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Melting Point Depression in Crystalline/Compatible Polymer Blends

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ABSTRACT: The determination of polymer/polymer interaction parameters (χ) from melting point data is critically reviewed with emphasis on two major areas. The first concerns variations of morphology with blend composition which can restrict attempts to calculate χ if nonequilibrium melting points are used. An equation is presented that relates the experimentally observed melting point change upon blending to the thermodynamic melting point depression and a morphological term that accounts for changes in lamellar thickness. Other morphological factors such as crystalline perfection and size are discussed. The second area of interest involves processes such as lamellar thickening during thermal analysis that can seriously impair determination of "true" crystalline melting points. Finally, methods for directly determining blend equilibrium melting points are discussed.

1. Introduction

In the past decade, blending or alloying polymers has been shown to be an excellent way of developing new materials exhibiting combinations of properties that cannot be obtained from any one polymer. Of special interest are those blends in which the component polymers are believed to be mixed on the molecular level. A large number of these "compatible" blends are composed of macromolecules that are chemically dissimilar. It is believed that specific interactions between unlike moieties are the driving force for miscibility in these systems. Chemically similar polymers can also exhibit compatibility. However, since the change in entropy upon mixing is small for two high molecular weight materials, the enthalpy of mixing cannot exceed a small critical value without phase separation occurring. It is for this reason that the rule of "like dissolves like" does not always apply to polymeric alloys.

There is a great deal of interest in compatible systems that contain at least one crystallizable component (crystalline/compatible blends). This is at least partially due to the fact that roughly one-half to two-thirds of all commercially significant polymers are crystalline or crystallizable. In these systems, the crystalline regions are phase separated from a miscible amorphous matrix.

Research on compatible blends, as well as polymer alloys in general, has expanded in the past 5–10 years as evidenced by the publication of a number of texts and review articles.[1-5] However, many questions remain unresolved. One of the most intriguing of these is the nature and extent of polymer/polymer compatibility. The most widely used technique for determining the magnitude of compatibility-inducing interactions in crystalline/compatible blends is melting point depression. The purpose of this article is to critically review this approach.

2. Background

Thermodynamic considerations predict that the chemical potential of a polymer will be decreased by the addition of a miscible diluent. If the polymer is crystallizable, this decrease in chemical potential will result in a decreased equilibrium melting point. Using the thermodynamic considerations of Scott,[6] Nishi and Wang[7] derived a relationship describing the melting point depression of a crystalline polymer due to the presence of a miscible diluent:

$$\frac{1}{T_m^{\circ\prime}} - \frac{1}{T_m^{\circ}} = \frac{-R\bar{V}_c}{\Delta H_f^{\circ}\bar{V}_a}\left[\frac{\ln V_c}{M_c} + \left(\frac{1}{M_c} - \frac{1}{M_a}\right)V_a\right] + \frac{-R\bar{V}_c}{\Delta H_f^{\circ}\bar{V}_a}(\chi V_a^2) \qquad (1)$$

where $\bar{V}$ is the molar volume of the polymer repeat unit, V the volume fraction of the component in the blend, ΔH_f° the perfect crystal heat of fusion of the crystallizable polymer, M the degree of polymerization, R the universal gas constant, T_m° the equilibrium melting point of the pure crystallizable component, $T_m^{\circ\prime}$ the equilibrium melting point of the crystalline material in the blend, and χ the polymer/polymer interaction parameter. The subscripts a and c denote the amorphous and crystalline components, respectively. The first term on the right-hand side of eq 1 reflects the entropy of mixing contribution to the equilibrium melting point depression while the second term reflects the enthalpy of mixing contribution.

In the case where the miscible diluent is polymeric, the entropy of mixing becomes negligible and the melting point depression will be largely enthalpic in nature. Equation 1 then reduces to

$$\frac{1}{T_m^{\circ\prime}} - \frac{1}{T_m^{\circ}} = \frac{-R\bar{V}_c}{\Delta H_f^{\circ}\bar{V}_a}(\chi V_a^2) \qquad (2)$$

The parameters of major interest in the preceding relationship are χ and V_a. Notice that for χ's less than zero, polymer/polymer interactions result in an equilibrium melting point depression. The smaller the value of χ, the greater the polymer/polymer interactions and the greater the melting point depression. Also note that $T_m^{\circ\prime}$ would

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be expected to decrease as V_a increases. Nishi and Wang speculate that for blend systems possessing χ's greater than zero, a melting point elevation should be observed. We feel that this hypothesis will be extremely difficult to prove since any system that would be predicted to have an equilibrium melting point elevation should form a multiphase (incompatible) system.

Referring to eq 2 one can see that if the variation of $T_m{}^{\circ\prime}$ with V_a is known, and values for $\Delta H_f{}^\circ$ and $T_m{}^\circ$ are available, a plot of $1/T_m{}^{\circ\prime} - 1/T_m{}^\circ$ vs. $V_a{}^2$ can be constructed that will yield a value of χ from the slope. It therefore appears that a relatively straightforward approach exists for determining the magnitude of interactions between components of crystalline/compatible blends. However, it is important to note that this approach has been developed from equilibrium conditions. Complications can arise if experimentally determined melting points are used in calculating χ. These complications can be divided into two major categories. The first deals with the possibility of morphological variations with composition. If this occurs, any variation in melting point due to morphology will be superimposed on the thermodynamic melting point depression. The second complication concerns processes such as lamellar reorganization, which can occur while melting points are determined via techniques such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA). These two areas will be discussed systematically in the following sections.

3. Nonequilibrium Melting

A. Morphology. (a) Crystal Thickness. If one desires to employ experimentally determined melting points to calculate χ, it is important to characterize any morphological changes with composition and determine how these changes would influence the observed melting points (T_m). The most important morphological influence on T_m's is the crystalline thickness (L). Consider an isothermally crystallized compatible blend composed of a semicrystalline polymer and an amorphous one. If significant polymer/polymer interactions occur (we assume that both polymers are high molecular weight), $T_m{}^{\circ\prime}$ will decrease as the concentration of the amorphous component increases. For a given crystallization temperature (T_c), one would therefore expect L to increase with increasing amounts of the amorphous component because of the decrease in the degree of supercooling at which crystallization occurs. Note that this variation of L with composition changes the observed melting point of the crystalline polymer in the blend in a manner opposite to that expected simply from thermodynamic considerations. In order to determine the relative magnitudes of these effects we performed a simple manipulation employing the Hoffman/Weeks relationship.[8] The melting points (nonequilibrium) of the pure crystallizable polymer (T_{m_A}) and the crystalline polymer in the blend (T_{m_B}) can be represented as follows:

$$T_{m_A} = T_{m_A}{}^\circ\left(1 - \frac{2\sigma_e}{\Delta H_f{}^\circ L_A}\right) \tag{3}$$

$$T_{m_B} = T_{m_B}{}^\circ\left(1 - \frac{2\sigma_e}{\Delta H_f{}^\circ L_B}\right) \tag{4}$$

where σ_e is the fold surface free energy and, from our previous definitions, $T_{m_A}{}^\circ = T_m{}^\circ$ and $T_{m_B}{}^\circ = T_m{}^{\circ\prime}$. If it is assumed that the surface free energies remain relatively constant upon blending,[9] we find by combining eq 3 and 4 that the difference in experimentally observed melting points between the pure polymer and the crystalline polymer in the blend (ΔT_m) can be expressed as

$$\Delta T_m = \Delta T_m{}^\circ + \frac{2\sigma_e}{\Delta H_f{}^\circ}\left(\frac{T_{m_B}{}^\circ}{L_B} - \frac{T_{m_A}{}^\circ}{L_A}\right) \tag{5}$$

where, $\Delta T_m{}^\circ = T_{m_A}{}^\circ - T_{m_B}{}^\circ$. Notice that the difference in melting point is composed of two terms, one due to the thermodynamic depression ($\Delta T_m{}^\circ$) and another due to the differences in crystal thickness. It is desirable at this point to substitute into eq 5 a relationship for L in terms of the crystallization temperature and material constants. There are a number of such relationships available; the selection of the proper one rests on whether or not crystal thickening at T_c occurs. Kinetic crystallization theory[10] yields the following relationship for the thickness of crystals formed initially at a given $T_c(l^*)$:

$$l^* = 2\sigma_e/\Delta F + \delta \tag{6}$$

where ΔF is the free energy difference between the supercooled liquid phase and the bulk crystal phase. The parameter δ will be discussed in detail subsequently. ΔF can be expressed as

$$\Delta F = \left(\frac{T_m{}^\circ - T_c}{T_m{}^\circ}\right)\Delta H_f{}^\circ \tag{7}$$

This relationship was originally derived for pure crystalline polymers but can be used for blends if the blend equilibrium melting point is substituted for $T_m{}^\circ$.[9] Equation 6 therefore becomes

$$l^* = \frac{2\sigma_e T_m{}^{\circ\prime}}{\Delta H_f{}^\circ(T_m{}^{\circ\prime} - T_c)} + \delta \tag{8}$$

Controversy exists as to whether crystals that form initially at a given supercooling thicken during isothermal crystallization. There is evidence that suggests that this process does not occur in solution-grown polyethylene single crystals.[11,12] However, for crystallization conducted at supercoolings lower than that normally obtainable from solution, a number of investigators have observed an increase in lamellar thickness and melting point with time during crystallization at T_c.[13-16] A simplifying assumption often made for this case is that the final lamellar thickness (L) is β times larger than the initial thickness (l^*). On the other hand, in a recent study on melt-crystallized polyethylene it was concluded from small-angle X-ray scattering (SAXS) measurements that thickening at T_c is not prominent.[17] Because of the controversial evidence, we will discuss eq 5 assuming both the presence and absence of lamellar thickening at T_c.

For the case in which no thickening takes place at T_c, substitution of eq 8 into eq 5 results in

$$\Delta T_m = \Delta T_m{}^\circ + \left(\frac{T_{m_B}{}^\circ}{\dfrac{T_{m_B}{}^\circ}{T_{m_B}{}^\circ - T_c} + \dfrac{\Delta H_f{}^\circ \delta_B}{2\sigma_e}} - \frac{T_{m_A}{}^\circ}{\dfrac{T_{m_A}{}^\circ}{T_{m_A}{}^\circ - T_c} + \dfrac{\Delta H_f{}^\circ \delta_A}{2\sigma_e}}\right) \tag{9}$$

Notice that given values for δ, $H_f{}^\circ$, and σ_e, eq 9 describes ΔT_m in terms of $T_{m_A}{}^\circ$ and $T_{m_B}{}^\circ$.

Before the implications of eq 9 are discussed, it is necessary to consider the nature of δ. This parameter, which results from the kinetic theory of crystallization, helps define the thickness of crystals that will form at a given

Table I
Parameters Used for Illustrative Calculations (PVF_2/PMMA)

$\chi = -0.3$
$\Delta H_f^\circ = 1600$ cal/mol
$T_m^\circ = 447$ K
$V_c = 34.0$ cm^3/mol
$V_a = 84.9$ cm^3/mol
$\sigma_e = 47.5$ ergs/cm^2
$\sigma = 9.8$ ergs/cm^2
$a = 5.43$ Å
$b = 4.45$ Å

Table II
Variation of ΔT_m, ΔT_m°, and l^* with Volume Fraction PMMA (V_a)

		$\delta = 10$ Å		$\delta = 20$ Å	
V_a	ΔT_m°, K	ΔT_m, K	l^*, Å	ΔT_m, K	l^*, Å
		$T_c = 427$ K			
0	0	0	118	0	128
0.1	0.3	<0.1	120	<0.1	130
0.2	1.3	0.2	125	0.4	135
0.3	2.9	0.4	135	0.8	145
0.4	5.1	0.7	153	1.3	163
0.5	7.8	1.0	185	1.9	195
0.6	11.2	1.3	250	2.4	260
0.7	15.1	1.6	438	2.9	448
		$T_c = 397$ K			
0	0	0	53	0	63
0.1	0.3	0.1	53	0.2	63
0.2	1.3	0.4	54	0.6	64
0.3	2.9	0.9	56	1.4	66
0.4	5.1	1.6	57	2.5	67
0.5	7.8	2.4	60	3.8	70
0.6	11.2	3.4	64	5.4	74
0.7	15.1	4.4	70	7.1	80

T_c. δ is the thickness that gives the crystals the necessary stability to form by creating a situation where the free energy of crystal formation is negative.[10]

Of importance in the analysis of eq 9 is whether δ would be expected to vary upon blending. The most exact form of δ is[10]

$$\delta = \frac{KT_c}{2b\sigma}\,\frac{2 + (1 - 2\psi)a(\Delta F)/2\sigma}{[1 - a(\Delta F)\psi/2\sigma][1 + a(\Delta F)(1 - \psi)/2\sigma]} \qquad (10)$$

where ψ, σ, and K are the adsorption parameter, side surface free energy, and Boltzmann constant, respectively. a and b are the width and thickness of the polymer molecule. By employing eq 2, 7, and 10 and parameters appropriate for the compatible poly(vinylidene fluoride)/poly(methyl methacrylate) (PVF_2/PMMA) blend system,[7,9] (Table I), we determined δ as a function of blend composition. The range of values calculated when the volume fraction of PMMA is varied from 0 to 0.7 (assuming that ψ is constant and equal to 0.2 or 0.5) is less than 1 Å. Therefore it appears that δ can be considered to be independent of blend composition. We do recognize that greater changes occur if δ is calculated for large undercoolings and large values of ψ. However, this behavior is not of concern since under these conditions the kinetic crystallization theory yields unreasonable values for l^* and δ and should not be utilized.[10]

It is appropriate at this point to direct attention back to eq 9. By employing the Nishi/Wang relationship and the parameters noted in Table I, we calculated for illustrative purposes the equilibrium melting point depression that would be expected at various compositions for a typical χ value of -0.3. We then substituted these values into eq 9 and determined how ΔT_m would vary with composition for different values of T_c and δ. Values for δ of 10 and 20 Å were selected since this range appears to be appropriate for a large body of polymers.[10] Also determined was the variation of lamellar thickness with composition (see eq 8). The results of these calculations are summarized in Table II. Notice that in all cases, the equilibrium melting point depression is considerably larger than that which would be observed experimentally. This results as a consequence of the increase in lamellar thickness upon blending. By rearranging eq 9, one can show that the effect of lamellar thickness can never completely offset the thermodynamic melting point depression, all other factors remaining constant. However, it is apparent that if investigators use experimentally determined T_m's to evaluate χ's, they may be significantly underestimating the magnitude of polymer/polymer interactions. It is important to realize that the preceding arguments are valid only if one is monitoring the true melting point of the as-formed crystals at a given T_c. Additional complications, such as lamellar reorganization during thermal analysis, will be discussed in a subsequent section.

There is little experimental evidence concerning the variation of L with composition for crystalline/compatible blends. Warner et al.[18] monitored L for the isotactic polystyrene (iPS)/atactic polystyrene system and observed no variation in L with composition. This is not surprising since one would expect that $\chi \approx 0$ for this system, resulting in no significant melting point depression or supercooling variation with composition. Khambatta et al.[19] studied blends of poly(ϵ-caprolactone) (PCL) and poly(vinyl chloride) (PVC) and observed that the L of PCL increased slightly with blend composition. This behavior is consistent with the supercooling argument. Somewhat more disturbing results were observed by Wenig and co-workers,[20] who studied the iPS/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend system. They reported a significant decrease in the iPS crystal thickness with increasing PPO content. This is contrary to what is expected and the explanation for this behavior is unclear at present.

We now discuss the implications of lamellar thickening at T_c upon eq 5. For this case the crystals initially formed are allowed to thicken by some factor β and we assume that β is independent of the degree of supercooling. Therefore, instead of directly substituting l^* (eq 6) into eq 5 we substitute βl^*, resulting in

$$\Delta T_m = \Delta T_m^\circ + 1/\beta\left[\frac{T_{m_B}^\circ}{\dfrac{T_{m_B}^\circ}{T_{m_B}^\circ - T_c} + \dfrac{\Delta H_f^\circ \delta_B}{2\sigma_e}} - \frac{T_{m_A}^\circ}{\dfrac{T_{m_A}^\circ}{T_{m_A}^\circ - T_c} + \dfrac{\Delta H_f^\circ \delta_A}{2\sigma_e}}\right] \qquad (11)$$

Assuming the values for PVF_2 and PMMA in Table I, we have calculated the variation of ΔT_m with composition at $T_c = 427$ K for different values of β and δ (Table III). Notice that as in the case of no thickening at T_c the equilibrium melting point depression is larger than the expected experimental melting point depression. However, this difference becomes less significant as the value of β increases. Data were calculated for $\delta = 0$ to show that at high β values the contribution of δ to ΔT_m becomes less significant. Therefore, for large values of β, eq 11 can be expressed as

$$\Delta T_m = \Delta T_m^\circ(1 - 1/\beta) \qquad (12)$$

This expression clearly shows that ΔT_m is less than ΔT_m° and that the greater the value of β, the smaller the difference between ΔT_m and ΔT_m°. It is important to remember that eq 12 has been derived by assuming β to be independent of blend composition and T_c. These assumptions are troublesome; in fact, it has been suggested that β will increase with increasing T_c.[10] Nevertheless eq

Table III
Variation of ΔT_m, $\Delta T_m°$, and L with Volume Fraction PMMA (V_a) (T_c = 427 K)

		δ = 0 Å		δ = 20 Å	
V_a	ΔT_m,° K	ΔT_m, K	L, Å	ΔT_m, K	L, Å
		β = 2			
0	0	0	216	0	256
0.1	0.3	0.2	219	0.2	259
0.2	1.3	0.6	230	0.8	270
0.3	2.9	1.4	250	1.8	290
0.4	5.1	2.5	286	3.2	326
0.5	7.8	3.9	349	4.9	389
0.6	11.2	5.6	479	6.8	519
0.7	15.1	7.6	856	9.0	896
		β = 3			
0	0	0	324	0	384
0.1	0.3	0.2	329	0.2	389
0.2	1.3	0.8	345	1.0	405
0.3	2.9	1.9	375	2.2	435
0.4	5.1	3.4	428	3.8	488
0.5	7.8	5.2	524	5.9	584
0.6	11.2	7.5	719	8.3	779
0.7	15.1	10.1	1283	11.1	1343

Table IV
Effect of Lateral Crystallite Size (x) on T_m[a]

x, Å	T_m, K	x, Å	T_m, K
∞	436.2	250	432.6
1000	435.3	100	427.3
500	434.4		

[a] L = 200 Å.

11 is interesting for illustrative purposes.

(b) Crystalline Size and Perfection. Another morphological factor that has been suggested to influence melting points is the degree of crystalline perfection. One might imagine that the presence of a noncrystallizable polymer could disrupt the packing of the crystalline component in the blend, resulting in defective, lower melting crystallites. To our knowledge there has been no direct evidence to substantiate this effect in compatible blends. A number of authors have commented on the perfection of the spherulitic superstructure in crystalline/compatible systems. In general, it has been observed that spherulites become more coarse and open as the concentration of the noncrystallizable component increases.[21,22] However, spherulitic order itself would not directly influence melting behavior. Melting points may however be affected if the individual lamellae within the spherulites become of dimensions such that side surface free energies are important. Consider the simple case of a square crystal with thickness L and lateral dimension "x". There will be surface free energies associated with the top or fold surfaces (σ_e) and the side surfaces (σ). Following the arguments of Hoffman and Weeks,[8] the free energy of formation (ϕ) of such a crystal can be expressed as

$$\phi = 2x^2\sigma_e + 4xL\sigma - x^2L(\Delta F) \qquad (13)$$

Setting $\phi = 0$ and substituting eq 7 into eq 13, we find

$$T_m = T_m°\left[1 - \frac{1}{\Delta H_f°}\left(\frac{2\sigma_e}{L} + \frac{4\sigma}{x}\right)\right] \qquad (14)$$

Equation 14 describes the T_m of a crystal in terms of its width and thickness. If the assumption is made that $x \gg L$, the term $4\sigma/x$ becomes much smaller than $2\sigma_e/L$, resulting in the classic Hoffman/Weeks expression.

It is important to consider what magnitude of a melting point decrease would be expected if lateral crystal size does indeed become smaller upon blending. For illustrative purposes we have performed sample calculations with $T_m°$, σ_e, σ, and $\Delta H_f°$ for poly(vinylidene fluoride). As shown in Table IV, melting points can decrease significantly with decreasing crystallite size. To our knowledge there have been only two experimental studies of crystallite size in crystalline/compatible blends, these being conducted by the wide-angle X-ray line-broadening technique (which yields a measure of a perpendicular distance through a set of parallel crystallographic planes). For blends of poly(ethylene oxide) and poly(methyl methacrylate) (PMMA) crystallized at a variety of supercoolings, both increases and decreases in apparent crystallite size were observed upon the addition of PMMA.[23] This contrasts with the iPS/PPO system, in which no variation of crystallite size was noted.[24] It is important to be aware that although the line-broadening technique would appear to be appropriate for this type of investigation, it is not clear whether the sizes measured are delineated by actual crystal surfaces, crystal offset, or a collection of crystalline defects.

B. Factors Associated with Thermal Analysis. Since investigators studying semicrystalline materials routinely use DTA or DSC to determine T_m's, it is important to be aware of factors that can complicate these dynamic experimental methods. Of prime importance is the determination of the "true" melting point and melting behavior of a specimen. Many semicrystalline polymers have been observed to anneal (i.e., reorganize to a higher melting form) during DTA/DSC temperature scans. This process apparently involves some type of lamellar thickening mechanism. A common technique used to determine if a polymer is prone to reorganization upon heating is to perform the thermal analysis at a variety of heating rates. For polymers that exhibit a single melting endotherm but whose behavior is complicated by lamellar thickening, increasing the heating rate will decrease the observed T_m since the lamellae are given less time to reorganize. This argument assumes that neither low polymer thermal conductivity or superheating is complicating the observed behavior. Some polymers have been shown to exhibit multiple (usually dual) melting endotherms, which are often believed to be the result of melting, followed by recrystallization and final melting. In this case, if the higher melting endotherm is associated with the melting of reorganized material, one would expect the magnitude of this endotherm to decrease with increasing heating rate.

There is no reason to believe that lamellar thickening is not a prominent process in the melting of semicrystalline blends. In fact, these systems pose interesting problems to those concerned with melting behavior. Consider a compatible blend of a high-T_g amorphous polymer and a semicrystalline polymer of low T_g. As a consequence of compatibility, the amorphous phase T_g increases as the concentration of the noncrystallizable component increases. One might intuitively expect that the increasing T_g of the amorphous regions would tend to inhibit lamellar thickening. Evidence suggesting this behavior has been observed for blends of semicrystalline PCL (T_g = −70 °C) and amorphous SAN (poly(styrene-*co*-acrylonitrile), T_g = 100 °C), a compatible system that exhibits dual melting behavior.[25] The DSC thermograms of melt-crystallized SAN/PCL blends show that as the concentration of SAN in the blends increases (increasing T_g), the higher temperature endotherm decreases in magnitude relative to the lower temperature endotherm (Figure 1). Notice also that the melting point of the lower temperature endotherm (T_{m_1}) increases in temperature with increasing SAN content, contrary to what would be expected from the discussion in the previous sections. The reason for this dis-

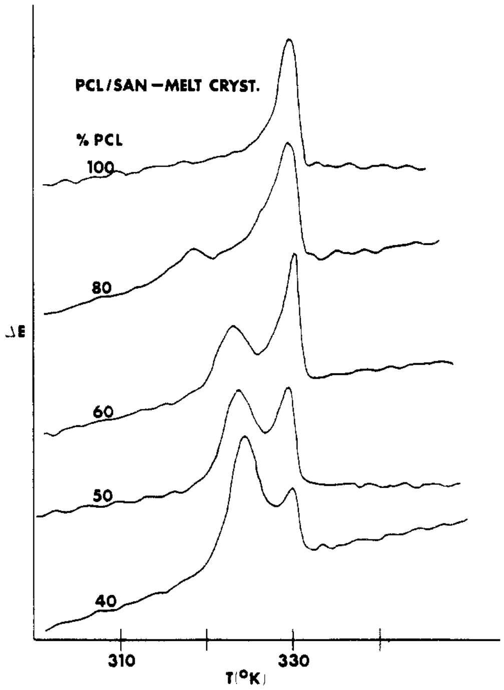

Figure 1. Representative DSC thermograms of melt-crystallized SAN/PCL blends. (Heating rate, 10 °C/min.)

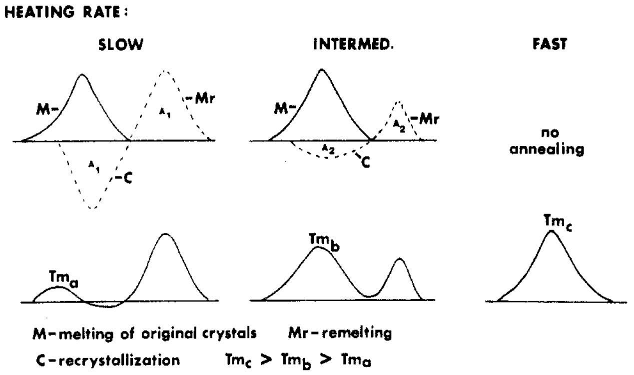

Figure 2. Schematic representation of the mechanism proposed to account for the melting behavior of melt-crystallized SAN/PCL blends. The top of the figure shows the melting of the original crystals (M), recrystallization (C), and remelting (Mr). The bottom portion of the figure shows the resultant thermograms that one would expect to observe experimentally. (Note that $T_{m_c} > T_{m_b} > T_{m_a}$.)

crepancy apparently arises from the inability of the DSC to determine the T_m of the as-formed crystals at conventional heating rates. This behavior is best rationalized by considering a melting mechanism that was previously proposed for this system.[25] We feel that a process consisting of melting of the crystals formed at T_c, recrystallization, and subsequent remelting is occurring (Figure 2). Two major consequences of this model are that as the heating rate is increased, T_{m_1} would be expected to increase in temperature and the higher melting endotherm would be expected to decrease in magnitude. Both of these effects were observed experimentally. With this melting mechanism as background, we are in a position to rationalize the variation of melting point with blend composition at a given heating rate. As stated previously, the blend amorphous phase T_g increases with increasing SAN content, resulting in a stiffer matrix surrounding the crystallites and possibly inhibiting crystal thickening. As a consequence of this variation in the tendency to undergo thickening, the magnitude of the recrystallization exotherm could be smaller for blends of high SAN content. Since the net effect of the recrystallization exotherm is to shift T_{m_1} to lower temperatures (see Figure 2), one would expect T_{m_1} to occur at higher temperatures for SAN-rich blends, as has been observed. It appears that the lower temperature endotherm is not representative of the melting of crystals formed at T_c but is a composite of the original melting and any recrystallization during heating.

A method used to determine the true T_m of crystals formed at T_c is to increase the heating rate such that crystal reorganization is minimized. Attempts to perform experiments at high rates on SAN/PCL blends were unsuccessful for a number of reasons, the foremost of which we believe is the problem of low polymer thermal conductivity. T_m's were observed to significantly increase at high heating rates, presumably because of the time necessary for heat to be transmitted throughout the sample. Another problem encountered at high heating rates was the loss of resolution between the two endotherms. It is apparent that the behavior of crystalline/compatible blends can be rather complex and that true experimental melting points can be difficult to determine.

4. Extrapolation Methods To Obtain Equilibrium Melting Points

To avoid potential complications due to changes in lamellar thickness, one can follow the methods of Hoffman and Weeks and directly determine $T_m^{\circ\prime}$ for a blend of given composition.[26-29] Although these methods are superior to the nonequilibrium procedure discussed previously, they are not without complications. The question of whether lamellar thickening occurs at T_c again becomes important. We will discuss the behavior that would be expected in both the presence and absence of this phenomenon. If we assume that the crystals initially formed at a given T_c do thicken by some factor β, the observed T_m can be expressed as follows:

$$T_m = T_m^\circ\left[1 - \frac{2\sigma_e}{\Delta H_f^\circ(\beta l^*)}\right] \qquad (15)$$

where $\beta l^* = L$, the final crystal thickness. By substituting the relationship for l^* in eq 8 into eq 15 and assuming δ to be small and β to be independent of T_c, one can express T_m as a linear function of T_c:[10]

$$T_m = T_m^\circ(1 - 1/\beta) + T_c/\beta \qquad (16)$$

T_m° (or $T_m^{\circ\prime}$) can be determined from a plot of T_m vs. T_c, where T_m° is the intercept of the extrapolated T_m's with the line defined by $T_m = T_c$. However, there are a number of factors that can potentially complicate this analysis. Determination of the true T_m of crystals formed at a given T_c can be difficult, as was discussed in the preceding section. In addition, it has been suggested that β will increase with increasing T_c, resulting in an overestimation of T_m°.[10] For the case of crystalline/compatible blends, it is not clear what influence (if any) blend composition and T_g have on the thickening behavior at T_c. Finally, it has been suggested that the effective value of σ_e is temperature dependent.[30] This can give rise to nonlinear T_m vs. T_c plots and cause considerable difficulties in determining reliable equilibrium melting points.

In the absence of thickening at T_c (i.e., $\beta = 1$), eq 8 is again substituted into eq 15; however, the δ term is not disregarded since this would result in $T_m = T_c$

$$T_m = T_m^\circ\left[1 - \frac{1}{\dfrac{T_m^\circ}{T_m^\circ - T_c} + \left(\dfrac{\Delta H_f^\circ \delta}{2\sigma_e}\right)}\right] \qquad (17)$$

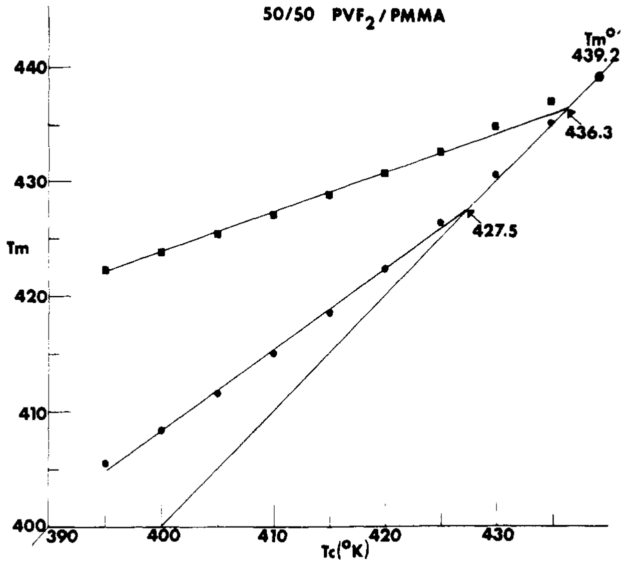

Figure 3. Theoretical plot of T_m vs. T_c for a 50/50 blend of PVF_2 and PMMA for different values of β ((■) $\beta = 2$; (●) $\beta = 1$). δ was assumed to be 15 Å in each case. The solid lines correspond to a least-squares fit for blends crystallized from 395 to 425 K.

which is an identity with eq 6 of ref 10. Again we have assumed that true melting points are available and have neglected any supercooling dependence of σ_e. Calculations have been performed by employing eq 17 and the parameters listed in Table I for a 50/50 PVF_2/PMMA blend (assuming $\delta = 15$ Å). These data are plotted in Figure 3. Notice that in this case that the deviation from linearity is apparent; however, this probably would not be discernible from experimental data encompassing a relatively small range of T_c's. In studies on the dependence of T_m on T_c, supercoolings of approximately 15–45 °C are usually employed. As can be seen in Figure 3, our calculated data are reasonably linear in this range. If one were to extrapolate these data to $T_m = T_c$, the observed $T_m^{\circ\prime}$ would be some 11 °C lower than the actual value. It is clear that if thickening at T_c is not significant, determination of $T_m^{\circ\prime}$ (or T_m°) by extrapolation can result in serious errors unless data at low supercoolings are obtained.

For illustrative purposes we have also performed sample calculations based on the data in Table I for the case where both thickening at T_c and δ are considered. Figure 3 shows the results for a 50/50 PVF_2/PMMA mixture assuming $\delta = 15$ Å and $\beta = 2$. Note that the curvature of this plot is much less than in the case of no thickening at T_c and linear extrapolation of the data at supercoolings from 15–45 °C results in an apparent $T_m^{\circ\prime}$ 3 °C less than the actual value. This deviation is much less than that for the case of no thickening at T_c and, in general, as β becomes larger, the apparent $T_m^{\circ\prime}$ obtained by extrapolation of data at conventional supercoolings will approach the actual $T_m^{\circ\prime}$. Including a supercooling dependence for β will result in more pronounced curvature of the T_m vs. T_c plot but will tend to give rise to a higher apparent $T_m^{\circ\prime}$ that may compensate for the underestimation of $T_m^{\circ\prime}$ through the "δ effect".

Another method of determining T_m° is to plot the observed melting point vs. $1/L$ and extrapolate to $1/L \rightarrow 0$. This technique arises directly from eq 3 and is somewhat less ambiguous than the T_m/T_c method since the exact relationship between L and T_c is not needed. Problems with the T_m vs. $1/L$ plots are associated with measuring T_m and L accurately. Determination of accurate T_m's can be difficult, as was discussed in the preceding section. L is usually measured by small-angle X-ray scattering (SAXS). Experimentally, the long period (crystalline + amorphous thickness) rather than L is obtained directly from the scattering curve. In a number of crystalline/compatible blends, it has been shown that the rejected, noncrystallizing second component resides in interlamellar regions.[19,20,31] Therefore, the measured long period and amorphous-phase thickness vary appreciably with blend composition but these variations are not simply related to L. One must therefore choose a theoretical model to extract L from the scattering curve and the values obtained can be dependent on the specific model chosen to interpret the data.[18]

It is interesting that in studies on pure crystalline polymers the T_m vs. T_c and T_m vs. $1/L$ approaches have yielded very similar values for T_m°.[10,32] This appears to be an indication that thickening at T_c is important in pure polymers. However, one should be careful when applying the T_m/T_c method to systems in which crystal thickening at T_c has not been established.

5. Conclusions

(1) An equation describing the experimentally observed melting point depression in binary crystalline/compatible blends in terms of the thermodynamic melting point depression and changes in lamellar thickness has been presented. This relationship predicts that the observed T_m depression can be significantly less than the thermodynamic depression due to the morphological term. This may result in a serious underestimation of χ if nonequilibrium T_m's are used in the usual Nishi/Wang expression.

(2) Melting points can decrease significantly with decreasing crystallite size. However, it is not clear what influence the addition of a second compatible polymer has on the lateral crystal size.

(3) Crystalline/compatible blends can exhibit complex melting behavior. DSC thermograms of SAN/PCL blends show that lamellar reorganization during thermal analysis can be a prominent complicating effect. Since this process is presumably T_g dependent, it might be expected that the tendency for reorganization would vary with composition if the blend components are of differing T_g. This behavior casts some doubt on one's ability to readily determine the true melting point of the crystals formed at a given T_c.

(4) Typical methods for determining the equilibrium melting point of the crystalline portion of a crystalline/compatible blend were critically reviewed. Plotting T_m vs. $1/L$ and extrapolating to $1/L \rightarrow 0$ appears to be, in principle, the most appropriate method for estimating equilibrium melting points. However, determination of L for crystalline/compatible blends is currently a difficult task.

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Registry No. PVF_2, 24937-79-9; PMMA, 9011-14-7.

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Mesophase Formation and Polymer Compatibility. The Poly(*p*-benzamide)–Polyacrylonitrile–Diluent System

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ABSTRACT: We report a study of phase equilibria for a ternary system involving a rigid polymer, unfractionated poly(*p*-benzamide) (PBA), a random coiled polymer, unfractionated polyacrylonitrile (PAN), and a diluent composed of *N*,*N*-dimethylacetamide + 3% LiCl. Three different PAN samples were used, covering a range of molecular weight between 60 000 and 160 000. Above a critical concentration of the two polymers, one observes a biphasic region composed of a nematic and an isotropic phase. Separation of the two phases by centrifugation, analysis of phase volume and composition, separation of PBA from PAN, and determination of the partition according to molecular weight were performed. The nematic phase contains the high molecular weight fraction of PBA, and the isotropic phase contains PAN + the low molecular weight fraction of the rigid polymer. Increasing the molecular weight of PAN causes an increase of the PAN/PBA ratio in the isotropic phase. The results are in satisfactory agreement with the theory of ternary systems composed of a rigid and a random coiled polymer. Minor deviations from theory involve a greater rejection of PBA by the flexible polymer and a lower amount of diluent in the isotropic phase than predicted. The role of polymer compatibility in the isotropic state is discussed.

In a previous paper[1] we reported the phase behavior of the system poly(*p*-benzamide) (PBA)–polyterephthalamide of *p*-aminobenzhydrazide (X-500)– *N*,*N*-dimethylacetamide (DMAc) + 3% LiCl. The results showed complete exclusion of X-500 from the mesophase that was formed above a critical concentration of the two polymers. X-500 was found only in the conjugate isotropic phase, which contained also the low molecular weight components of PBA. The segregation of X-500 in the isotropic phase was in qualitative agreement with Flory's theory of phase equilibria involving monodisperse rodlike and random coiled polymers.[2] The fractionation of PBA was also expected from the theory of mixtures of rodlike molecules[3,4] and from previous results obtained with binary systems.[5]

Some aspects of the behavior of the ternary systems remained, nevertheless, unclarified. The theoretical basis for incompatibility[2] rests on entropy considerations based on the interference of the random coil with the mutual orientation of the rodlike molecules in the mesophase. Compatibility between rodlike molecules is assisted by the lack of such an interference. We were concerned by the possible role of the degree of flexibility of the nonrodlike component and of the polymer "compatibility", as usually defined in the case of isotropic mixtures of two random coiled polymers.[6] In the latter case, compatibility is prevalently based on enthalpy parameters that reflect favorable interaction between molecules. A contribution from such an effect is not included in the above theories.[2-4] Therefore, we considered of interest the comparison of phase diagrams involving polymers with large differences in their chemical constitution. Furthermore, theory[2-4] only describes the behavior of two extremes: rigid rods and random coils. Are polymers of intermediate rigidity (e.g., wormlike chains) expected to enter the mesophase or the isotropic solution? The study of these problems is relevant not only to the thermodynamics of liquid crystalline solutions but also to the processing of two-polymer systems.

In the present paper we describe the behavior of the PBA–polyacrylonitrile (PAN)–DMAc + 3% LiCl systems. With respect to the PBA–X-500–DMAc + 3% LiCl system previously reported, the present system exhibits a much greater difference between the chemical constitution of the rigid and the flexible polymers. Moreover, while X-500 exhibits a partial degree of rigidity,[7-9] PAN conforms with the random coil model. We also study the role of the

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