement. Other polymers, like poly(phenylene oxide) [18] and poly(-ethylene terephthalate) [19], form large fractions of the rigid amorphous phase, and the bulk density is therefore not indicative of the crystalline content. Other interfacial effects can result in curvature in the plot of enthalpy vs. specific volume [3,20]. In some cases, only a single measurement is taken [15,16] which could lead to larger errors of extrapolation.

In the present work, we offer another approach to evaluate the equilibrium heat of fusion, and implement this approach using fast
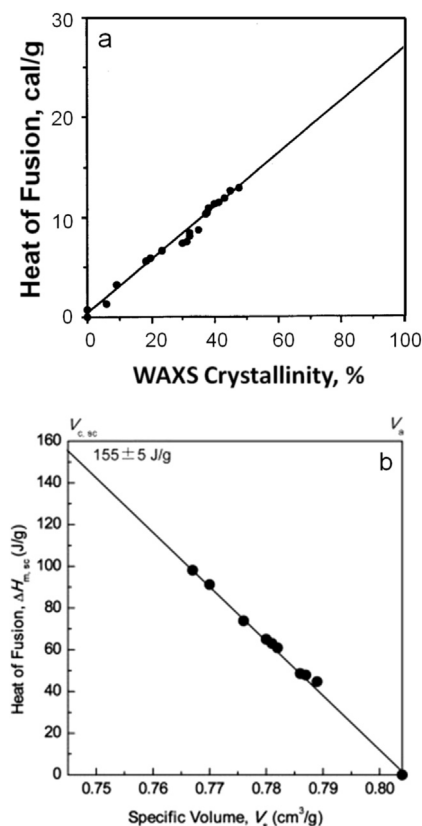
scanning calorimetry (FSC) [21–23]. This work was motivated by our earlier thermal studies of silk fibroin protein, and the desire to determine Δh_f^0 for this biomaterial. Using DSC or its temperature modulated variant, TMDSC, it was not possible to obtain Δh_f^{meas} for silk fibroin because of interference from the degradation process [24]. The slow scanning rates, β, available in DSC, which commonly range from about 0.17 K/s (1 K/min) to 0.5 K/s (30 K/min), do not allow heating of milligram-size samples fast enough to avoid degradation. To circumvent this difficulty, we took advantage of the very fast heating rates of FSC ($\beta \geq 100$ K/s) to study silk fibroin protein. With this technique we were able to heat nanogram-size samples fast enough to observe the melting endotherm of silk [24].

Here, we propose an approach for using FSC to determine $\Delta h_f^0(T_m)$, where T_m is the measured melting peak temperature. A set of samples having different masses and the same (or different) crystallinities is used to obtain endotherm areas, Δh_f^{meas} [J], from heat flow rate vs. temperature in FSC. Heat flow rate is then converted to heat capacity [J/K] and the sample mass is estimated in the way described previously [25]. The value of Δh_f^0 is then found from the slope of a plot of Δh_f^{meas} vs. the product mass*crystallinity. Advantages include: reduction of error in the measurement; ability to use a single DSC scan to obtain the crystallinity for comparison to the FSC; applicability to all types of polymers, copolymers, and blends regardless of degree of crystallinity; and of particular interest in this work, applicability to biomaterials which may require fast scanning rates of FSC to prevent degradation.

As in the case of DSC thermal measurement, to implement the FSC approach, some prior knowledge of thermal properties is required. *Viz.*, the solid state or liquid state specific heat capacity, $c_p^{solid}(T)$ or $c_p^{liquid}(T)$ [J/(gK)], must be known from literature. The degree of crystallinity should be known by using another experiment. The FSC method is outlined in the following section, and then applied to polyethylene (PE) to demonstrate proof of principle using a polymer whose solid and liquid state heat capacities are available in the ATHAS data bank [26]. The temperature dependent enthalpy of fusion, $\Delta h_f^0(T)$, for polyethylene is also known [16,27] allowing direct comparison of this value to the one obtained from FSC as a check. Then the method is applied to silk fibroin, yielding a first estimate of the equilibrium heat of fusion of silk crystals, $\Delta h_f^0(silk) \sim (137 \pm 7)$ J/g.

2. Materials and methods section

2.1. Materials

A narrow fraction of linear polyethylene (PE) with a weight average molecular weight of 60,700 g/mol and polydispersity index of 1.13 was purchased from the Société Nationale des Pétroles d' Aquitaine (SNPA), France. For DSC tests, a compression molded film (~100 μm thick) of the polyethylene was used. For FSC tests, the as-received PE granules were solvated at 2 wt% concentration in xylene at the reflux temperature, then spin coated using a Headway research grade spin caster. To obtain samples thin enough for FSC studies, five to nine droplets of PE in hot xylene were deposited onto sugar-coated glass slides, at 2000 rpm for 60 s. The samples were dried and then floated off the slides by immersion in distilled water. Tiny PE fragments were collected and dried prior to mounting in the FSC. PE masses and heat capacities can be found in Supplementary Information Table 1.

Silk fibroin sample preparation has been described in several prior publications [25,28]. Therefore, details of the silk samples, including a list of their masses and crystallinities, have been placed in the Supplementary Information Table S2.

Regarding the heating of these samples, beside the expected thermal lag, resulting in temperature gradients of a few Kelvin on

Fig. 1. Extrapolative methods for obtaining the equilibrium heat of fusion, Δh_f^0. a.) Measured heat of fusion for poly(phenylene sulfide), PPS, vs. crystallinity from X-ray diffraction [10]. The y-coordinate of the intersection of the line of best fit at 100% crystallinity gives the equilibrium heat of fusion for PPS. b.) Measured heat of fusion vs. specific volume for poly(lactic acid), PLLA [8]. The y-coordinate of the intersection of the line of best fit to the specific volume of the crystal unit cell gives the equilibrium heat of fusion of PLLA. Figure used with permission of the publisher, John Wiley and Sons, 2007.