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Miscibility and Volume Changes of Mixing in the Poly(vinyl chloride)/Poly(methyl methacrylate) Blend System

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ABSTRACT: The thermodynamic miscibility of a poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) blend system was investigated. Specific volume–temperature relationships of PVC, PMMA, and their blends as well as the volume change of mixing, Δv_m, of the blends in the liquid state were obtained by dilatometry. The equation of state parameters and the molecular parameters of PVC, PMMA, and polymer blends were determined according to the lattice fluid theory of Sanchez and Lacombe. The Δv_m observed did not agree well over the whole composition range with that predicted from the theory. It was experimentally shown that the miscibility of this blend system depended on composition and that Δv_m of a blend with a PVC composition of 0.8 is much more negative. The enthalpy of mixing, ΔH_m, was also predicted by using the pair molecular parameter. PVC/PMMA blends exhibited negative values of Δv_m and ΔH_m over the entire composition range. These indicated that the blend system studied here was thermodynamically miscible in the liquid state.

Introduction

The miscibility and phase behavior of polymer blends have been extensively studied, and several books on polymer blends have been published recently.[1-4] The miscibility has been assessed by the turbidity of the polymer blend film, the presence of one or two glass transition temperatures (T_g), the presence of one or two mechanical or dielectric relaxations, and the band shift of infrared spectra. A single composition-dependent T_g or single relaxation indicates miscibility of the polymer blend, whereas two T_g's or relaxations indicate immiscibility.

The thermodynamics of polymer blends has been mainly focused on theoretical calculations of Gibbs free energy of mixing, ΔG_m, or enthalpy of mixing, ΔH_m. Miscibility of polymer blends requires that ΔH_m be negative because a small entropy of mixing, ΔS_m, for polymer blends is insufficient to overcome an unfavorable (positive) ΔH_m. Sanchez and Lacombe[5,6] pointed out the important role of the volume change of mixing, Δv_m, of polymer blends on the thermodynamic miscibility of polymer blends in the liquid state. However, few studies of Δv_m have been carried out despite its importance because dilatometric measurements in the equilibrium liquid state are difficult.

In a previous paper,[7] we reported on the thermodynamics of a polystyrene/poly(2-chlorostyrene) blend system. For this blend system, specific volume–temperature relationships of each homopolymer and its blend as well as the volume change of mixing, Δv_m, of the blends were obtained in the liquid state by dilatometry. The equation of state parameters and the molecular parameters of each homopolymer and the blend were determined according to the lattice fluid theory of Sanchez and Lacombe. Theoretical values of Δv_m for any blend composition were estimated from the theory of Sanchez and Lacombe by using the observed value of Δv_m for a certain blend composition. Theoretical and observed values of Δv_m agreed quite well, and the enthalpy of mixing, ΔH_m, was also predicted by using the pair molecular parameters. These two values of Δv_m and ΔH_m were negative, indicative of miscibility of this blend system in the liquid state.

The miscibility of blend system poly(vinyl chloride) (PVC)/poly(n-alkyl methacrylate) has been studied by many workers.[8-10] The miscibility of this blend system is very delicate, depending upon the molecular weight of each homopolymer, blend preparation, and so on. PVC/poly(methyl methacrylate) (PMMA) blend systems are also reported to take a variety of miscibilities. Schurer et al.[11] and Huarng et al.[12] reported the miscibility of this system only at lower PVC content. Parmer et al.[8] stated that this system is miscible over the entire composition range. On the contrary, Razinskaya et al.[13] reported immiscibility. Their conclusions are subtly different because of different blend preparation, the molecular weight of each homopolymer, and tacticity of PMMA.[14-16] The role of specific interactions on the miscibility could be present in these blends.[15,17-20] Three types of specific interaction have been considered: the type of hydrogen bridge interaction between the carbonyl group and the methyne proton, the type of dipole–dipole interaction between the carbonyl group and the carbon–chlorine bond, and the type of Lewis acid–base interaction between the carbonyl oxygen of an ester as an electron donor and the hydrogen of the CHCl group as an electron acceptor. As mentioned above, the miscibility of this system has been discussed widely but not completely elucidated. There are few discussions of the miscibility based on thermodynamics for this system. In this study, the miscibility behavior of this system in the liquid state is discussed thermodynamically for the whole composition range, according to the lattice fluid theory of Sanchez and Lacombe.

Experimental Section

Material. PVC and PMMA samples were kindly supplied by Mitsui Toatsu Chemicals, Inc., and Mitsubishi Rayon Co., Ltd., respectively. PVC was purified by precipitation of tetrahydrofuran (THF) solution into methanol. PMMA was also purified by precipitation of chloroform solution into hexane. Each purified sample was dried under vacuum. The molecular weights of PVC ($M_w = 1.2 \times 10^5$, $M_w/M_n = 2.1$) and PMMA ($M_w = 9.5 \times 10^4$, $M_w/M_n = 2.0$) were determined relative to standard polystyrene by gel permeation chromatography using THF as eluent. Each polymer and PVC/PMMA blends with compositions of 20/80, 50/50, and 80/20 [PVC/PMMA] were completely dissolved in 3 wt % 2-butanone and were prepared by casting on a Petri dish at 50 °C. To remove the last trace of solvent and thermal history,

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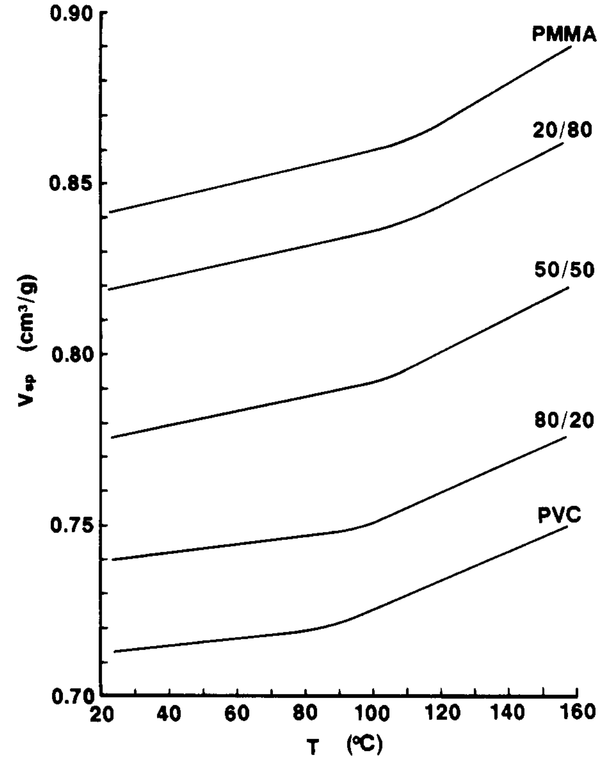

Figure 1. Specific volume versus temperature for PVC and PMMA and 20/80, 50/50, and 80/20 PVC/PMMA blends.

these films obtained were dried under vacuum at 150 °C and were quenched to 0 °C by ice water. Again these films were completely dried under vacuum.

Densities of blend films at 23 °C as a reference state were measured by a flotation method using a mixed solvent of carbon tetrachloride and cyclohexane, whose density was determined by a pycnometer. This mixed solvent could not swell two homopolymers and polymer blends at all. In fact, density change of samples was not observed during an experimental time of about 10 h.

Dilatometry. A dry specimen was confined by dry mercury in a dilatometer composed of a capillary with a uniform inner diameter. Dilatometers containing mercury alone, PVC, PMMA, and 20/80, 50/50, and 80/20 blends were heated at a heating rate of 0.5 °C/min from room temperature to 155 °C in an oil bath. The meniscus height of the mercury in the capillaries of dilatometers, which was almost the same in all cases, was measured every 2 °C by using a precise cathetometer (0.005-cm precision). The volume expansion of the mercury and the capillary glass due to an uncertain temperature gradient in the unimmersed part was corrected by using the data of a dilatometer containing only mercury. Since this volume expansion could be assumed to be the same for all the dilatometers, the volume expansion for the dilatometer of the homopolymer or polymer blend might be compensated by using the apparent expansion coefficient obtained from the dilatometer of mercury itself, which is obtained by the true expansion coefficient of mercury.[21]

Results and Discussion

The total observed volume change, ΔV_{obs}, in each dilatometer was measured at the temperature range from 25 to 155 °C and corrected to specific volume using a method described elsewhere.[7] Figure 1 shows specific volumes of PVC, PMMA, and blends with various compositions as a function of temperature. The specific volume–temperature curves of the polymer blends exhibit a single inflection at the glass transition, indicating that the 20/80, 50/50 and 80/20 polymer blends are miscible. The polymer blends, however, show a relatively broad glass transition region, although one cannot see it clearly in Figure 1. This broadening is remarkable in a 20/80 polymer blend, which is also observed more clearly in a differential scanning calorimeter (DSC) thermogram, and it reduces with an increase of PVC content. The broadening of the glass transition region owing to mixing can be seen in other miscible polymer blends.[8,22,23] This behavior suggests that PVC and PMMA blends mix in a rather microheterogeneous state.

Table I
Thermodynamic State Parameters and Molecular Parameters of PVC, PMMA, and Their Blends at 150 °C

	PVC	80/20	50/50	20/80	PMMA
ρ, g/cm³	1.337_8	1.297_9	1.227_0	1.164_8	1.128_7
$\alpha \times 10^4$, deg^{-1}	5.35	5.62	5.93	6.02	6.73
$\tilde{v}$	1.091	1.098	1.104	1.106	1.123
v^*, cm³/mol	13.06	11.34	9.74	8.68	8.04
$\tilde{T}$	0.535_5	0.549_0	0.562_0	0.567_0	0.598_0
T^*, deg	790	771	753	746	707
$\Delta v_{\mathrm{m,sp}}$, cm³/g		−0.0089	−0.0073	−0.0039	

Thermodynamic quantities such as density, temperature, and expansion coefficient of each homopolymer and polymer blend are important state parameters. They are obtained from the equation of state of the polymer liquid, i.e., the lattice fluid theory of Sanchez and Lacombe.[5,6] At atmospheric pressure the Sanchez–Lacombe equation of state for polymer liquids is expressed by the equations[5,6]

$$\tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}] = 0 \tag{1}$$

$$T\alpha = \left[\frac{\tilde{T}}{1 - \tilde{\rho}} - 2\right]^{-1} \tag{2}$$

where $\tilde{\rho}$ and $\tilde{T}$ are the reduced density and temperature, respectively. The expansion coefficient, α, experimentally obtained at a fixed temperature for each homopolymer and polymer blend, is used to obtain the values of $\tilde{\rho}$ and $\tilde{T}$ from eqs 1 and 2. The values of characteristic volume and temperature, v^* and T^*, for each homopolymer can be calculated according to a previously mentioned method.[7] The v^* of polymer blend is evaluated by the specific volume change of mixing, $\Delta v_{\mathrm{m,sp}}$, obtained experimentally

$$\Delta v_{\mathrm{m,sp}} = \frac{1}{\rho_1^* v_1^*}\{(w_1 + Qw_2)\tilde{v}v^* - w_1\tilde{v}_1 v_1^* - Qw_2\tilde{v}_2 v_2^*\}$$

$$Q \equiv \frac{\rho_1^* v_1^*}{\rho_2^* v_2^*} \tag{3}$$

where subscripts 1 and 2 represent PVC and PMMA, respectively, w is the weight fraction, and ρ^* is the characteristic density. Thus, all the molecular parameters such as v^* and ϵ^* $(=kT^*)$ as well as the equation of state parameters were estimated for each homopolymer and polymer blend.

The following combining rules of the polymer blend system were assumed

$$v^* = \phi_1^2 v_1^* + 2\phi_1\phi_2 v_{12}^* + \phi_2^2 v_2^* \tag{4}$$

$$\epsilon^* v^* = \phi_1^2 v_1^* \epsilon_{11}^* + 2\phi_1\phi_2 v_{12}^* \epsilon_{12}^* + \phi_2^2 v_2^* \epsilon_{22}^* \tag{5}$$

where ϕ is the mole fraction. We can evaluate the intrinsic molecular-pair parameters v_{12}^* and ϵ_{12}^* independently of the composition of polymer blend, using eqs 4 and 5 and the v^* and ϵ^* values of each homopolymer and polymer blend. Thermodynamic quantities and the molecular parameters of each homopolymer and polymer blend are listed in Table I. The $\Delta v_{\mathrm{m,sp}}$ of any composition of polymer blend could be predicted by using v_{12}^* obtained as shown by the solid line in Figure 2. $\Delta v_{\mathrm{m,sp}}$ was negative over the

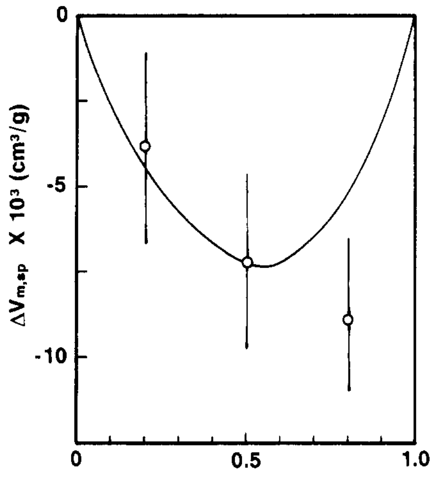

Figure 2. Volume change of mixing, Δv_m, versus weight fraction of PVC. The solid line represents the theoretically predicted curve, and the circles are the experimental results.

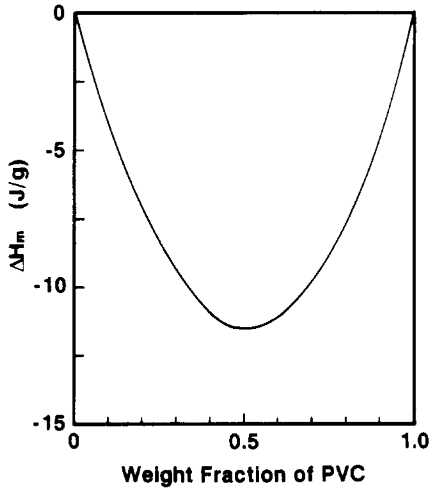

Figure 3. Theoretically predicted heat of mixing, ΔH_m, as a function of weight fraction of PVC.

entire composition range, indicating miscibility of the polymer blend in the liquid state. The observed value did not agree well with the predicted $\Delta v_{m,sp}$ shown by the solid line in a higher PVC content range, though the experimental error of $\Delta v_{m,sp}$ is large. The experimental Δv_m of a 80/20 polymer blend deviates negatively, indicating that it is probably more miscible.

The heat of mixing, ΔH_m, is defined by

$$\Delta H_m = \gamma N[-\rho\epsilon^* + \phi_1\rho_1\epsilon_{11}^* + \phi_2\rho_2\epsilon_{22}^*] \quad (6)$$

where γN is the total number of mers in the polymer blend system. One can also obtain theoretical ΔH_m, using eqs 5 and 6, although it contains large error as well as Δv_m. The predicted value of ΔH_m is plotted in Figure 3. ΔH_m was negative over the entire composition range, indicating that this blend system is miscible. Although direct measurements of ΔH_m were carried out by Ichihara et al.,[24] Karasz and MacKnight et al.,[25,26] Tager et al.,[27,28] and Paul and Barlow et al.,[29-31] our method mentioned here is also available to discuss thermodynamic miscibility.

We also investigated the sorption properties of CO_2 for a polymer blend in the glassy state at 25 °C.[32] The solubility coefficient, k_D, a Henry's law constant, of the polymer blend deviated negatively from semilogarithmic additivity. From the mixing rule of k_D of the polymer blend system developed thermodynamically from the Flory–Huggins theory for ternary system,[1,33] we obtained the negative value of the interaction parameter of PVC/PMMA, $\chi = -0.257$, as a gross approximation. Consequently this blend system is said to be miscible in the liquid and glassy states.

In conclusion, the equation of state and specific volume–temperature relations obtained by dilatometry can qualitatively predict thermodynamic miscibility for the polymer blends in the liquid state. PVC/PMMA polymer blends exhibited negative values of Δv_m and ΔH_m over the entire composition range, suggesting the presence of the specific interaction between PVC and PMMA.

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