Crystallization behaviour of a semicrystalline miscible blend

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A theoretical model has been developed to explain the crystallization behaviour in a thermodynamically miscible blend of a semicrystalline and amorphous polymer. The model predicts the growth rate and half-time for the maximum crystallization, and relates the observable melting temperatures to the equilibrium melting temperatures in each blend. A complete equation that contains morphological, entropic and enthalpic contributions has been developed for this purpose.

(Keywords: polymer blends; semicrystalline miscible blends; crystallization

INTRODUCTION

Scientific and industrial interest in polymer blends has been gaining steady and significant momentum in the past few years. A market growth of 9% each year until 1996 has been forecast by Kossoff and Associates[1] for thermoplastic polymer blends. From a scientific point of view, however, polymer blends can be divided into three basic groups:

Group 1 Miscible blends, such as:
PPO–PS
PVDF–PMMA

Group 2 Near-miscible blends, such as:
PS–PVME
PES–PEO
PVC–PBA

Group 3 Immiscible blends, such as:
PE–PMMA
PP–PC

The above abbreviations and the mathematical symbols used here are defined in the 'Notation' at the end of the paper.

Miscibility is defined by a single T_g and $\partial^2\Delta G/\partial\phi^2 > 0$. The group 1 blends do not show a phase separation within the accessible temperature ranges, whereas the blends in group 2 show a detectable phase transition of predominantly lower critical solution temperature (*LCST*) type. The miscibility is a result of a favourable combination of two sets of quantities: (a) the match between physical quantities such as volumes and expansion coefficients and (b) chemical structures that allow a specific interaction to occur between the functional groups of the blend constituents. The latter is generally more important in high-molecular-weight polymeric mixtures than the former. In the absence of these favourable parameters, a mixture of two polymers will be heterogeneous with two T_g values.

The structure–property relationships in these three groups of polymeric blends are different. In the majority of cases miscible blends provide the ultimate properties that one would hope to achieve from blending practice.

The high-performance and engineering thermoplastics used in applications normally contain a certain level of crystallinity. The crystallinity region provides high-temperature strength and environmental resistance for the polymer. It is therefore important to know how the crystals are affected when a semicrystalline polymer is blended with an amorphous one that has favourable interactions. The aim of this paper is to explain, theoretically, the crystallinity behaviour of such a mixture.

BACKGROUND TO THE SUBJECT

The addition of an amorphous polymer to a semicrystalline polymer, which forms a thermodynamically miscible blend, has a dramatic effect on the crystallization behaviour of the latter. Ullman *et al.*[2] have shown that the lamellar thickness of poly(vinylidene fluoride) (PVDF) blended with poly(methyl methacrylate) (PMMA) decreases as the concentration of PMMA increases. The thickness of the amorphous layer and the long period increase as PMMA concentration increases. Cimmino *et al.*[3] have shown that the spherulite radial growth rate of poly(ethylene oxide) (PEO) decreases, and its half-time of crystallization increases at a given crystallization temperature, when it is blended with PMMA or poly(vinyl acetate) (PVAc). Various authors[4–6] have reported an observable depression on the melting of crystals in miscible blends. Alfonso *et al.*[7] reported that the kinetics and the thermodynamic parameters governing the crystallization of blends need modification.

Given the above information, there is no comprehensive theoretical model available to explain these observations. Sanchez *et al.*[8] have offered a theoretical model with various degrees of approximations for crystallization behaviour from a dilute solution. Flory[9] has related the observable melting-point depression to entropy and enthalpy of the crystalline units in the mixtures. This equation has been widely used but was found to be inadequate for describing the melting-point depression in blends[7,10]

In this paper a more comprehensive model describing the crystallization behaviour of a semicrystalline polymer

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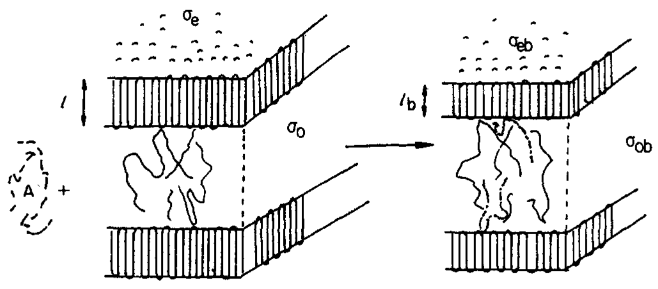

Figure 1 Schematic presentation of crystalline/amorphous regions of a homopolymer with and without the other component. The symbols are defined in the 'Notation'. The amorphous polymer (A) is referred to as component 1, and the semicrystalline polymer as component 2

in the presence of an amorphous polymer is presented. The observable melting point is related to an equilibrium melting point in each blend. These treatments are only valid when the two components are thermodynamically miscible. The semicrystalline component is generally referred to as component 2 and the amorphous polymer as component 1. Component 1 (*Figure 1*) is excluded from the crystalline region. The symbols used in this figure are defined in the 'Notation'.

THE EQUILIBRIUM MELTING TEMPERATURE IN BLENDS

In a semicrystalline homopolymer the change in free energy of melting per mole of crystalline unit is given by:

$$\Delta G_u(T) = \Delta H_u - T\Delta S_u \tag{1}$$

where ΔH_u and ΔS_u are heat of fusion and entropy changes on melting. For an infinitely large crystal with an equilibrium melting temperature of T_m^* then $\Delta G_u(T_m^*) = 0$ or:

$$T_m^* = \Delta H_u/\Delta S_u \tag{2}$$

Assuming ΔS is constant over the temperature range of T_m to T_m^* then equation (1) can be written as:

$$\Delta G_u(T_m) = \Delta H_u - T_m\left(\frac{\Delta H_u}{T_m^*}\right) = \Delta H_u\left(\frac{T_m^* - T_m}{T_m^*}\right) \tag{3}$$

Also at T_m:

$$n\Delta G_u(T_m) = 2\sigma_e \tag{4}$$

Combining equations (3) and (4) gives:

$$T_m = T_m^*\left(1 - \frac{2\sigma_e}{\Delta H_u n}\right) \tag{5}$$

This equation often appears in the literature and relates the observable melting to the equilibrium melting temperatures in homopolymers. Blundell *et al.*[11] have used this equation to calculate the equilibrium melting temperature of poly(ether ether ketone) (PEEK).

For blends, however, the difference in free energy of the crystalline unit can be written as[8]:

$$n\Delta G_{ub}(T) = n\Delta G_u(T) + \Delta G_M \tag{6}$$

$$\Delta G_{ub}(T) = \Delta H_u - T\Delta S_u + \Delta g_M \tag{7}$$

where the heat of fusion of the crystalline unit in the blend is assumed to be equal to that of the homopolymer. If we start with an athermal mixture, where the heat of mixing is zero, then equation (7) becomes:

$$\Delta G_{ub}(T) = \Delta H_u - T\Delta S_u - T\Delta s_M \tag{8}$$

At $T = T_{mb}^*$ we have:

$$T_{mb}^* = \Delta H_u/\Delta S_{ub} \tag{9}$$

where

$$\Delta G_{ub}(T_{mb}) = \Delta H_u\left(1 - \frac{T_{mb}}{T_{mb}^*}\right) - T_{mb}\Delta s_M \tag{10}$$

As in equation (4):

$$\Delta G_{ub}(T_{mb}) = 2(\sigma_e/n)_b \tag{11}$$

By combining equations (10) and (11) and rearranging we have:

$$\frac{1}{T_{mb}} = \left(\frac{1}{T_{mb}^*} + \frac{\Delta s_M}{\Delta H_u}\right)\left(\frac{1}{1 - (2\sigma_{eb}/\Delta H_u n_b)}\right) \tag{12}$$

This equation relates the observable melting temperature to the equilibrium melting temperature in athermal polymer blends. It is shown by Cimmino[3] and Ullman[2] that:

$$\sigma_{eb} = \phi_1^{\alpha}\sigma_e \qquad n_b = (1 - \phi_1)^{\beta} n \tag{13}$$

where α and β are constants and need to be evaluated for each system.

In equation (12) if $\Delta s_M \rightarrow 0$ then:

$$T_{mb} = T_{mb}^*\left(1 - \frac{2\sigma_e}{\Delta H_u n_b}\right) \tag{14}$$

If the heat of mixing of the amorphous region is not ignored, then equation (7) with a similar treatment as that of equation (12) gives:

$$T_{mb} = T_{mb}^*\left(1 - \frac{2\sigma_{eb}}{\Delta H_u n_b} + \frac{\Delta g_M}{\Delta H_u}\right) \tag{15}$$

where the Δg_M is the difference in free energy per mole of crystalline unit between amorphous and crystalline polymer. Equation (15) is a general form of the equation that relates the observable melting temperature to the equilibrium melting temperature of the blend. This equation will be expanded in the following sections to explain the crystallization behaviour of the blend.

THE SPHERULITIC GROWTH RATE

The common equation used to describe the radial growth rate of a semicrystalline polymer is given by Hoffman *et al.*[12] as:

$$G = G^0 \exp\left(-\frac{C_1}{T - T_g + C_2}\right)\exp\left(-\frac{4\sigma_e\sigma_0}{RT}\frac{1}{\Delta G_u(T)}\right) \tag{16}$$

where G^0 is a pre-exponential factor that is inversely proportional to $\bar{M}_n$ of the polymer[13]. The other two terms describe kinetic and energetic parts of the growth rate respectively. C_1 and C_2 are constants and will be defined later. $\sigma_e\sigma_0$ is the product of the fold and lateral free energies[12].

Using equations (3) and

$$C_3 = 4\sigma_e\sigma_0/R\Delta H_u$$

this equation becomes:

$$G = G^0(\bar{M}_n)\exp\left(-\frac{C_1}{T - T_g + C_2}\right)\exp\left(-\frac{C_3 T_m^*}{T(T_m^* - T_m)}\right) \tag{17}$$

For the crystalline unit in the blend, however, it becomes:

$$G_b = G_b^0(\bar{M}_n)\exp\left(-\frac{C_1}{T - T_{gb} + C_2}\right) \times \exp\left(-\frac{C_4 T^*_{mb}}{T[T^*_{mb} - T_m + T^*_{mb}(\Delta g_M/\Delta H_u)]}\right) \qquad (18)$$

where

$$C_4 = 4(\sigma_e\sigma_0)_b/R\Delta H_u$$

For a miscible blend where $\Delta g_M < 0$, equation (18) indicates a slower rate of spherulitic growth in the blend than that of the homopolymer. This has been shown experimentally by Cimmino for various PEO blends. According to this equation the radial growth rate should continue to decrease as the concentration of the amorphous polymer increases. It is conceivable that at some value of Δg_M, where the thermodynamic miscibility is preferred, the last term in equation (18) vanishes and crystal growth ceases.

For an athermal mixture the radial growth rate is similarly given by:

$$G_b = G_b^0(\bar{M}_n)\exp\left(-\frac{C_1}{T - T_{gb} + C_2}\right) \times \exp\left(-\frac{C_4 T^*_{mb}}{T[T^*_{mb} - T_m - (TT^*_m\Delta s_m/\Delta H_u)]}\right) \qquad (19)$$

In this equation $-T\Delta s_M$ is also negative, which implies that the growth in such a mixture is also slower than the crystallizable homopolymer component.

The values of C_1 and C_2 for miscible blends with a single T_g are given by a WLF equation, where:

$$\log a_T = \log\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{B}{2.303}\left(\frac{1}{f(T)} - \frac{1}{f(T_g)}\right) \qquad (20)$$

$$f(T) = f(T_g) + \Delta\alpha(T - T_g) \qquad (21)$$

$$C_1 = \frac{B(T - T_g)}{2.303 f(T_g)} \simeq 450\ (\mathrm{K}) \qquad C_2 = \frac{f(T_g)}{\Delta\alpha} \simeq 52\ (\mathrm{K}) \qquad (22)$$

Hence

$$\log a_T = \frac{-C_1}{T - T_{gb} + C_2} \qquad (23)$$

This principle is expected to be applicable for a miscible blend although the C_1 and C_2 values could vary slightly. Alfonso *et al.*[7] have derived an expression, based on the diffusion of the two polymers, to replace the transport factor.

THE CRYSTALLIZATION TIME IN THE BLEND

Ullman *et al.*[2] have shown that the total level of crystallinity in the blends decreases exponentially as the concentration of the amorphous polymer increases. The time to achieve such a level of crystallinity can be obtained from Avrami equations:

$$W_{cb} = W_{max}\left[1 - \exp\left(-\frac{4\pi}{3} N_{0b} G_b^3 (t - t_0)^m\right)\right] \qquad (24)$$

The nuclei density, N_{0b}, varies with the temperature and molecular dimension of the crystallizable unit. t_0 is the induction time. At $t = t_{1/2}$ where $W_{cb} = \frac{1}{2}W_{max}$ and for $m = 3$ we have:

$$(t_{1/2})_b = \frac{1}{G_b}\left(\frac{3\ln 2}{4\pi N_{0b}}\right)^{1/3} + t_0 \qquad (25)$$

where G_b is given by equation (18). The slower spherulitic growth rates, as mentioned earlier, imply that longer times are required to reach half of the maximum crystallization in the blend compared with that of the homopolymer. $(t_{1/2})_b$ and G_b for blends are composition-dependent and from equation (25) it appears that G_b is concentration-dependent too. However, for each blend composition G_b decreases linearly with $(t_{1/2})_b$, as shown by Van Antwerppen[13] for poly(ethylene terephthalate) (PET).

EVALUATION OF Δg_M AND Δs_M

According to standard thermodynamic practice Δg_M is equivalent to the change in chemical potential per mole of crystalline unit. This is given by Flory[9] using his lattice model as:

$$\Delta\mu_{2u} = \frac{RTV_u}{V_1}\left[\frac{\ln\phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_1\right] + \frac{RTV_u}{V_1}\chi_{12}\phi_1^2 \qquad (26)$$

For an athermal mixture where $\chi_{12} = 0$ equation (26) becomes:

$$-T\Delta s_M = \frac{RTV_u}{V_1}\left[\frac{\ln\phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_1\right] \qquad (27)$$

At extremely low concentrations of amorphous polymer where $\phi_1 \to 0$ it reduces to:

$$-T\Delta s_M \simeq \frac{RT}{r_2}\frac{V_u}{V_1}\ln\phi_2 \qquad (28)$$

This is the change in the entropy of athermal mixtures which often appears in the literature. However, substituting equation (28) into equation (12) gives:

$$\frac{1}{T_{mb}} = \left(\frac{1}{T^*_{mb}} - \frac{RV_u}{r_2 V_1}\ln\phi_2\right)\left(1 - \frac{2\sigma_{eb}}{\Delta H_u n_b}\right)^{-1} \qquad (29)$$

Equation (29) is only applicable to athermal mixtures. For non-athermal mixtures the complete version of equation (26) should be used. The χ_{12} interaction parameter in this equation is concentration, temperature and pressure dependent. It seems advantageous to replace this parameter by an alternative interaction parameter, namely X_{12}, which is concentration-independent. X_{12} is still temperature- and pressure-dependent. According to Flory's equation-of-state theory[14]:

$$\Delta\mu_{2u} = \Delta\mu_{2u}^{comb} + \Delta\mu_{2u}^{res} \qquad (30)$$

where

$$\Delta\mu_2^{res} = RT\chi_{12}\phi_1^2 = P_2^*V_2^*\left[3\tilde{T}_2\ln\left(\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} + \tilde{P}_2(\tilde{v} - \tilde{v}_2)\right] + \frac{V_2^*\theta_1^2}{\tilde{v}}\frac{S_2}{S_1}(X_{12} - T\tilde{v}Q_{12}) \qquad (31)$$

For details of derivations and applications of this equation see refs. 14 and 15. Substituting equation (31) in equation (26) and the resultant into equation (15) and

Table 1 The Q_{12} and X_{12} ratio

Blend	X_{12} (J cm^{-3})	$Q_{12} \times 10^{-3}$ (J cm^{-3} K^{-1})	$Q_{12} \times 10^{-3}/X_{12}$ (K^{-1})	Ref.
DPS-PVME	−1.86	−3.00	1.6	16
CPE-EVA	−4.20	−10.80	2.5	17
CPE-PBA	−1.01	−2.63	2.6	17
PVC-PMMA	−3.04	−6.08	2.0	17
PVC-PBA	−12.80	−25.60	2.0	18
PVC-PPrA	−15.11	−30.00	2.0	18
PVC-PPeA	−10.47	−22.00	2.0	18
PES-Phenoxy	−1.5	−2.70	1.8	19
PES-PEO	−40.00	−48.20	1.2	7

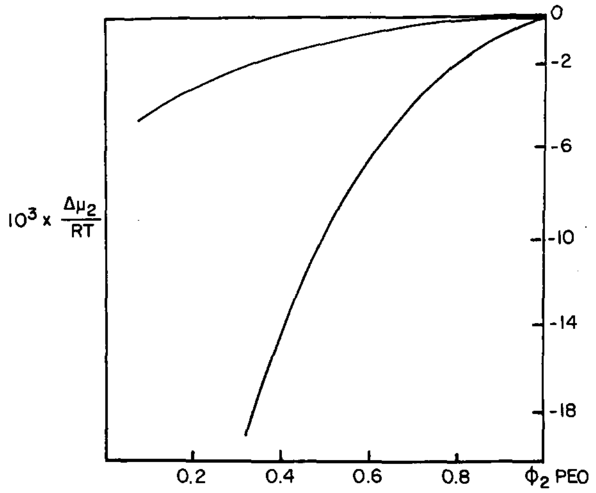

Figure 2 The chemical potential changes per mole of PEO in the mixtures of PES–PEO at 25°C

rearranging gives:

$$T_{\mathrm{mb}} = T^*_{\mathrm{mb}}\left(1 - \frac{2\sigma_{\mathrm{eb}}}{\Delta H_{\mathrm{u}} n_{\mathrm{b}}}\right) + \frac{T^*_{\mathrm{mb}}}{\Delta H_{\mathrm{u}}}\frac{RTV_{\mathrm{u}}}{V_1}\left[\frac{\ln\phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_1\right] + \frac{T^*_{\mathrm{mb}}}{\Delta H_{\mathrm{u}}}\frac{V_{\mathrm{u}}}{V_1}P^*_2V^*_2\left[3\tilde{T}_2\ln\left(\frac{\tilde{v}_2^{1/3}-1}{\tilde{v}^{1/3}-1}\right) + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} + \tilde{P}_2(\tilde{v} - \tilde{v}_2)\right] + \frac{T^*_{\mathrm{mb}}}{\Delta H_{\mathrm{u}}}\frac{V_{\mathrm{u}}}{V_1}\frac{V^*_2}{\tilde{v}}\frac{\theta_1^2 S_2}{S_1}(X_{12} - T\tilde{v}Q_{12}) \quad (32)$$

This equation relates the observable melting temperature to the equilibrium melting temperature of a crystalline unit in the blend at atmospheric pressure, $\tilde{P}_2 \approx 0$, or at any given pressure. The first term in this equation is related to the morphology of the crystals in the blend, the second term is the change in combinatorial entropy of the mixture and the last two terms are related to entropy and enthalpy of the interactions. The numerical solutions of these two terms are given by Rostami *et al.*[15]. These two terms vanish as the heat of the mixing goes to zero.

The concentration-independent quantity, X_{12}, is related to the heat of mixing via:

$$\Delta H_{\mathrm{m}} = (\omega_1 v^*_{1\mathrm{sp}} + \omega_2 v^*_{2\mathrm{sp}})\left(\frac{\phi_1 P^*_1}{\tilde{v}_1} + \frac{\phi_2 P_2}{\tilde{v}_2} - \frac{P^*}{\tilde{v}}\right) \quad (33)$$

where

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1\theta_2 X_{12} \quad (34)$$

The X_{12} value is normally obtained by measuring the heat of mixing of oligomeric analogues in a microcalorimeter and using equations (33) and (34) to obtain a value of X_{12}.

The Q_{12} factor, however, arises from the entropy of interactions in the amorphous region. Data for X_{12} and Q_{12} for some polymeric blend systems cited in the literature are listed in *Table 1*. From this table the ratio between X_{12} and Q_{12} seems to be constant, leading to an empirical relation:

$$Q_{12} \simeq 2.0 \times 10^{-3} X_{12}\ \mathrm{K}^{-1} \quad (35)$$

Using the values of X_{12} and Q_{12} given in this table and other required information given in ref. 6 the $\Delta\mu_{2\mathrm{u}}/RT$ of PES–PEO has been calculated for room temperature. The result is plotted in *Figure 2*.

THE MELTING-POINT DEPRESSION IN BLENDS

Although there is some ambiguity in the definition of the observable crystalline melting temperature[20], nevertheless many authors[2–4,9,16,20] have reported detectable differences between the melting behaviour of a semicrystalline polymer on its own and its blend. Almost invariably in all cases the observable melting point of the semicrystalline homopolymer is generally depressed in the blends. Equation (36) given by Flory[9] has been widely used to describe this behaviour. It has also been used to obtain the usual Flory–Huggins interaction parameter:

$$\frac{1}{\phi_1}\left(\frac{1}{T_{\mathrm{mb}}} - \frac{1}{T_{\mathrm{m}}}\right) = \frac{RV_{\mathrm{u}}}{\Delta H_{\mathrm{u}} V_1}(1 - \chi_{12}\phi_1) \quad (36)$$

Many authors have experienced difficulties in fitting this equation to their experimental data[5,7,10]. The principal difficulties are:

(1) This equation has been derived at conditions of observable melting temperatures, not at thermodynamic equilibrium temperatures.

(2) The plot of the left-hand side of equation (36) *versus* the right-hand side has an intercept with the y axis that contains information on the crystalline morphology[5] but has been ignored.

(3) The concentration dependence of the interaction parameter adds a restriction on plotting the left-hand side of equation (36) *versus* ϕ_1 to obtain a single value for χ_{12}.

A modified version of this equation has been used by other authors[4,6] with an added constant factor that is related to the morphology of the crystalline region. These approaches have not been entirely satisfactory.

Equation (32) contains all the necessary ingredients needed to explain the melting-point depression of the crystalline unit in the blends. It takes into account the morphology of the crystalline units, residual and combinatorial entropies and the enthalpy of mixing of a semicrystalline polymer with an amorphous one. At $T = T_{mb}$ this equation can be rearranged to give:

$$\begin{aligned}\Delta H_u\left(\frac{1}{T_{mb}} - \frac{1}{T^*_{mb}}\right) = &-\frac{RV_u}{V_1}\left[\frac{\ln \phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_1\right] \\ &- \frac{P^*_2 V^*_2}{T_{mb}}\frac{V_u}{V_1}\left[3\tilde{T}_2 \ln\left(\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right)\right. \\ &\left. + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} + \tilde{P}_2(\tilde{v} - \tilde{v}_2)\right] \\ &- \frac{V^*_2 V_u}{T_{mb}}\frac{\theta_1^2}{\tilde{v}}\frac{S_2}{S_1}(X_{12} - T_{mb}\tilde{v}Q_{12}) \\ &+ \frac{1}{T_{mb}}\frac{2\sigma_{eb}}{\Delta H_u n_b}\end{aligned} \qquad (37)$$

This equation relates the observable melting point to the equilibrium melting point via four terms: first the morphological term, second the combinatorial entropy, third the residual entropy and fourth the enthalpic term. Verification of this equation requires a careful d.s.c., X-ray diffraction and calorimetric analysis of the semicrystalline blends.

In a specific situation where $\sigma_{eb} = \sigma_e$, $n_b = n$ and $T^*_{mb} = T^*_m$ equation (37) reduces to:

$$\begin{aligned}\Delta H_u\left(1 - \frac{T_{mb}}{T^*_m}\right) = &\left(1 - \frac{T_m}{T^*_m}\right) \\ &- \frac{RT_{mb}V_u}{V_1}\left[\frac{\ln \phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_1\right] \\ &- \frac{P^*_2 V^*_2 V_u}{V_1}\left[3\tilde{T}_2 \ln\left(\frac{\tilde{v}_2^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right)\right. \\ &\left. + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} + \tilde{P}_2(\tilde{v} - \tilde{v}_2)\right] \\ &- \frac{V^*_2 V_u}{V_1}\frac{\theta_1^2}{\tilde{v}}\frac{S_2}{S_1}(X_{12} - T_m\tilde{v}Q_{12})\end{aligned} \qquad (38)$$

which is simpler than equation (37) but assumes equal equilibrium melting point for the crystalline region in the homopolymer and the blend.

This equation relates the observable T_m of the homopolymer to that of the blend. The T^*_m of the homopolymer is still required to take into account the morphological changes in the crystalline blend. The last two terms in this equation disappear for athermal mixtures.

CONCLUSION

The spherulitic radial growth rates in a miscible blend of semicrystalline and amorphous polymer are shown to be slower than that of the semicrystalline homopolymer. The half-time crystallization in the blends is higher than that of the homopolymer. The observable melting temperature in a blend is related to the blend's equilibrium melting temperature via four terms, morphology, entropies and enthalpy. The observable melting-point depression in the blend is not easily related to the observable melting temperature of the homopolymer without any simplifying assumption. The present theory requires careful experimental work for verification.

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NOTATION

PPO	poly(2,6-dimethylphenylene oxide)
PS	polystyrene
DPS	deuterated polystyrene
PVDF	poly(vinylidene fluoride)
PMMA	poly(methyl methacrylate)
PVME	poly(vinyl methyl ether)
PES	poly(ether sulphone)
PEO	poly(ethylene oxide)
PVC	poly(vinyl chloride)
PBA	poly(butyl acrylate)
PE	polyethylene
CPE	chlorinated polyethylene
PP	polypropylene
PC	polycarbonate
EVA	ethylene vinyl acetate
PVAc	poly(vinyl acetate)
PEEK	poly(ether ether ketone)
PET	poly(ethylene terephthalate)
T_g	glass transition temperature
ΔG_u	Gibb's free energy difference per mole of crystalline unit of the homopolymer (J mol^{-1} of crystalline unit)
ΔH_u	heat of melting of the crystalline unit in the homopolymer (J mol^{-1} of crystalline unit)
ΔS_u	entropy differences (J mol^{-1} K^{-1} of crystalline unit)
n	number of crystalline units, which is equivalent to the lamella thickness
σ_e	surface free energy of chain-folded surface (J cm^{-2})
σ_o	lateral surface free energy (J cm^{-2})
Δg_M	difference in the free energy of mixing per mole of crystalline component (J mol^{-1} of crystalline component)
T_m	observable melting point (K)
T^*_m	equilibrium melting point of the homopolymer (K)
G	spherulitic radial growth rate (μm s^{-1})
α, β	constants
f	free volume fraction
$\Delta\alpha$	difference in the thermal expansion coefficients (K)
w_c	volume crystallinity at time t
w_{max}	maximum volume crystallinity
N_0	density of nuclei (nuclei μm^{-1})
$\Delta\mu_{2u}$	chemical potential per mole of crystalline unit (J cm^{-3} mol)
V_{2u}	molar volume of the crystalline unit
V_1	molar volume of the amorphous polymer unit
ϕ_i	volume fraction of component i
r_i	chain length of polymer i

χ_{12}	Flory–Huggins interaction parameter per crystalline unit
P_2^*	hard core pressure of component 2
V_2^*	hard core volume of component 2
$\tilde{v}_2$	reduced volume of component 2
$\tilde{v}$	reduced volume of the blend
$\tilde{P}_2$	reduced pressure of component 2
$\tilde{T}_2$	reduced temperature of component 2
θ_i	surface site fraction of component i
X_{12}	enthalpic interaction energy (J cm^{-3})
Q_{12}	entropic contact energy (J cm^{-3} K^{-1})
S_i	surface-to-volume ratio of component i
ω_i	weight fraction of component i
$v_{i\mathrm{sp}}^*$	hard core specific volume (cm^3 g^{-1})
ΔH_{M}	heat of mixing (J g^{-1})
Δb_{M}	partial molar entropy difference

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