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Some comments on the degree of crystallinity defined by the enthalpy of melting

Hsin-Lung Chen*
Department of Chemical Engineering, Chang Gung College of Medicine and Technology, Kwei-San, Taoyuan, Taiwan, R.O.C.

and Jenn Chiu Hwang
Department of Chemical Engineering, Yuan Ze Institute of Technology, Nei-Li, Taoyuan, Taiwan, R.O.C.

In this communication we try to provide a straightforward but critical discussion on the meaning of the degree of crystallinity defined by the enthalpy of melting. We show that the widely used crystallinity obtained by $\Delta h_f/\Delta h_f^0$ can be called the 'equivalent weight crystallinity', signifying the amount of perfect crystals that can be melted by the measured enthalpy of melting. The equivalent weight crystallinity does not only depend on the amount of the crystals, but also on the perfection of the crystals: a crystal with higher perfection has larger equivalent weight. The weight fraction of the chain-folded crystals is derived based on the same model and assumptions underlying the Thomson–Gibbs equation. A reason is also offered for the frequently observed difference between the crystallinity determined by the density and that obtained by the enthalpy of melting.

(Keywords: degree of crystallinity; semicrystalline polymers; chain-folded crystals)

Introduction

Defining the degree of crystallinity precisely has been a long-term challenge to polymer scientists. To achieve this one must know how to define the crystalline and amorphous phases precisely. Such a task was complicated by the presence of the crystal–amorphous interphase and intracrystalline defects in the semicrystalline polymers. Should the intracrystalline defects be counted as the crystalline or amorphous material, and what criteria should be used to fix the interphase position? These two are among those difficult questions which should be answered in order to provide an exact definition of the degree of crystallinity[1]. The crystallinities used today are all defined by simplified models. The two-phase model (a perfectly crystalline + a perfectly amorphous phase), although the simplest, is still the most widely used model. The degree of crystallinity can be determined easily from the enthalpy of melting as:

$$w_c = \frac{\Delta h_f}{\Delta h_f^0} \qquad (1)$$

where Δh_f and Δh_f^0 are the experimentally measured enthalpy of melting and the bulk enthalpy of melting, respectively. The two-phase model assumes that a semicrystalline polymer contains a perfectly crystalline and a perfectly amorphous phase, and the boundary between these two phases is perfectly sharp[1,2]. However, the morphologies of semicrystalline polymers are much more complicated than this idealized two-phase description. The crystalline phase in semicrystalline polymers is believed to be composed of crystals with chain folds on the surfaces; consequently, a more realistic model would be a crystalline phase containing chain-folded crystals and a liquid-like amorphous phase.

Since the model underlying equation (1) is not consistent with the real morphologies in the semicrystalline polymers, we can ask 'what is the real meaning of the crystallinity given by equation (1)?'. This question has not really been examined, although equation (1) has been used so extensively, and in general the crystallinity thus obtained has still been treated as the amount of chain-folded crystals in the sample. In this communication, we try to provide a critical discussion of the crystallinity defined by the enthalpy of melting based on some straightforward considerations which may have been neglected previously. First, we will show that the crystallinity given by equation (1) can be termed as the 'equivalent weight crystallinity'. Secondly, we will derive the weight fraction of chain-folded crystals using the same model and assumptions underlying the well-known Thomson–Gibbs equation. Finally, we will provide one reason why the crystallinity determined by the enthalpy of melting differs from that measured by the density when the ideal two-phase model is used.

The meaning of equation (1)

In the differential scanning calorimetry experiment, the measured enthalpy of melting, Δh_f, is generally normalized by the total weight of the semicrystalline polymer. Therefore, the total enthalpy of melting is given by:

$$\Delta H_f = W \Delta h_f \qquad (2)$$

where W is the total weight of the semicrystalline polymer. Now let us assume that the semicrystalline

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* To whom correspondence should be addressed

Table 1 List of parameters

Parameter	Definition	Unit
W	Total weight of the semicrystalline polymer	g
ΔH_f	Total enthalpy of melting measured experimentally	joule
Δh_f	$\Delta h_f = \Delta H_f/W$; enthalpy of melting per unit weight of the semicrystalline polymer	joule g^{-1}
W_c	Weight of the chain-folded crystals in the sample	g
Δh_f^c	$\Delta h_f^c = \Delta H_f/W_c$; enthalpy of melting per unit weight of the chain-folded polymers	joule g^{-1}
W_c^e	'Equivalent weight'; the weight of perfect crystals to be melted by the amount of heat of ΔH_f	g
Δh_f^0	Bulk enthalpy of melting; the enthalpy of melting per unit weight of 100% perfect crystal	joule g^{-1}
w_c^e	$w_c^e = W_c^e/W = \Delta h_f/\Delta h_f^0$; the equivalent weight crystallinity	
w_c	$w_c = W_c/W = \Delta h_f/\Delta h_f^c$; the weight fraction of chain-folded crystals in the semicrystalline polymer	

polymer contains a crystalline phase composed of chain-folded crystals and a liquid-like amorphous phase. This model is identical to that used in deriving the Thomson–Gibbs equation, where the chain folds are counted as part of the crystalline phase and the crystalline phase is assumed to have a defined melting point (m.p.). If Δh_f^c is the enthalpy of melting normalized by the weight of the chain-folded crystals in the polymer, then the total enthalpy of melting can also be written as:

$$\Delta H_f = W_c \Delta h_f^c \tag{3}$$

where W_c is the weight of the chain-folded crystals actually melted.

Now we can ask a question, 'if the amount of heat ΔH_f is taken to melt the perfect crystals, what weight of the perfect crystals would be melted?'. This is expressed as:

$$\Delta H_f = W_c^e \Delta h_f^0 \tag{4}$$

Equation (4) means that if the amount of heat ΔH_f is taken to melt the perfect crystals, the weight of the perfect crystals to be melted is W_c^e. Thus, W_c^e can be called the 'equivalent weight'.

From equations (2) to (4), two definitions for the degree of crystallinity can be obtained:

$$w_c^e = \frac{W_c^e}{W} = \frac{\Delta h_f}{\Delta h_f^0} \tag{5}$$

$$w_c = \frac{W_c}{W} = \frac{\Delta h_f}{\Delta h_f^c} \tag{6}$$

The crystallinity defined by equation (5) is identical to that given by the ideal two-phase model, i.e. equation (1). It can be seen that equation (1) does not yield the true weight fraction of the chain-folded crystals in the polymer, but only provides the 'equivalent weight fraction' of the perfect crystals that can be melted by ΔH_f. Consequently, w_c^e can be called the 'equivalent weight crystallinity'. The definitions of the parameters considered above are summarized in *Table 1*.

One problem associated with the equivalent weight crystallinity is that it does not only depend on the amount of the crystals, but also on the perfection of the crystals. If the weight of two chain-folded crystals of different perfections is identical, the crystal of higher perfection (e.g. crystal with lower surface free energy and larger thickness) has larger equivalent weight than the crystal of lower perfection. It is also noted that the use of the equivalent weight crystallinity is not restricted to a certain type of morphology pertaining to the semicrystalline polymer. As far as the equivalent weight crystallinity is concerned, all the materials contributing to melting will be counted as the 'crystalline portion' and their amount will be converted into the equivalent weight irrespective of the morphology associated with the semicrystalline polymer.

Weight fraction of the chain-folded crystals

The true weight fraction of the chain-folded crystals is given by w_c in equation (6). Since $\Delta h_f^c < \Delta h_f^0$, it is expected that $w_c > w_c^e$. To determine w_c, it is necessary to know the value of Δh_f^c. Following the derivation of the well-known Thomson–Gibbs equation[1], the free energy of melting at temperature T is given by:

$$\Delta h_f^0\left(1 - \frac{T}{T_m^0}\right) - \Sigma\sigma_i A_i = \Delta h_f^c\left(1 - \frac{T}{T_m}\right) \tag{7}$$

where T_m^0 is the equilibrium m.p., $\Sigma\sigma_i A_i$ is the total surface free energy, and T_m is the m.p. of the chain-folded crystals. If the surface free energy is assumed to be independent of temperature, then:

$$\Delta h_f^0 - \Sigma\sigma_i A_i = \Delta h_f^c$$

$$\frac{\Delta h_f^0}{T_m^0} = \frac{\Delta h_f^c}{T_m}$$

Thus

$$\frac{\Delta h_f^c}{\Delta h_f^0} = \frac{T_m}{T_m^0} \tag{8}$$

Equation (8) is also a statement that the entropy of melting of the chain-folded crystals is the same as that of the perfect crystals. This is a consequence of assuming the temperature independence of $\Sigma\sigma_i A_i$, or that the entropic contribution to the surface free energy is negligible.

From equations (5), (6) and (8), w_c is given by:

$$w_c = \left(\frac{\Delta h_f}{\Delta h_f^0}\right)\left(\frac{T_m^0}{T_m}\right)$$

$$= w_c^e\left(\frac{T_m^0}{T_m}\right) \tag{9}$$

Based on the same assumptions underlying the Thomson–Gibbs equation, the weight fraction of the chain-folded crystals is given by the product of the equivalent weight crystallinity and the ratio of the equilibrium m.p. to the m.p. of the chain-folded crystals. It can be seen that the correction factor is the melting point ratio, T_m^0/T_m, which is greater than unity.

Crystallinity determined by the density

The degree of crystallinity can also be defined from the volume of melting, by simply replacing the enthalpy of melting in equations (5) and (6) with the corresponding specific volume of melting. It is noted that w_c^e defined by the volume of melting is not necessarily equal to that defined by the enthalpy of melting, and this is frequently observed experimentally. For instance, Glotin and Mandelkern have found for polyethylene that the crystallinity (i.e. the equivalent weight crystallinity) determined by the density is always larger than that obtained by the enthalpy of melting[3]. This may be ascribed to the difference in the equivalent weight converted from these two properties of melting. For a simple example, suppose the crystalline phase in a semicrystalline polymer contains 1 g of chain folds; the volume of melting of this amount of chain folds corresponds to that of 0.6 g of perfect crystals, but on the other hand, the enthalpy of melting of 1 g of chain fields does not have to correspond to the enthalpy of melting of 0.6 g of perfect crystals. This consequently leads to the difference between the w_c^e determined by density and that obtained by the enthalpy of melting.

Concluding remarks

The main objective of this communication is to clarify the meaning of equation (1). Because equation (1) has been so widely used, it is necessary to know its real meaning to avoid misinterpretation of the crystallinity derived from it. Equation (9) was not derived with the intention to replace equation (1). It is well known that the morphologies of semicrystalline polymers are complicated, and they may vary from one polymer to another. As a consequence, the model employed here (i.e. a chain-folded crystalline phase with a defined m.p. and a liquid-like amorphous phase) may not be consistent with the real morphology of some semicrystalline polymers. In addition, the assumptions used in deriving equation (9) further complicate its accuracy for the determination of the real crystallinity. Therefore, we think that equation (5) is still the most practical, since it measures the crystallinity in terms of the 'equivalent weight', regardless of the morphology of the polymers. But one thing to be kept in mind when interpreting the crystallinity obtained by equation (5) is that the equivalent weight crystallinity depends not only on the amount of the crystals but also on the perfection of the crystals. Finally, the difference between the equivalent weight crystallinity measured by the density and that determined by the enthalpy of melting may be due to the difference in the converted equivalent weight. This factor should be considered when comparing the equivalent weight crystallinities determined by these two methods.

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