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Notes

Melting Point Depression in Multicrystalline Blends: PVF_2/PMMA

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Introduction and Theory

The melting temperature (T_m) of a crystalline polymer is often lowered when it is blended with another polymer with which it is compatible.[1-5] This lowering is due to the entropy of mixing and also due to the interaction between both components of the blend, which is the source of an enthalpic term.[6,7] The melting point depression effect allows a direct determination of the interaction parameter between the components.[2,3] In order to avoid the influence of kinetic factors, equilibrium melting temperatures derived from Hoffman–Weeks plots[8] have been used.[3] Assuming a high degree of polymerization for both components, the entropic term in Scott's equation[2] for thermodynamic mixing of two polymers can be neglected. The melting point depression is then given by

$$\frac{T_{m\alpha}{}^\circ - T_{b\alpha}{}^\circ}{T_{m\alpha}{}^\circ} = -\frac{BV_2}{\Delta H_2}\phi_1{}^2 \qquad (1)$$

where $T_{m\alpha}{}^\circ$ and $T_{b\alpha}{}^\circ$ are the equilibrium melting temperatures of the pure and blended crystals (which will be called hereafter α-crystals), respectively, B is the interaction energy density (negative), V_2 is the molar volume of the repeating unit of the crystallizable polymer, ΔH_2 is the enthalpy of fusion per mole of repeating units and, ϕ_1 is the volume fraction of the noncrystallizable component.

Equation 1 was derived[2,3] based on the implicit assumption that only one type of crystal is present in the system, yielding a single melting point. However, polymeric blends very often show multiple melting peaks in DSC thermograms[1,3,5] arising either from the melting of different crystal forms or from reorganization processes occurring on heating. This is the case of PVF_2/PMMA blends, for which at least three different endotherms have been observed.[3] Then in order to get reliable values for the interaction parameter from eq 1, one should take into account the presence of all of the crystal types in the blend, as will be discussed below.

PVF_2/PMMA Blends

When PVF_2/PMMA blends are annealed below 420 K, a predominant peak appears in the DSC thermogram which corresponds to the melting of the so-called α-crystals. Morra observed[3] that application of eq 1 for this range of crystallization temperatures yields a straight line, in agreement with the results of Nishi and Wang.[2] However, when the blends are annealed above 425 K, two new crystal types, γ and γ', of higher melting points, become predominant, i.e., with a $\gamma + \gamma'$ crystalline fraction larger than that of the α-crystals. We denote by $\gamma + \gamma'$ the sum of both crystallinities corresponding to γ and γ'. It was also shown[3] that γ-crystals are nucleated from the melt whereas γ'-crystals seem to result from a reorganization of α-crystals, i.e., from a crystal–crystal transition. The higher the crystallization temperature and the longer the crystallization time, the more α-crystals transform to γ'-crystals and the larger is the γ'-peak. For crystallization temperatures above 425 K, the plot $(T_{m\alpha}{}^\circ - T_{b\alpha}{}^\circ)/T_{m\alpha}{}^\circ$ vs. $\phi_{PMMA}{}^2$ yields[3] a convex curve above the straight line corresponding to the same plot for T_c below 420 K. It will be shown here, based on very simple thermodynamic considerations, that the observed increased values and the composition dependence of the interaction parameter[3] can partly be due to a misapplication of eq 1.

In deducing eq 1, one uses the entropy and enthalpy of mixing of the volume fractions of both components, whereas in multicrystalline blends there are different coexisting crystals which are not involved in the mixing process until their respective melting points are reached. Therefore, when using eq 1, one should renormalize ϕ_1 with respect to the total volume fraction of the blend which is actually taking part in the redissolution process of the α-crystals. In other words, it is suggested to apply the lattice model and Scott's equation for thermodynamic mixing of two polymers to a reduced matrix of volume $1 - \phi_{\gamma+\gamma'}$, where $\phi_{\gamma+\gamma'}$ represents the volume fraction of those crystals of higher melting point already present in the blend when the melting of α-crystals takes place. Hence the renormalized volume fractions in the reduced lattice are $\phi_1/(1 - \phi_{\gamma+\gamma'})$ and $(\phi_2 - \phi_{\gamma+\gamma'})/(1 - \phi_{\gamma+\gamma'})$ for the first and the second component, respectively. Because the renormalization factor depends on the crystallization temperature T_c, it is not possible to give a simple and rigorous correction of eq 1 for the equilibrium melting point depression. However, if $1/(1 - \phi_{\gamma+\gamma'})$ does not change very drastically in the range of T_c temperatures used for the extrapolation of the Hoffman–Weeks plots, one can approximate

$$\frac{T^\circ_{m\alpha,\gamma+\gamma'} - T^\circ_{b\alpha,\gamma+\gamma'}}{T^\circ_{m\alpha,\gamma+\gamma'}} = -\frac{BV_2}{\Delta H_2}\phi_1{}^2\zeta_{\text{eff}}(\phi_1) \qquad (2)$$

with an effective value $\zeta_{\text{eff}} = [1/(1 - \phi_{\gamma+\gamma'})]^2$ for each composition.

It is interesting to note that when $(T^\circ_{m\alpha,\gamma+\gamma'} - T^\circ_{b\alpha,\gamma+\gamma'})/T^\circ_{m\alpha,\gamma+\gamma'}$ is plotted vs. $\phi_1{}^2$ without including the factor ζ_{eff}, the experimental points will fall above the straight line which results from plotting $(T^\circ_{m\alpha,\gamma+\gamma'} - T^\circ_{b\alpha,\gamma+\gamma'})/T^\circ_{m\alpha,\gamma+\gamma'}$ vs. $\phi_1{}^2\zeta_{\text{eff}}$, with a tendency to approach it for the limiting values $\phi_1 = 0$ and $\phi_1 = 1$. This is just the effect observed by Morra in PVF_2/PMMA blends.[3]

From Morra's results two thermograms corresponding to $\phi_{PMMA} = 0.142$ and $\phi_{PMMA} = 0.599$ have been chosen, in which the α-peak appears clearly defined and isolated ($T_c = 432.7$ K). Taking as a first approximation the ratio of the areas under the DSC peaks as the ratio of the respective crystallinities, renormalization factors have been calculated for both compositions, obtaining $\zeta = 2.5$ and $\zeta = 1.4$, respectively. These values are in good agreement with the ones, $\zeta = 2.7$ and $\zeta = 1.4$, derived from the ratio between the experimental melting point depressions for high and low temperatures assuming eq 2 to be valid. It implies that the observed increased values can be lowered by only renormalizing the volume fraction involved in the

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mixing process associated with the melting of the α-crystals. In this way the convex curve associated with the plot $(T_m^\circ - T_b)/T_m^\circ$ vs. ϕ_1^2 is transformed into a straight line with a slope nearly the same as that of the low-temperature data. Moreover, one can derive from eq 2 the renormalization factor for each composition and therefore predict the $\gamma + \gamma'$ crystalline function, which is found to increase with PVF$_2$ content, in qualitative agreement with the DSC observations of the same author.[3]

Conclusions

In conclusion, when applying eq 1 to multicrystalline blends, one should renormalize the volume fractions by excluding the volume associated with crystals not involved in the melting and mixing processes under consideration. Otherwise one can erroneously interpret the results and obtain an apparent composition dependence for the interaction parameter. These arguments offer a plausible explanation for the melting point depression effects observed by Morra et al.[3] in PVF$_2$/PMMA blends.

Registry No. Poly(vinylidene fluoride) (homopolymer), 24937-79-9; poly(methyl methacrylate) (homopolymer), 9011-14-7.

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Homopolymer-Induced Microphase Separation of a Homogeneous Diblock Copolymer

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In a series of recent papers, Hong and Noolandi[1] developed a theory for the phase behavior of various multicomponent polymer systems containing block copolymers. One of the novel features of the theory was the fact that it predicted a particular range (temperature and molecular weight) where a block copolymer by itself can be in a homogeneous state but the addition of a homopolymer will cause the mixture to form a heterogeneous morphology containing microdomains. The purpose of the present Note is to provide experimental verification of this predicted behavior.

Details of the synthesis and characterization of the polymers described here can be found in previous publications from this laboratory[2,3] and in the doctoral thesis of Torradas.[4] The homogeneous diblock copolymer was comprised of a 30 000 molecular weight block of 1,2-polybutadiene (>99% 1,2 addition) and a 100 000 molecular weight block of 1,4-polybutadiene (36% cis 1,4; 51% trans 1,4; 13% 1,2); this copolymer will be referred to by the code 30/100. The two homopolymers employed here were matched in microstructure with the individual block moieties of the copolymer; thus homopolymers are designated 30K 1,2B and 100K 1,4B. As in previous work, specimens of these polymers and various blends were prepared by spin casting[5] from cyclohexane. Specimens were lightly cross-linked with high-energy electrons to facilitate handling. Methods of contrast enhancement for transmission microscopy and techniques employed on our Rheovibron dynamic viscoelastometer have been reported in detail elsewhere.[2,6-8]

Table I
Location of Loss Tangent (3.5 Hz) Maxima for Homopolymers, Binary Homopolymer Blends, and the 30/100 Block Copolymer

specimen	% 30K 1,2B	% 100K 1,4B	% 30/100	$T(\tan\delta_{\max})$, °C
30K 1,2B	100	0	0	9.1
blend 1	75	25	0	9.8 and −82.2
blend 2	50	50	0	13.6 and −77.3
blend 3	23	77	0	14.8 and −76.5
100K 1,4B	0	100	0	−79.1
30/100	0	0	100	−57.0

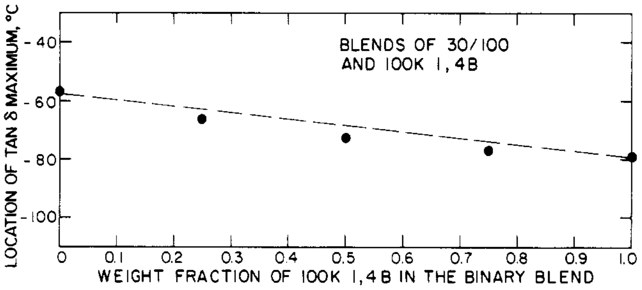

Figure 1. Temperature of the maximum in the loss tangent (3.5 Hz) for blends of 30/100 and 100K 1,4B.

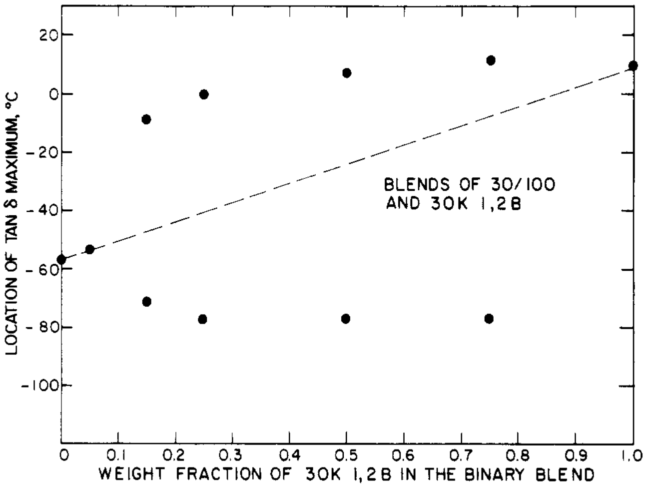

Figure 2. Temperature of the maximum in the loss tangent (3.5 Hz) for blends of 30/100 and 30K 1,2B.

Table I gives the locations of the loss tangent (3.5 Hz) peaks for the two homopolymers, the diblock copolymer, and the homopolymer blends. As discussed in more detail elsewhere,[2,4] the two homopolymers form two-phase blends (two damping peaks) over the entire range examined whereas the 30/100 block copolymer is homogeneous (a single, intermediate transition). When the 30/100 copolymer is blended with 100K 1,4B, homogeneous blends are obtained as indicated in the loss tangent data shown in Figure 1 and in the featureless transmission electron micrographs[4] not shown here. Thus the 100K 1,4B homopolymer does not induce microphase separation of the 30/100 diblock. In Figure 2, however, there is clear evidence that addition of an appropriate amount (around 10%) of the 30K 1,2B homopolymer results in the appearance of two loss tangent maxima. Transmission

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