

Miscibility of Poly(vinylidene fluoride) and Poly(styrene-*co*-methyl methacrylate) Blends

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ABSTRACT: The miscibility of poly(vinylidene fluoride) (PVDF) and poly(styrene-*co*-methyl methacrylate) (SMMA) blends was examined as a function of copolymer composition. PVDF was miscible with SMMA copolymers having an styrene content less than 13 vol%. The segmental interaction parameters were determined by combining the equilibrium melting point depression of PVDF and the binary interaction model. According to the binary interaction model, the maximum styrene content in SMMA for the blend to be miscible was predicted as 18.5 vol% which agrees well with an experimental result.

KEY WORDS Miscibility / Binary Interaction Model / Poly(vinylidene fluoride) / Poly(styrene-*co*-methyl methacrylate) / Melting Point Depression / Segmental Interaction Parameter /

Recently, many studies¹⁻¹² have been carried out on the miscibility of polymer blends containing a copolymer, because miscibility can be attained for a certain range of copolymer composition even though the pairs of their corresponding homopolymers are immiscible. This phenomenon has been successfully understood based on the binary interaction model proposed by Kambour *et al.*¹ In this model, a thermodynamic interaction parameter between a polymer pair is governed by the interaction parameters between the segmental pairs with different chemical structure. More recently, Paul *et al.*,²⁻⁶ Karasz *et al.*^{7,8} and others⁹⁻¹² have further extended the above binary interaction model to several types of blends containing copolymers and applied the model to interpret the effect of copolymer composition on the miscibility of blends.

Blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) have been studied extensively and reported to be miscible,¹³⁻¹⁷ while blends of PVDF and

polystyrene (PS) is a well-known immiscible pair. In this study, the miscibility for blends of PVDF and poly(styrene-*co*-methyl methacrylate) (SMMA) was examined as a function of copolymer composition and interpreted in terms of the segmental interaction parameters, which are determined by combining the binary interaction model with the data obtained from the equilibrium melting point depression. It is also attempted to predict the critical copolymer composition for the blends to be miscible using the calculated segmental interaction parameters and the binary interaction model.

EXPERIMENTAL

Materials

PVDF ($M_w = 1.0 \times 10^5$ g/mol) and PMMA ($M_w = 1.5 \times 10^5$ g mol⁻¹) were obtained from Pennwalt Co. and Lucky Inc. respectively and used as received without further purification. SMMA was synthesized by bulk polymerization in a sealed glass ampule using benzoyl

peroxide as an initiator at 60°C. The copolymer was purified by pouring the reaction mixture into methanol and dried in a vacuum oven at 100°C for 24 h. The methyl methacrylate content in the copolymer was determined by the elemental analysis based upon the weight of carbon atom. The copolymer composition and glass transition temperature are listed in

Table I.

Preparation of Blends

The blends of PVDF/SMMA were prepared by dissolving the component polymers in *N,N*-dimethylformamide. The solutions were cast on aluminum dish and dried in a vacuum oven 60°C for 72 h.

Thermal Analysis

Thermal analysis was performed on a Du Pont 910 differential scanning calorimeter equipped with a mechanical cooling accessory. For the measurement of glass transition temperature (T_g), the sample were melted at 200°C for 5 min, quenched into liquid nitrogen to prevent the crystallization of PVDF, and heated from -70°C to 150°C at a heating rate of 20°C min⁻¹. The glass transition tempera-

Table I. Properties of SMMA copolymers

Sample	Copolymer composition	Intrinsic viscosity	T_g
	vol% of styrene	dl g ⁻¹	°C
SMMA2	1.9	1.24	127
SMMA9	8.9	1.08	122
SMMA13	13.6	1.15	121
SMMA24	24.0	1.10	117

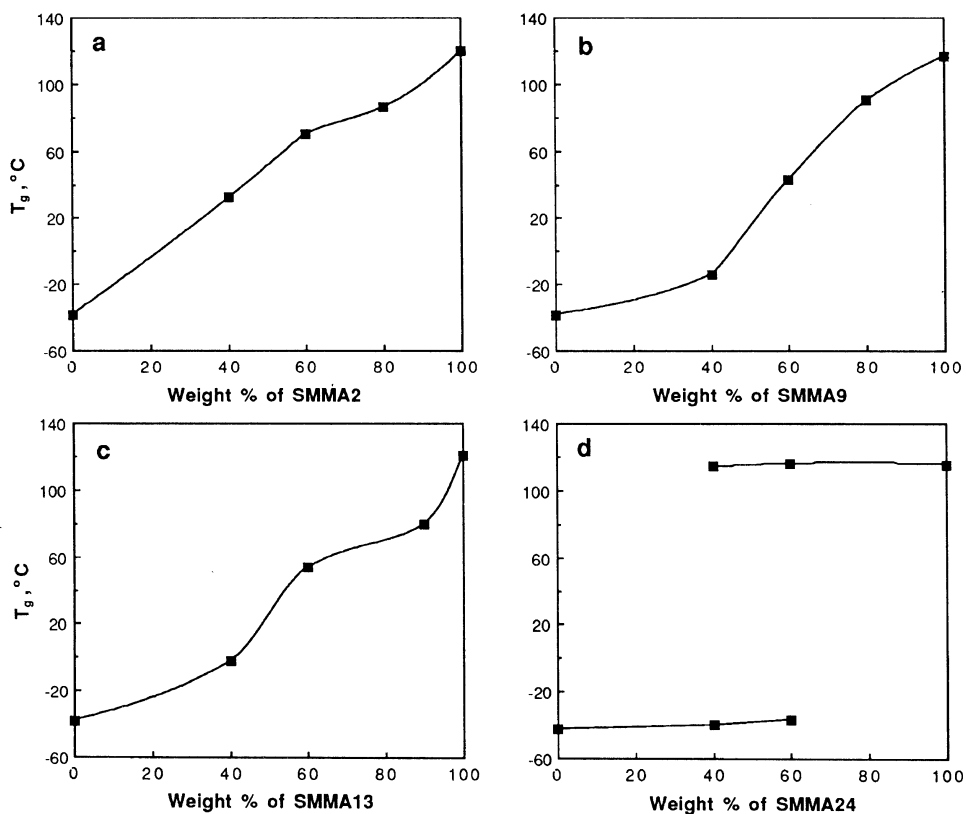


Figure 1. Glass transition behaviors for (a) PVDF/SMMA2, (b) PVDF/SMMA9, (c) PVDF/SMMA13, and (d) PVDF/SMMA24 blends.

ture was taken as the midpoint of the heat capacity change. The isothermal crystallization from the melt was also carried out to determine the equilibrium melting temperature. The samples were melted at 200°C for 5 min, cooled quickly to the crystallization temperature (T_c), and kept at T_c for at least 20 min. After isothermal crystallization was terminated, the samples were cooled to room temperature, and then heated to 200°C at a heating rate of 20°C min⁻¹ for measuring the melting temperature (T_m).

RESULTS AND DISCUSSION

The existence of a single and composition dependent glass transition temperature between those of pure components is a widely used criterion in determining the miscibility of a polymer blend. Figure 1 shows that blends of PVDF/SMMA2, PVDF/SMMA9 and PVDF/SMMA13 have a single glass transition temperature between those of components, indicating that mixtures are completely miscible over the entire blend ratio. However, PVDF/SMMA24 blend shows two glass transition temperatures located at nearly the same temperatures as those of component polymers, indicating that the blend is immiscible.

In order to obtain quantitative information about the thermodynamic interactions in the blends, we used the Nishi–Wang equation:¹⁸

$$T_m^0 - T_m = -T_m^0 \frac{BV_{2u}}{\Delta H_{2u}} \phi_1^2 \quad (1)$$

where $\Delta H_{2u}/V_{2u}$ means the latent heat of fusion of pure crystalline component per unit volume, B is the interaction parameter between blend components, ϕ_1 is the volume fraction of the amorphous component and T_m^0 and T_m are melting temperature of the pure crystallizable polymer and of the blend, respectively. However as Morra and Stein¹⁷ have pointed out, the directly measured melting points are not equilibrium values since they have a

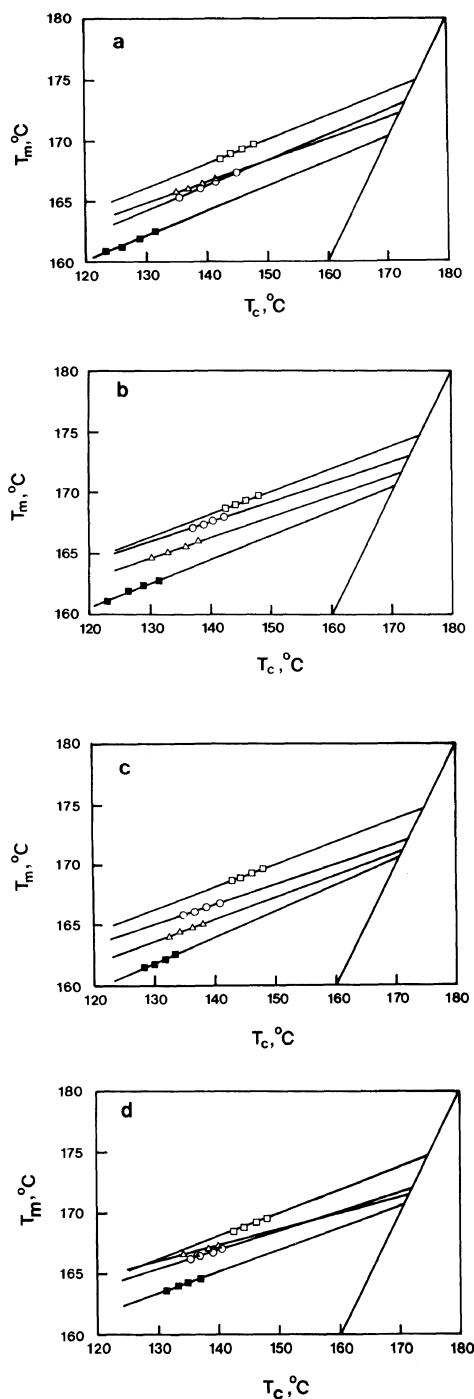


Figure 2. Hoffman–Weeks plots for (a) PVDF/PMMA, (b) PVDF/SMMA2, (c) PVDF/SMMA9, and (d) PVDF/SMMA13 blends: (□) 100; (○) 90; (△) 80; (■) 70 wt% PVDF.

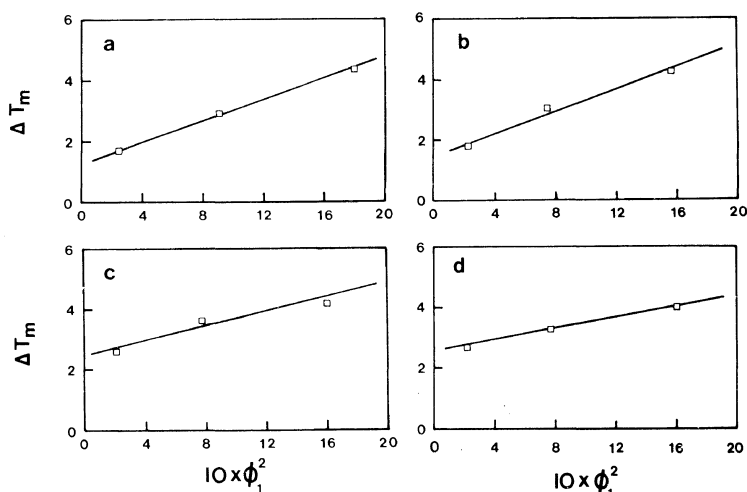


Figure 3. Plots of ΔT_m versus ϕ_1^2 for (a) PVDF/PMMA, (b) PVDF/SMMA2, (c) PVDF/SMMA9, and (d) PVDF/SMMA13 blends.

contribution from finite lamellar thickness. To eliminate the effect of finite lamellar thickness from the melting temperature, the method of Hoffman-Weeks¹⁹ has been used and the equilibrium melting temperatures for pure PVDF and blends of given compositions were determined. Figure 2 represents the Hoffman-Weeks plots to obtain the equilibrium melting temperatures for pure PVDF and PVDF/SMMA blends.

The interaction parameter between both components B can be easily derived from eq 1 if one knows the equilibrium melting point depression for a given composition. The weight fractions were converted into volume fractions using the molar volumes of monomeric units determined by group contribution method.²⁰ By using the data of $V_{2u} = 36.4 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta H_{2u} = 1,600 \text{ cal mol}^{-1}$,²¹ B values were calculated from the slopes of Figure 3. The results are listed in Table II. Negative B 's for PVDF/PMMA, PVDF/SMMA2, PVDF/SMMA9 and PVDF/SMMA13 support the fact that these systems are miscible. It is also found that B value decreases as the styrene content in SMMA increases. This indicates that the styrene unit in SMMA plays an unfavorable role for the miscibility of PVDF/SMMA

Table II. Interaction parameters for the miscible blends

Blend Pair	$B/\text{cal cm}^{-3}$
PVDF/PMMA	-1.72
PVDF/SMMA2	-1.69
PVDF/SMMA9	-1.11
PVDF/SMMA13	-0.91

blends.

In mixture of a homopolymer A and a random copolymer $C_y D_{1-y}$, the interaction parameter B can be expressed as eq. 2:²

$$B = yB_{AC} + (1-y)B_{AD} - y(1-y)B_{CD} \quad (2)$$

where B_{ij} is the segmental interaction parameter and y is the volume fraction of C units in the copolymer. This equation represents that the overall interaction parameter B can be expressed in terms of the segmental interaction parameter B_{ij} 's and the copolymer composition.

To apply eq 2 to PVDF/SMMA blends, we let vinylidene fluoride = A, styrene = C and methyl methacrylate = D. The segmental interaction parameter B_{ij} 's were calculated from the nonlinear regression of eq 2, using the four B values (see Table II) for four PVDF/SMMA

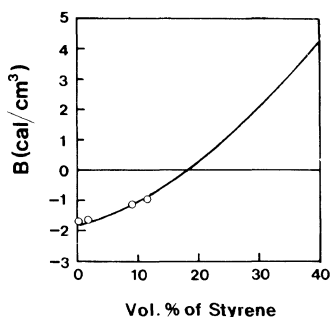


Figure 4. The dependence of interaction parameter B on the copolymer composition. Circles are experimental values and the solid line was computed from eq 2 by using B_{AD} , B_{AC} and B_{CD} .

blend differing in SMMA composition y :

$$B_{AD} = -1.87 \text{ cal cm}^{-3}$$

$$B_{AC} = 28.42 \text{ cal cm}^{-3}$$

$$B_{CD} = 24.72 \text{ cal cm}^{-3}$$

The negative values ($-1.87 \text{ cal cm}^{-3}$) of B_{AD} means that PMMA is miscible with PMDF and this value is comparable with the reported value ($-2.98 \text{ cal cm}^{-3}$).²² The positive values of B_{AC} and B_{CD} imply that PS/PMMA and PVDF/PS blends are immiscible. The signs of B_{ij} values are reasonable, recalling the miscibility for the corresponding homopolymer pairs. However, the absolute magnitudes of these values are somewhat large in a practical sense. This may be caused by many assumptions included in theories for the calculation of B_{ij} values.

The binary interaction model (eq 2) can predict the maximum styrene content y_{\max} in the SMMA copolymer where the heat of mixing of the blend is zero. Equation 2 can be solved for y after letting the overall B value be zero, and inserting calculated segmental B_{ij} values. The calculated y value is approximately 18.5 vol%. This value agrees well with an experimental result that PVDF/SMMA24

blend shows double glass transition temperatures, indicating the blend is immiscible. The dependence of overall B values on the copolymer composition is shown in Figure 4 where the solid line was computed from eq 2 by using the three calculated B_{ij} values.

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