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Interactions in poly(vinylidene fluoride)/poly(methyl methacrylate-co-ethyl methacrylate) blends

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Summary

The interaction parameters B for blends of poly(vinylidene fluoride) (PVDF) with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and five methyl methacrylate/ethyl methacrylate copolymers (PMEMA) were determined by measurements of melting point depression of PVDF. The B values are negative, indicating an attractive intermolecular interaction. The intramolecular interaction parameter between MMA and EMA segments in PMEMA was found to be +3.25 cal/cm^3, indicating a repulsive interaction between different monomer segments in the copolymer.

Introduction

There are many polymer blend systems in which a homopolymer A is miscible with a copolymer B/C over a certain range of copolymer composition even though it is immiscible with either homopolymer B or homopolymer C. These systems include blends of poly(methyl methacrylate) (PMMA) with poly(styrene-co-acrylonitrile) (1-4), PMMA with poly(α-methyl styrene-co-acrylonitrile) (5,6), poly(vinyl chloride) with poly(ethylene-co-vinyl acetate) (7) and poly(2,6-dimethyl-1,4-phenylene oxide) with poly(o-chlorostyrene-co-p-chlorostyrene) (8). Recent theories (9-11) have suggested that the intramolecular interaction between different monomer units in the copolymer is an important factor in determining the miscibility of these blends. Indeed, the intramolecular interaction parameters have been found to be positive for several homopolymer/copolymer blends (2,9,10,12).

Poly(vinylidene fluoride) (PVDF) is miscible with PMMA (13-19) and with poly(ethyl methacrylate) (PEMA) (16,20-22). The intermolecular interaction parameters of these blends have been determined by measurements of melting point depression of PVDF. The present study deals with the interaction of PVDF with various poly(methyl methacrylate-co-ethyl methacrylate) (PMEMA). From the measured intermolecular interaction parameters, the intramolecular interaction parameter between MMA and EMA segments in PMEMA is then evaluated.

Experimental

PVDF was obtained from Scientific Polymer Products, Inc. PMMA (Elvacite 2010) and PEMA (Elvacite 2042) were obtained from Du Pont. Two PMEMA samples containing 30% and 60% by weight of methyl methacrylate, respectively, were obtained from Polysciences, Inc. Three additional PMEMA samples were prepared by bulk polymerization at 60°C for 24 h using 0.3% by weight of azobisisobutyronitrile as initiator. The copolymers were purified by precipitation of the 2-butanone solutions into excess methanol. The methyl methacrylate contents of the three PMEMA samples as determined by ^{1}H-NMR are 16, 42 and 80% by weight, respectively.

The blends were prepared by solution casting using dimethylformamide as solvent. Solvent was first allowed to evaporate at 110°C. The blends were then dried under vacuum at 110°C for 48 h.

The melting points (T_m) of samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter. Samples were first heated to 170°C using a heating rate of 20°C/min and kept at this temperature for 5 minutes before being cooled to 25°C to ensure all samples had the same thermal history. The samples were re-scanned 24 h later using a heating rate of 20°C/min. The peak of the melting endotherm was recorded as T_m of the sample.

Results and discussion

For a miscible blend containing a crystallizable component such as PVDF, the melting point depression of the crystalline polymer by the miscible diluent is used to calculate the intermolecular interaction parameter B using the equation (13,20)

$$T_m = T_m^\circ + B(V_{2u}/\Delta H_{2u})T_m^\circ \phi_1^2$$

where T_m° and T_m are the melting points of pure PVDF and PVDF in the blend respectively, $\Delta H_{2u}/V_{2u}$ is the heat of fusion per unit volume of repeating unit for PVDF [44.0 cal/cm^3 (13)] and ϕ_1 is the volume fraction of the non-crystallizable polymer in the blend. B is obtained from a plot of T_m against ϕ_1^2. A typical plot is shown in Figure 1. The B values for all the blends are given in Table 1. Each of the B values is an average of three determinations. The B values for PVDF/PMMA and PVDF/PEMA blends are in good agreement with those reported by Paul and co-workers (16).

Following the binary interaction model by Paul and Barlow (11), the interaction parameter B for PVDF/PMEMA blends can be expressed as

$$B = B_{MMA/VDF}\phi_{MMA} + B_{EMA/VDF}\phi_{EMA} - B_{MMA/EMA}\phi_{MMA}\phi_{EMA}$$

Table 1. B values for blends

Blend	B/cal cm^{-3}
PVDF/PMMA	-4.43
PVDF/PEMA	-2.66
PVDF/PMEMA(16% MMA)	-2.83
PVDF/PMEMA(30% MMA)	-4.00
PVDF/PMEMA(42% MMA)	-4.07
PVDF/PMEMA(60% MMA)	-4.80
PVDF/PMEMA(80% MMA)	-4.52

where $B_{MMA/VDF}$ and $B_{EMA/VDF}$ are the intermolecular interaction parameters, $B_{MMA/EMA}$ is the intramolecular interaction parameter between different monomer segments in PMEMA, and $\emptyset_{MMA}$ and $\emptyset_{EMA}$ are the volume fractions of MMA and EMA in PMEMA respectively. If $B_{MMA/EMA}$ equals to zero, B is then a weighted average of the intermolecular interaction parameters according to the copolymer composition. With the exception for PVDF/PMEMA(16% MMA) blends, the other four B values are significantly more negative than the weighted average values as shown in Figure 2. This indicates that $B_{MMA/EMA}$ is positive. $B_{MMA/EMA}$ is found to be +3.25 cal/cm^3 by using a least-squares analysis to obtain the best fit of the experimental data. The positive $B_{MMA/EMA}$ indicates a repulsive interaction between the two different monomer segments in the copolymer. The indication is consistent with the fact that PMMA is immiscible with PEMA (23-25).

In the present and other studies (13,14,16,20,21), PVDF is crystallized under large undercooling and the measured melting point is not the thermodynamic equilibrium melting point. The use of non-equilibrium melting point to calculate interaction parameter has been critized as it may result in an underestimation of the interaction parameter (26). However, the interaction parameter for PVC/poly(ϵ-caprolactone) blend obtained from non-equilibrium melting point measurements (27) is in excellent agreement to that from equilibrium melting point measurements (28). The interaction parameter for PVDF/PMMA blend is -8.33×10^6 J/m^3 (-2.11 cal/cm^3) based on the equilibrium melting points of PVDF obtained at low crystallization temperatures (17-18). This value is less negative than the values obtained from non-equilibrium melting point measurements (13,16). On the other hand, based on the equilibrium melting points of PVDF obtained at high crystallization temperatures, the interaction parameter varies between -5.40×10^6 and -2.96×10^7 J/m^3 (-1.29 and -7.07 cal/cm^3) depending on the composition of the PVDF/PMMA blend (17,18). The apparent composition dependence of interaction parameter could be due to the failure of taking into consideration the presence of

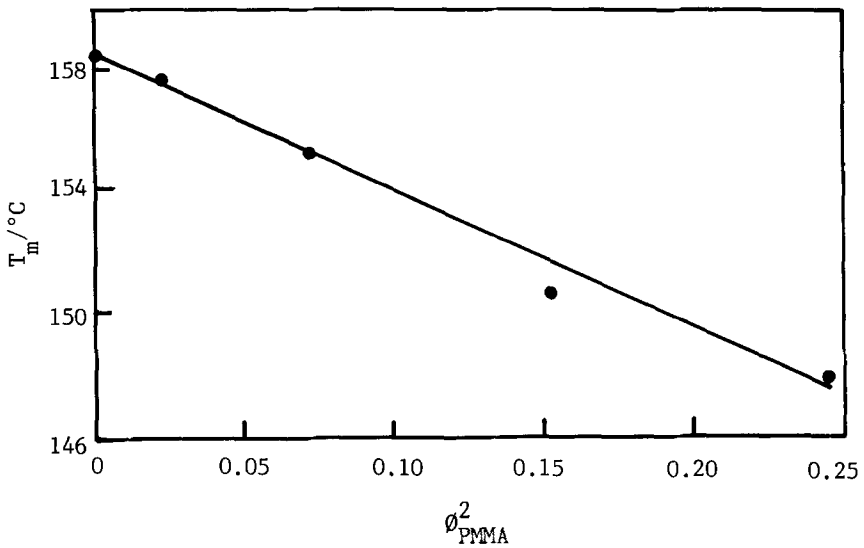

Figure 1. Melting point depression plot for PVDF/PMMA blends.

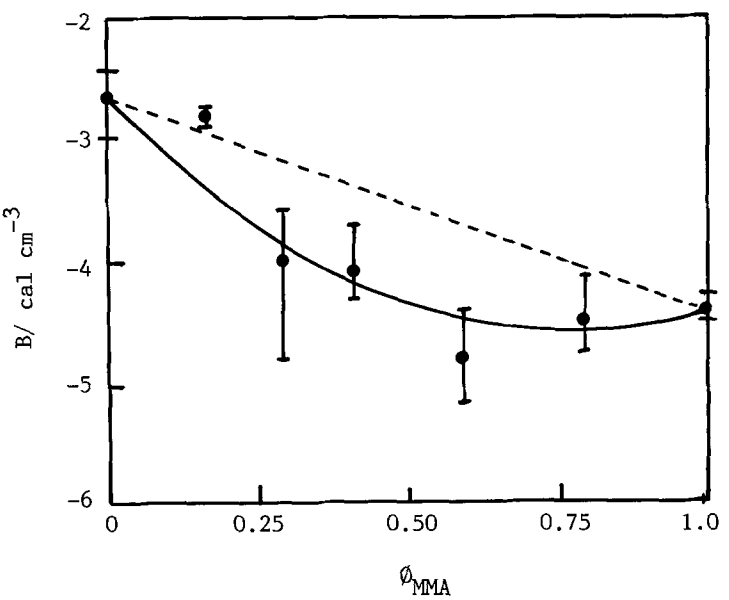

Figure 2. Effect of copolymer composition on B.

$B_{MMA/EMA} = 0$ (- - - - - - -);

$B_{MMA/EMA} = +3.25$ cal/cm^3 (———).

other crystalline forms of PVDF (29). These illustrate the complexity in the measurements of interaction parameter for blend containing PVDF. Although non-equilibrium melting points of PVDF are used in the present study, we believe that the result is valid at least qualitatively, i.e. the intramolecular interaction between MMA and EMA is repulsive.

Acknowledgement

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