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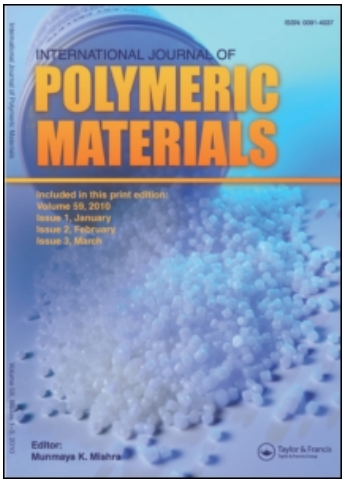

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Calculation of the Interaction Parameters in Hydrogen-Bonded Polymer Blends

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The values of the interaction parameters in the hydrogen-bonded polymer blends were calculated from the sorption isotherms and the glass transition temperatures and found to be mostly negative. The values of the interaction parameters calculated by the sorption isotherms are reasonable in magnitude but those calculated by the glass transition temperatures are much larger in magnitude. However, the values by either method had the same composition order in the studied blends.

Keywords: Interaction parameter; hydrogen bond; polymer blends

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1. INTRODUCTION

The miscibility of dissimilar polymers is enhanced by favourable intermolecular interactions. Of the various secondary interaction forces commonly encountered, hydrogen bonding has been the subject of many investigations [1–3].

In a previous investigation [4], modified polystyrenes containing 5% or 15% p-hydroxystyrene (designated as PHS-5, PHS-15) as hydrogen-bond donors were blended with poly(methyl methacrylate) (PMMA) as acceptors. The glass transition temperatures (T_g) of the

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polymer blends were measured. And water vapour sorption experiments in the polymer blends were also performed. The polymer blends were known to be miscible because the films are transparent and there is a single glass transition temperature for each composition [4].

In this communication, the T_g values and the sorption isotherm data were used to estimate the values of the interaction parameters in the hydrogen-bonded blends. The composition dependence of the values of the interaction parameters in the hydrogen-bonded blends is also discussed.

2. GLASS TRANSITION TEMPERATURE

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Lu and Weiss [5] derived an equation that relates the glass transition temperature, T_g, and a binary interaction parameter, χ, for miscible binary polymer blends. In their derivation, the enthalpy of mixing was written as a Van laar expression, and the T_g was formally treated as a second-order Ehrenfest transition [6]. The equation for a strong specific interaction is as follows:

$$T_{gm} = \frac{\omega_1 T_{g_1} + k_0 \omega_2 T_{g_2}}{\omega_1 + k_0 \omega_2} + \frac{A\omega_1\omega_2}{(\omega_1 + k_0\omega_2)(\omega_1 + b\omega_2)(\omega_1 + c\omega_2)^2} \tag{1}$$

$$A = \frac{-\chi R(T_{g_1} - T_{g_2})c}{M_1 \Delta C_{p1}} \tag{2}$$

$$k_0 = \Delta C_{p_2}/\Delta C_{p_1} \tag{3}$$

where T_{gm}, T_{g_1} and T_{g_2} are the glass transition temperatures of miscible blend, polymer 1 and polymer 2, respectively. ω_i and ΔC_{pi} are the weight fraction and the change in the specific heat at T_{gi} of polymer i, respectively. ρ_i and M_i are the density and the molar mass per chain segment of polymer i, respectively. $c = \rho_1/\rho_2$, $b = M_1/M_2$, R is the gas constant. These three equations can be used to estimate the χ values.

3. SORPTION ISOTHERM

The sorption isotherm data can be used to calculate Flory's thermodynamic interaction parameter χ [7], from the following equation:

$$\chi = [\ln(a_A/V_A) - V_B]/V_B^2 \tag{4}$$

where a_A is the solvent activity equal to relative pressure and V_A and V_B are the volume fractions of solvent and polymer.

4. RESULTS AND DISCUSSION

The method for estimating χ_{12} values was carried out by using equations (1), (2) and (3). The T_{gm} values were taken from reference 4. For the PMMA/PHS-5 blends, the k, c and b values were estimated to be 0.988, 1.1255 and 1.048, respectively. And for the PMMA/PHS-15 blends, the k, c and b values were 0.966, 1.1043 and 1.064, respectively. The χ_{12} values were calculated by using the above-mentioned values and are listed in Table I. All the χ_{12} values are negative.

The isotherm data were also taken from reference 4. For simplification, we replaced V_A by C_A (mass fraction of solvent) because the density of polymers is close to 1 g/cm^3 and the solvent is

TABLE I Binary interaction parameters

PMMA/PHS-5	χ_{12} (*vapor sorption*)	χ_{12} (*estimated from* T_{gm})
90/10		−5.60
80/20	−2.84	−13.08
70/30		−13.46
60/40		−10.04
50/50	−1.28	−9.99
31/69		−11.93
20/80	0.54	−6.47
PMMA/PHS-15	χ_{12} (*vapor sorption*)	χ_{12} (*estimated from* T_{gm})
75/25	−1.511	−9.96
50/50	−1.122	−4.47
25/75	−0.772	−4.26

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water. The χ values were calculated according to equation (4). The plots of χ vs. C_A are shown in Figures 1 and 2. Figure 3 is obtained by extrapolation of χ to zero concentration. The extrapolation was done first by a polynominal regression of data in Figures 1 and 2 (in all cases, correlation coefficients higher than 0.99), then putting C_A to zero concentration. Because the shapes of the curves of 80 and 100% PHS-5 in Figure 1 are more concave, this will cause bigger error in the extrapolation. However, negative deviation from the additivity rule is observed in both blend systems except in 80% PHS-5. Therefore the binary interaction parameter χ_{12} can be estimated from the following equation:

$$\chi_{12} = (\chi - \phi_1\chi_1 - \phi_2\chi_2)/(\phi_1\phi_2) \tag{5}$$

where χ, χ_1, χ_2 are the interaction parameters of the blend, polymers 1 and 2, respectively. ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2. The values of ϕ_1 and ϕ_2 were approximated by using the weight fractions because the density difference between PMMA and PHS-5 (or PHS-15) is small. The calculated χ_{12} values are also listed in Table I and mostly negative.

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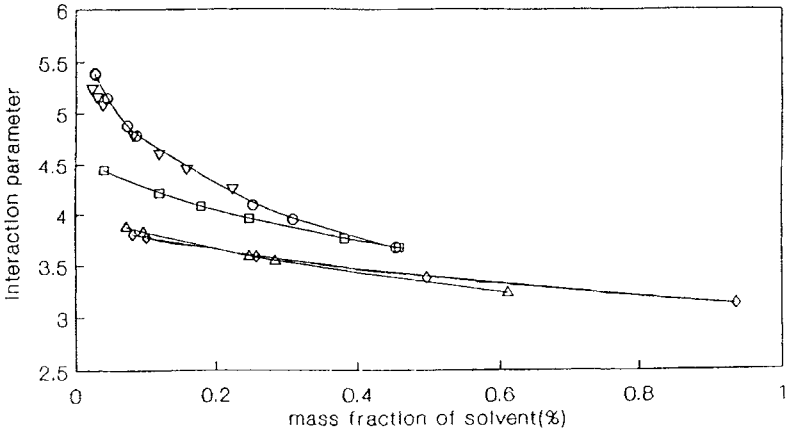

FIGURE 1 Thermodynamic interaction parameters of PMMA/PHS-5 blends Δ PMMA, ◇ PMMA/PHS-5 (80/20), □ PMMA/PHS-5 (50/50), ▽ PMMA/PHS-5 (20/80), ○ PHS-5.

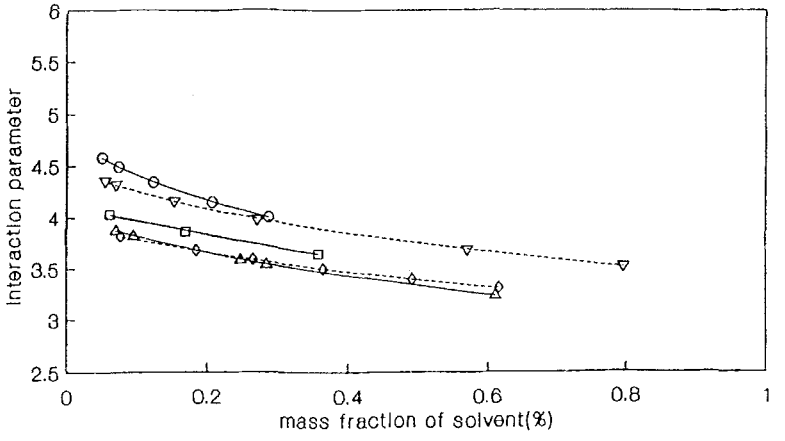

FIGURE 2 Thermodynamic interaction parameters of PMMA/PHS-15 blends Δ PMMA, ◇ PMMA/PHS-15 (75/25), □ PMMA/PHS-15 (50/50), ▽ PMMA/PHS-15 (25/75), ○ PHS-15.

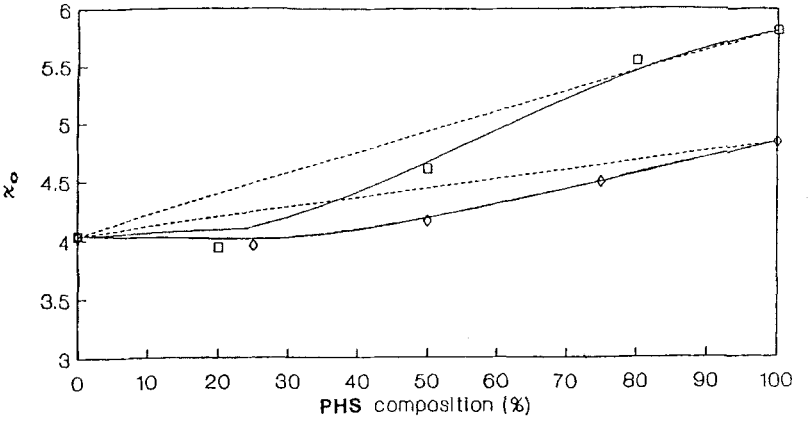

FIGURE 3 Interaction parameters at zero solvent concentration. □ PMMA/PHS-5, ◇ PMMA/PHS-15.

The following comments can be drawn from the above calculations. The χ_{12} values calculated from the glass transition temperatures are larger in order of magnitude. The χ_{12} values calculated from the sorption isotherm data are reasonable in magnitude but not exact because of the errors involved in extrapolation. If the estimated χ_{12} values of the

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PMMA/PHS-5 blends from T_g data in Table I are used as an indicator of miscibility, the three compositions of the PMMA/PHS-5 (80/20, 70/30, 31/69) blends seems to be more miscible than the rest of the blends. The χ_{12} values by either method have the same composition order as follows: PMMA/PHS-5 (20/80) > PMMA/PHS-5 (50/50) > PMMA/PHS-5 (80/20), PMMA/PHS-15(25/75) > PMMA/PHS-15 (50/50) > PMMA/PHS-15 (75/25). For PMMA/PHS-5 blends, the ones rich in PMMA are more miscible than those rich in PHS-5. For the PMMA/PHS-15 blends, the ones rich in PMMA are much more miscible than those rich in PHS-15 owing to the self-association (form hydrogen bonds) of PHS-15 [4]. Overall speaking, the χ_{12} values calculated by either method are mostly negative in accordance with the miscibility criterion.

5. CONCLUSION

The binary interaction parameters (χ_{12}) in the hydrogen-bonded polymer blends were estimated using the sorption isotherm and glass transition temperature data. The values show that the blends rich in PMMA are more miscible than those rich in PHS-5 (or PHS-15).

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