Polymer Bulletin 11, 517–521 (1984)

Polymer Bulletin

Behavior

Melting Point Elevation in Compatible Polymer Blends

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Summary

An expression is presented which relates the experimentally observed melting point depression in crystallizable, compatible polymer blends to changes in lamellar thickness and thermodynamic considerations. Considering a given crystallization temperature, this relationship suggests that one should observe a depressed blend melting point, despite an increase in lamellar thickness over the pure crystallizable material. Possible explanations for the melting point elevation observed in some compatible blends are discussed.

Introduction

In the past several years there has been considerable interest in compatible polymer blends in which at least one of the components is crystallizable. Of particular interest in these crystalline/compatible mixtures has been the melting behavior of the crystalline component since this can potentially be related to the degree of intermolecular interaction between the constituent polymers. In the majority of melting studies on such systems one observes a decrease in the experimentally determined (non-equilibrium) melting point as more of a second compatible polymer is added to the blend. However, a number of investigators have recently observed an elevation of the melting point of the crystalline polymer in the compatible blend over that of the pure crystallizable polymer crystallized at the same temperature (T_c) (1-4). In this note we would like to discuss the possible origins of this melting point elevation.

Background

We consider an isothermally crystallized compatible blend composed of two high molecular polymers, one of which is semi-crystalline. On the basis of the Nishi-Wang treatment (5), the equilibrium melting point of the crystallizable polymer in the mixture should be less than that of the pure crystallizable polymer if significant intermolecular interactions occur between the component polymers. In other words, one would expect an equilibrium melting point depression if the polymer-polymer interaction parameter (χ) is negative. The magnitude of the equilibrium melting point depression will be a function primarily of the magnitude of any polymer-polymer interactions and the concentration of the crystallizable component in the blend.

The expression describing the melting point depression due to a miscible polymeric diluent is (5):

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

where T_m° is the equilibrium melting point of the pure crystallizable component, $T_{m_B}^{\circ}$ the equilibrium melting point of the crystalline material in the blend, R the universal gas constant, $\bar{V}$ the molar volume of the polymer repeat unit, ΔH_f° the perfect crystal heat of fusion of the crystallizable polymer and V the volume fraction of the component in the blend. The subscripts a and c denote the amorphous and crystalline component respectively. It has been suggested that if χ is positive, one should observe an equilibrium melting point elevation (5). From a strictly mathematical viewpoint this is correct. However, a mixture of two high molecular weight polymers in which χ is positive would form an incompatible system in which the phase separated molecules would be expected to be surrounded by molecules of their own kind. In this case one would expect the thermodynamic criteria upon which Eqn. 1 is based to be invalid and crystallization and subsequent melting to be similar to that in the pure bulk state.

Miscible systems can be formed in situations where χ is positive but the mixing must be driven by the combinatorial entropy, which is ignored in Eqn. 1. Considering the entropy of mixing in Eqn. 1 leads to the conclusion that in a miscible system (irrespective of whether χ is positive or negative) one would expect an equilibrium melting point depression. Melting behavior like that of the pure state would be expected in an incompatible mixture.

If the pure crystallizable polymer and the blend of this polymer with a compatible amorphous one are crystallized at the same T_c, the thickness of the lamellae in the blend would be expected to be larger than that of the pure polymer because of the decreased supercooling at which the blend crystallizes. Taken by itself, this increased lamellar thickness would result in an increased blend melting point and, in fact, this has been suggested to be the origin of the observed melting point elevation (1). However, superimposed on this effect will be an expected decrease in experimental melting point due to thermodynamic effects (i.e. polymer-polymer interactions). By employing a simple manipulation of the Hoffman-Weeks expression (6) we have shown that (7):

$$\Delta T_m = \Delta T_m^{\circ} + \frac{2\sigma_e}{\Delta H_f^{\circ}} \left(\frac{T_{m_B}^{\circ}}{L_B} - \frac{T_m^{\circ}}{L} \right) \qquad (2)$$

assuming that the surface free energy (σ_e) remains constant upon blending (8). In this expression, $\Delta T_m = T_m - T_{m_B}$ is the difference in experimentally observed melting points between the pure crystalline polymer and the crystalline polymer in the blend (B), $\Delta T = T_m^{\circ} - T_{m_B}^{\circ}$ the difference in equilibrium melting points, and L and L_B the crystalline thicknesses of the crystalline polymer in the pure state and in the blend,

Table 1

Predicted crystal thickness and melting point for pure PVF_2 and PVF_2/PMMA blends crystallized at 427 K.

	L(Å)	T_m(K)	ΔT_m°(K)
PVF_2	216	437.0	----
80 PVF_2/20 PMMA	230	436.4	1.3
60 PVF_2/40 PMMA	286	434.5	5.1
40 PVF_2/60 PMMA	479	431.4	11.2

respectively. Examination of Eqn. 2 shows that ΔT_m is composed of two terms, one due to the thermodynamic depression(ΔT_m°) and another due to changing crystal thickness. Notice that these two terms work in opposition: polymer-polymer interactions act to cause a melting point decrease for the crystals in the blend whereas the crystal thickness term results in a melting point elevation. Substitution of the expression for L and L_B from the kinetic theory of crystallization (9) into Eqn. 1 and subsequent rearrangement results in:

$$\Delta T_m = \Delta T_m^{o} (1 - 1/\beta) \qquad (3)$$

for the case were thickening at T_c is important (β is the factor by which the crystals thicken at T_c). Examination of Eqns. 2 and 3 shows that within the constraints of this model, the thermodynamic term offsets the crystal thickness term in all cases. In other words, despite the increase in crystal thickness in the blend, the experimentally observed melting point for the blend should always be lower than that of the pure crystalline polymer crystallized at the same T_c, all other factors remaining constant.

Discussion

For illustrative purposes, Table 1 compares the expected crystal thicknesses and melting points for poly(vinylidene fluoride) (PVF_2) and several compositions of a compatible blend of PVF_2 and poly(methyl methacrylate) (PMMA) based upon Eqns. 2 and 3. For the purpose of these sample calculations, parameters such as σ_e,ΔH_f°, etc. were obtained from the literature (5,8). β was assumed to be equal to 2. T_c was taken to be 427K (a supercooling of 20° for pure PVF_2) and χ was assumed to be -0.3 (5). Note that one would expect the thickness of the PVF_2 crystals to be significantly larger in the blends as compared to pure PVF_2. However, the expected thermodynamic depression in the blend due to the polymer-polymer interactions is such that the observed blend melting point should actually be considerably less than that of pure PVF_2. When considering only crystal thickness and thermodynamic effects it is possible to see blend melting points which are larger than the pure polymer but this can happen only for specimens crystallized at different T_c's.

The question which now must be addressed is why does one occasionally observe a melting point elevation upon blending? One possibility is a variation in σ_e but, at least for the case of PVF_2 and PMMA, σ_e has been found to remain constant upon blending (8). In at least one case, the apparent elevation has been rationalized on the basis of a mechanism in which the as-formed crystals thicken to a higher melting form during thermal analysis. The details of this mechanism have been presented in a previous publication (3) and will not be reiterated here except to note that it can account for an apparent blend melting point elevation.

It is also conceivable that crystallite perfection changes upon blending. A number of publications have appeared in which it has been shown that crystal perfection increases in pure crystalline polymers as T_c increases or if one anneals the polymer at temperatures relatively close to T_m (10-12). On the basis of this work it might be expected that crystal perfection would increase as the concentration of the crystallizable polymer in a compatible blend decreases since the degree of supercooling decreases. The case of the pure crystallizable polymer and crystalline/compatible blend are not strictly analogous since the blend contains a relatively high concentration of "impurities". High molecular weight impurities retard crystal growth rates but it is unclear at present what (if any) direct influence they have on crystalline perfection. The blend melting point would be expected to increase with increasing crystal perfection, all other factors remaining constant. Unfortunately there have been very few experimental studies of crystal perfection in crystalline/compatible blends to date (13) and one must therefore consider this issue unresolved.

In addition to crystal perfection, crystallite size (lateral crystalline order) may also change upon blending. This may also influence experimental melting points with T_m decreasing with decreasing size. There have been two studies of crystallite size in crystalline/compatible blends and both were conducted using the wide angle x-ray line broadening technique (13,14). In one of these studies (14), lateral crystalline order was seen to change significantly upon blending but it is extremely difficult to ascertain what influence this actually has on the observed melting points since one must also take into account any other morphological changes and thermodynamic considerations. Nevertheless,if lateral order increases significantly,it is possible that one could observe a melting point elevation for the blend.

Conclusions

An expression 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 shows that despite the increase in crystal thickness in the blend, the experimentally observed melting point for the blend should always be lower than that of the pure crystalline polymer crystallized at the same T_c, all other factors remaining constant. Other possible rationales for the melting point elevation observed in some compatible blends are discussed.

Acknowledgements

The authors would like to thank the Celanese Plastics and Specialties Company and the General Electric Foundation for partial support of this work.

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Accepted May 9, 1984