Volume Contraction on Mixing in Poly(vinyl ethylene-co-1,4-butadiene)/Polyisoprene Blends

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ABSTRACT: The volume changes on two sides of phase boundary in a lower critical-solution-temperature (LCST) type phase diagram of poly(vinyl ethylene-co-1,4-butadiene) (V-BR) with polyisoprene (IR) blends were obtained in liquid state by dilatometry. The volume change on mixing was clearly observed in the specific volume-temperature relationship. Considering a blend composition dependence of the specific volume, we found the volume contraction below LCST, whereas the volume expansion above LCST. Furthermore thermal expansion coefficients of V-BR, IR and their blends were determined in this work.

KEY WORDS Miscibility / Volume Contraction on Mixing / Dilatometric Measurement / Vinyl Polybutadiene / Polyisoprene / Liquid-Liquid Phase Transition / Thermal Expansion Coefficient /

The miscibility of polymer-polymer blends can be, in general, observed, if an existence of strong interaction, such as hydrogen bonding, charge transfer and complex formations, is predicted between dissimilar polymer chains.¹⁻⁷ In this condition, an enthalpy of mixing ΔH_{mix} is negative due to a favorable energy contribution to the polymer miscibility. Since the mixtures of high molecular weight components are characterized by a nearly negligible value of combinatorial entropy of mixing ΔS_{mix} , ΔH_{mix} has played an important role in attaining homogeneous phase on mixing. In some miscible blends, however, the strong interaction were not observed. One of the familiar cases is the miscibility in poly-(2,6-dimethyl-1,4-phenyl ether) (PPE)/poly-(styrene) (PS) blend.⁸ Although the strong interaction between PPE and PS has not been observed in current investigations, the blend of PPE with PS may be an excellent miscible blends. Thus, the miscibility still leads us difficulty to comprehend, except that the

hydrogen bond is formed between dissimilar polymer chains.

One can approach to this subject taking account of the equation of state.^{10,11} The Flory equation of state based on Prigogine corresponding state theory adopted the free volume changes on miscible blending between component polymer A and B. A reduced volume of blend deviates generally from straight nature of additivity in reduced volume vs. reduced temperature plot. Thus the volume contraction on mixing should be observable in many miscible blends.

In our previous studies, the blend of poly(vinyl ethylene-co-1,4-butadiene) (V-BR) with polyisoprene (IR) was expected to be an ideal mixing in high molecular weight polymer mixtures due to a possibility of nearly negligible heat of mixing¹²⁻¹⁴ and analogous molecular properties in monomer units. However, our results have suggested that the free volume contribution to the blend miscibility influenced considerably a phase behavior, i.e., the lower

critical solution temperature (LCST) in an observable temperature range, the reversibility between heterogeneous and homogeneous phase and the composition dependence of Flory–Huggins interaction parameter χ . On the other hand, Sakurai and his co-workers^{15,16} reported that the miscibility of V-BR/IR and V-BR/Poly(styrene-*co*-butadiene) (SBR) blends with various microstructures (vinyl content in V-BR) was interpreted by the contribution of random copolymerization based on lattice theory. A few difference in each monomeric interaction parameter χ_{12} which is determined by their small angle neutron scattering (SANS) experiment was found to dominate the blend miscibility with random copolymer. Roland and his collaborator^{17–21} conducted their investigation of miscibility for V-BR/IR and poly(vinyl ethylene) (PVE)/IR blends in a careful way. They concluded that the V-BR/IR blends were nearly ideal mixture, because no chemical interaction between V-BR and IR was provided by both the infrared spectroscopy and NMR study, and that the morphological homogeneity was also confirmed by both ^1H and ^{13}C NMR.²¹

Since the excess volume of mixing for the blend might be attributed to the composition dependence of χ parameter, we attempted to confirm the volume contraction of the blends with a density gradient tube and dilatometer.

EXPERIMENTAL

Materials

The polymer samples used in this study were V-BR (32.3) and IR, supplied by Nippon Zeon Co., Ltd. The figure in parenthesis represents the vinyl content in wt% of V-BR. The structural formula of both the samples are illustrated in Figure 1. IR (Nipol 2200 $\bar{M}_w = 730,000$, $\bar{M}_w/\bar{M}_n = 1.84$) was commercial polymer, while V-BR (32.3) ($\bar{M}_w = 214,000$, $\bar{M}_w/\bar{M}_n = 1.03$) was prepared by polymerizing 1,3-butadiene in hexane or benzene with a *n*-butyllithium catalyst in combination with

Figure 1. Schematic representation of V-BR and IR.

diglyme (diethylene glycol dimethyl ether) at 40°C. 1,2-unit content in V-BR was limited with adding the fixed amount of diglyme. The higher 1,2-unit content in V-BR was achieved with the large amount of diglyme, because the electron acceptability of diglyme which is a polar molecule can magnify the ionic strength in carbon-lithium bond.

The blend samples were prepared by precipitation from 5 wt% toluene solutions in ethanol. The precipitated samples were dried under vacuum at 40°C for a week.

Measurements

The densities of polymer films were measured by use of a gradient column composed of water and methanol. All density measurements were made at 25°C. A sedimentary film in the gradient column was stopped at the point where the density of water–methanol solution equaled to that of the film. When the film stayed for more than 15 min at the same density solution, we determined the density of the film. In this short time scale, a swelling effect of polymers in the solution was neglected because of no sinking or no floating. The average of three measurements for each samples was taken as the experimental value.

The temperature variation in the specific volume was determined by a method well-known in dilatometry.^{22–25} For dilatometric measurements, a common Pyrex glass dilatom-

eter composed of a capillary and a reservoir was used. The samples were sealed in the reservoir, and the mercury was poured into as enveloped the samples in it. The dilatometer was placed in an oil thermostat, with a temperature control at $\pm 0.1^\circ\text{C}$. The relative volumes obtained at intervals of 2 or 5°C were converted to the absolute volumes based on the density at 25°C . In order to achieve an equilibrium condition, the dilatometer was annealed to an isothermal setting at each temperatures for more than 2 hours. Our blend samples of V-BR (32.3) with IR was found to occur a reversible behavior between double T_g and single T_g states. Thus, one can easily determine a physical quantities both in the heterogeneous region and in homogeneous region, even though the measurements to determine the physical quantities are carried out many times in one sample. The temperature variation of the blends in the specific volume was defined with the relative volume in third run. The specific volume obtained in third run was almost the same as that in the second run.

RESULTS AND DISCUSSION

An excess volume of mixing caused from volume change on mixing can not be permitted in an ideal mixture for Flory–Huggins lattice theory. According to the lattice theory, the specific volume of polymer blend is directly proportional to blend composition; a straight line nature is expected between the specific volumes of component polymers. However, the volume change on mixing must, in practice, be included in an occurrence of the blend miscibility, since the liquid structure and condition exert on a mixing state. This structural effect has been pointed out in V-BR (32.3)/IR blend as the Flory–Huggins interaction parameter χ depended upon the blend composition.¹⁴ Thus, the volume change on mixing with the blend composition should be found in the V-BR (32.3)/IR.

In order to confirm the volume change on

Figure 2. Density of V-BR (32.3)/IR blends at 25°C against blend composition. The solid curve which presents the average density is given as second order function of blend composition.

Table I. Density of the samples, measured by density gradient tube in methanol–water solution at 25°C

V-BR (32.3)/IR	Density/ 10^3 kg m^{-3}
0/100	0.8990
30/70	0.8976
50/50	0.8960
70/30	0.8939
100/0	0.8899

mixing, we evaluated the temperature variation of specific volume with dilatometry. In the dilatometric measurement, a precise determination of density at 25°C is the most important. The density of the blend at 25°C was expressed as a quadratic function of blend composition. Figure 2 shows experimental densities and an approximate curve. The scattered densities attributed to an experimental error were averaged by the approximation of quadratic expression. The densities of both component polymers and 30/70, 50/50 and 70/30 blends at 25°C are shown in Table I. The upward curve of density against blend composition represents the presence of volume contraction. The absolute specific volumes based on the densities at 25°C are the criterion in estimating each specific volumes at various temperatures.

The temperature variation of specific volume

Figure 3. Temperature variation of specific volume for V-BR (32.3). The monotonic increase of specific volume is shown with raising temperature.

Figure 4. Temperature variation of specific volume for IR. The monotonic increase of specific volume is shown with raising temperature.

for the component polymers was examined on account of clarifying the absence of both a specific inflection point and a curvature in the observable temperature range. The experimental specific volumes of V-BR (32.3) and IR are presented in Figures 3 and 4, respectively. A monotonic increase of specific volume for the component polymers is obviously shown in the plot of specific volume versus temperature. In both the figures, a solid line is accurately drawn by a least square expression for all data. Each slopes of the straight lines represent thermal expansion coefficients of component polymers that are one of the physical quantities. The thermal expansion

Table II. Thermal expansion coefficients of the samples

V-BR (32.3)/IR	Temperature/°C	Thermal expansion coefficient/deg.
0/100	0—100	7.844×10^{-4}
30/70	0—63	7.964×10^{-4}
	63—100	8.728×10^{-4}
50/50	0—58	7.910×10^{-4}
	58—100	8.406×10^{-4}
70/30	0—64	8.098×10^{-4}
	64—100	8.359×10^{-4}
100/0	0—100	7.937×10^{-4}

Figure 5. Temperature variation of specific volume for V-BR-(32.3)/IR 30/70 blend. The dotted line represents a linearly extrapolated specific volume-temperature relationship above LCST phase boundary temperature, at which phase separation takes place.

coefficients are shown in Table II. A difference between the thermal expansion coefficient of V-BR (32.2) and that of IR is relatively small. Thus, in V-BR (32.3) and IR, one can easily find that a thermal property of both component polymers is almost identical to each other. In accordance with Flory equation of state theory, the system in which pure component polymers have the similar thermal expansion coefficients exhibits largely extent of miscible condition due to small unfavorable contribution, such as free volume effect, to the miscibility. In our blend system, the origin of miscibility may be interpreted by the similar thermodynamic manner.

A result of dilatometry for the V-BR (32.3)/IR 30/70 blend is presented in Figure 5.

Since we have recognized the phase transition in the V-BR (32.3)/IR blend to take place for a short time length, the temperature variation of specific volume in the dilatometric measurement can be observed in the equilibrium state at which the blend system is under a given set of condition. In Figure 5, the solid line represents a monotonic increase of specific volume with raising temperature up to LCST phase boundary temperature, whereas the broken line represents other monotonic increase above the boundary temperature. The both lines are drawn by the least square expression for the data with a correlation function being 0.999. In the specific volume versus temperature plot, the point of inflection is clearly revealed at near the phase boundary temperature which has been already reported. The temperature on the inflection point is 64°C, which we call the binodal temperature in the LCST phase behavior for V-BR (32.3)/IR blend.

As to a thermodynamic interpretation of the temperature variation of specific volume, the specific volumes V are replaced by change of thermal expansion coefficient $\Delta\alpha$ as follows

$$\Delta\alpha = \frac{V - V_{bn}}{T - T_{bn}} \quad (1)$$

where T is the temperature, T_{bn} the binodal temperature and V_{bn} the specific volume at the binodal temperature. As shown in Figure 6, horizontal solid lines on the two sides of T_{bn} are the slopes of two straight line in the specific volume versus temperature plot. There is a discontinuity in the $\Delta\alpha$ at T_{bn} , so that a presence of discontinuity in the second derivative (curvature) of the chemical potential is revealed at atmospheric pressure. Since the thermal expansion coefficient below LCST is smaller than that above LCST, the volume contraction on mixing can be realized in the V-BR (32.3)/IR blend.

Similar results in both the 50/50 and 70/30 blends are shown in Figure 7 and 8, respectively. The point of inflection appears at near the phase boundary temperature in LCST

Figure 6. Variation of thermal expansion coefficient of V-BR (32.3)/IR (30/70) blend as a function of temperature difference between the actual temperature T and temperature T_{bn} at which phase separation takes place.

Figure 7. Temperature variation of specific volume for V-BR (32.3)/IR 50/50 blend. The dotted line represents a linearly extrapolated specific volume-temperature relationship above LCST phase boundary temperature, at which phase separation takes place.

Figure 8. Temperature variation of specific volume for V-BR (32.3)/IR 70/30 blend. The dotted line represents a linearly extrapolated specific volume-temperature relationship above LCST phase boundary temperature, at which phase separation takes place.

phase diagram. These results are summarized in Table II.

Tsujita and his co-workers²⁸ recently reported that the volume contraction of mixing in the specific volume–temperature relationships of blends of PS and poly(2-chlorostyrene) were obtained in the liquid state by dilatometry. On the other hand, the volume expansion of mixing in the miscible polymer blends of poly(vinyl nitrate) (PVN) with poly(vinyl acetate) (PVAc) were indicated by dilatometric method in our previous publication.^{25–27} We concluded that the both fairly large depression of the thermal expansion coefficients and volume expansion suggested the existence of a strong interaction between PVN and PVAc at certain blend composition. Currently, several investigators have also offered that the volume expansion of mixing occurred in a few polymer pairs^{29–31}. Therefore, both volume expansion and contraction on mixing have been observed in the miscible systems which indicated the existence of strong interaction between dissimilar polymer pairs.

In the present work, the specific interactions, such as hydrogen bonding, charge transfer and ion complex formations, are hardly considered in the V-BR (32.3)/IR blends for which chemical structures consist of carbon and hydrogen. Coming to think of the miscible condition in the V-BR (32.3)/IR blends with the absence of specific interaction, one can find out the difference of miscibility between presence and absence of specific interactions. One of the approaches for a solution of the riddle is an evaluation of the thermodynamic condition permitted at each temperatures. Let us consider a blend composition dependence of the specific volume at respective temperatures.

Figure 9 shows the specific volume against blend composition at 25°C below LCST. In the miscible blends at below LCST, a negative volume deviation of blends from the additivity is clearly seen in Figure 9. The negative deviation reflects directly the volume contraction of mixing. We may predict that there is a

Figure 9. Composition dependence of specific volume at 25°C. The volume contraction which deviates from the volume additivity is observed for V-BR (32.3)/IR blends.

Figure 10. Composition dependence of specific volume at 65°C. The volume additivity is obtained for V-BR (32.3)/IR blends.

certain stereo structure for achieving the miscible state due to the absence of specific interaction between V-BR (32.3)/and IR. Thus, a compactness on mixing sets in below LCST, so that ΔV_{mix} becomes to be negative. As shown in Figure 10, the specific volumes of the blends at 65°C, in the vicinity of which the phase transition between homogeneous and heterogeneous states occurs, are expressed well by a straight line those of V-BR (32.3) and IR, as a function of blend composition. We should allow it to be the additivity of volume. On the other hands, rising higher temperature above LCST, the volume expansion due to phase separation is observed at 100°C in Figure 11.

Figure 11. Composition dependence of specific volume at 100°C. The volume expansion which is represented as a positive deviation from additivity between the volume of component polymers is observed for V-BR (32.3)/IR blends.

A positive volume deviation of blends from additive straight line drawn between specific volumes of pure component polymers is obviously found. There may be unfavorable effects for miscibility with rising temperature, *i.e.*, increases of repulsion with increasing mobility and interface with increasing heterogeneity.

From the results of temperature dependence of volume changes on mixing, we can consider a balance of following two effects on the blend miscibility; (1) the existence of certain stereo structure for achieving the miscible compact state, and (2) the unfavorable effect on the miscibility. Consequently, the volume contraction takes place below LCST, while the volume expansion occurs above LCST. When the both effects are compensated each other in the vicinity of LCST phase boundary temperature, one can observe the additivity of volume against blend composition. Therefore, we would attribute the formation of certain stable stereo structure without any strong interactions to the fundamental reason of miscibility in V-BR (32.3)/IR blends.

CONCLUSION

The volume changes on mixing for the

V-BR (32.3)/IR blends exhibiting LCST phase behavior have been indicated by dilatometric measurements. The thermal expansion coefficients for V-BR (32.3), IR and their blends were also determined. When the dilatometric measurements for the blends were carried out with raising temperature, an inflection point in a specific volume-temperature plot was obviously observed at near the phase boundary temperature. Thus, the phase transition in this system should be identical to a second order phase transition in which there is a discontinuity in the second derivative of the chemical potential. Studying further the volume changes of mixing against blend composition, we obtained that the volume contraction on mixing took place below LCST, while the volume expansion on demixing occurred above LCST. Therefore, we predicted a stable structure which favors the miscibility. It is interesting that the strong intermolecular interactions are not always necessary to get miscible polymer blends. More detailed microscopic, structural and thermodynamic investigation being now conducted.

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