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UCST Phase Behavior and the Miscibility Valley in Blends of Poly(vinyl ethylene-*co*-1,4-butadiene) and Hydrogenated Terpene Resin

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ABSTRACT: The phase behavior of blends of hydrogenated terpene resin and polybutadiene with various 1,2-unit contents was investigated by customary cloud point measurements. UCST type phase diagrams were drawn for the seven polybutadienes for which 1,2-unit content was varied. The Flory–Huggins interaction parameters, χ_{ij}, were determined by fitting the cloud points with binodal curves. By means of the mean field approximation, the locus of the UCSTs was simulated against copolymer composition, using the determined χ_{ij} parameters. The new miscible concave curve, namely the miscibility valley, against copolymer composition at the critical blend composition was found in the present study.

Introduction

The miscibility of polymer–polymer blends has been predicted according to thermodynamics.[1-3] Many liquid–liquid phase transitions have been explored on the basis of the mean field approximation.[4,5] The major phase transition is a lower critical solution temperature (LCST) type phase behavior. In this case of copolymer/homopolymer and copolymer/copolymer blends,[6-8] the so-called miscibility windows have been predicted and observed, in which a locus of LCSTs is delineated against copolymer composition as a convex curve. On the other hand, an upper critical solution temperature (UCST) type phase behavior has also been observed recently. Therefore, a further study on a locus of UCSTs against copolymer composition is very interesting due to its interdisciplinary nature.

In our previous study,[9] it was predicted that a locus of UCSTs is delineated against copolymer composition as a concave curve, named the miscibility valley. A miscibility valley type phase behavior was found in blends of poly(carbonate) and poly(styrene-*co*-methacrylic acid). However, the observed miscibility valley lay in a limited range of copolymer composition due to the difficulty of preparing poly(styrene-*co*-methacrylic acid) over a whole range of copolymer composition, and a hydrogen bonding formation was revealed by FT-IR spectroscopy. In order to perform a fundamental study on the miscibility of polymer blends against copolymer composition, it is important to satisfy the following conditions: (1) preparing the random copolymer over the whole range of copolymer composition and (2) an intermolecular interaction being only the van der Waals dispersion force. Therefore, a pair of polymers consisting of carbon and hydrogen have to be chosen for a study on the phase behavior. One of the remarkable pairs is a blend of polybutadiene and terpene resin. The polybutadiene can be regarded as a copolymer of poly(vinylethylene-*co*-1,4-butadiene) (PVB)[10-12] consisting of 1,4- and 1,2-units, although it is prepared by polymerizing 1,3-butadiene. On the other hand, terpene resin is a nonpolar oligomer. This blend can be investigated by changing copolymer composition, and its miscibility is dependent on the combinatorial entropy term. Polybutadiene has been shown to be practically miscible with various terpene resins in the whole range of copolymer composition, i.e. the 1,2-unit.[13] If the terpene resin is hydrogenated, one can observe the critical temperature within an experimental temperature range between the glass transition and degradation temperatures.

Table I. Sample Characteristics

sample	1,2-linkage/ %	M_w	M_w/ M_n	T_g/ °C	density/ g cm^{-3}
PVB (10.0)	10.0	285 000	1.09	−96	0.8945[a]
PVB (24.3)	24.3	222 000	1.04	−79	0.8929[a]
PVB (32.3)	32.3	214 000	1.03	−73	0.8925[a]
PVB (47.4)	47.4	214 000	1.03	−62	0.8916[a]
PVB (54.3)	54.3	267 000	1.06	−55	0.8909[a]
PVB (60.0)	60.0	224 000	1.04	−48	0.8907[a]
PVB (70.4)	70.4	232 000	1.05	−38	0.8886[a]
Clearon-P125		1 185	1.32	73.5	0.9974[a] (1.0220[b])

[a] Obtained by a water–methanol density gradient culumn. [b] Estimated from the thermal expansion coefficient in the liquid state.

In this study, the miscibility of blends of polybutadiene and hydrogenated terpene resin is investigated by changing the blend composition and copolymer composition. The UCST type phase behavior and miscibility valley are found and thermodynamically investigated according to the mean field approximation.

Experimental Section

The polymer samples used in this study were polybutadiene with various 1,2-unit contents (PVB), supplied by Nippon Zeon Co., Ltd. The figure in parentheses represents the 1,2-unit content (%) of PVB. PVB was prepared by polymerizing 1,3-butadiene in hexane with *n*-butyllithium catalyst in combination with diglyme (diethylene glycol dimethyl ether) at 40 °C. PVB was purified by precipitation from 5 wt % toluene solution in methanol. The hydrogenated terpene resin used was Clearon-P125 supplied by Yasuhara Chemical Co., Ltd. Clearon-P125 was prepared by hydrogenating dipentene resin. The dipentene resin was synthesized by oligomerizing dipentene monomer in toluene with chlorinated aluminum anhydride at 35–40 °C. After the toluene and residual monomer were removed, the dipentene resin was hydrogenated in hexane with stabilized nickel by blowing hydrogen gas. The FT-IR spectrum for Clearon-P125 was reported in a previous paper.[14] Their molecular characteristics are shown in Table I.

The densities of PVB 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 the water–methanol solution was equal to that of the film. The density of the film was determined after it remained at the same level of the solution density for more than 1 h. In this short time scale,

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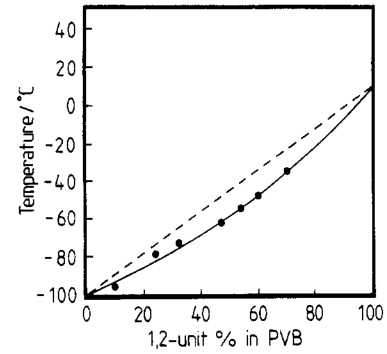

Figure 1. Glass transition temperature of PVB against the 1,2-unit content. The solid line is drawn by using the Fox equation.

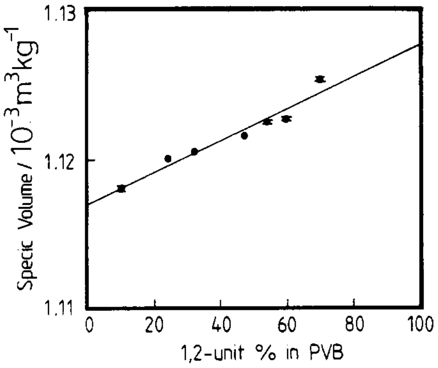

Figure 2. Volume additivity of PVB against the 1,2-unit content.

a swelling effect of polymers in the solution was neglected, as no sinking or floating was observed.

The T_g's of the PVB samples were measured using a duPont DSC at a rate of 10 °C min^{-1}. The T_g was taken to be the intermediate temperature between the top and bottom points of an inflection between the base line and tangential line at the inflection points of DSC.

The phase dissolution temperature (T_d) was obtained with various cooling rates using a light scattering photometer (OPTEC GP-5). Before the cooling measurements were made, the temperature was raised to 170 °C to achieve a miscible state. A He–Ne gas laser beam of 632.8-nm wavelength was applied vertically to the film specimen. The goniometer traces of the scattered light from the film were recorded during cooling at various constant rates.

Results and Discussion

Figure 1 shows the variation of the T_g of PVB with the microstructure composition. As the 1,2-unit content of PVB increases, the corresponding T_g increases accordingly, and this is in good agreement with the Fox equation.[15] Thus, in this article, PVB will be regarded as a random copolymer consisting of 1,2- and 1,4-units. In order to apply the mean field approximation to the oligomer/copolymer blends, a volume additivity of the copolymer has to be found against the copolymer composition. Figure 2 shows specific volumes of PVB plotted against the 1,2-unit. The closed circles with error bars are averaged specific volumes of three observations, and the solid line is drawn by the least squares method. The specific volume varies according to the additivity. It suggests the possibility of an application of the Flory–Huggins lattice model to the blend miscibility. In the following discussion, the lattice theory with mean field approximation is used to explain thermodynamic liquid–liquid phase transition.

First, cloud points were determined to draw a temperature–blend composition phase diagram by using the light scattering technique on temperature variation. According to the customary criterion, phase dissolution temperatures (T_d) were determined using light scattering measurements. The light scattering profile from the immiscible blend, having a modulated structure, shows a peak in the scattering intensity as a function of scattering angle. The variation of scattered light intensity was monitored with cooling from 160 to 100 °C. As it is clearly shown in Figure 3, the temperature at which the scattering intensity begins to increase is defined as T_d. The T_d of the PVB (54.3)/Clearon-P125 blend was found to depend upon the cooling rate. By straight line extrapolation to zero cooling rate, the cloud point can be determined, as demonstrated in Figure 4. Such experiments were carried out for the blends with more than 60 wt % of Clearon-P125. To draw a liquid–liquid phase diagram of blends of various PVBs and Clearon-P125, the density of Clearon-P125 which was presented in our previous paper was used. The observed cloud points for PVB (54.3)/Clearon-P125 against the blend composition are shown in Figure 5. It is pertinent that the cloud points produce convex curves when plotted against the blend composition. This is the so-called UCST type phase diagram. The cloud point data were fitted to the binodal curve calculated according to the Flory–Huggins free energy of mixing (per unit volume of the mixture), where the solid line is a calculated binodal curve and closed circles are the cloud points. This curve-fitting belongs to the Koningsveld manner.[16] For the calculation, the conventional temperature dependence of the χ parameter was evaluated as $\chi = A + B/T$. The estimated χ parameter is listed in Table II. Similar UCST type phase diagrams were also obtained in other PVB blends that contain various 1,2-units. For instance, the phase diagrams for PVB (10.4)/Clearon-P125 and PVB (70.4)/Clearon-P125 are shown in Figures 6 and 7, respectively. In these

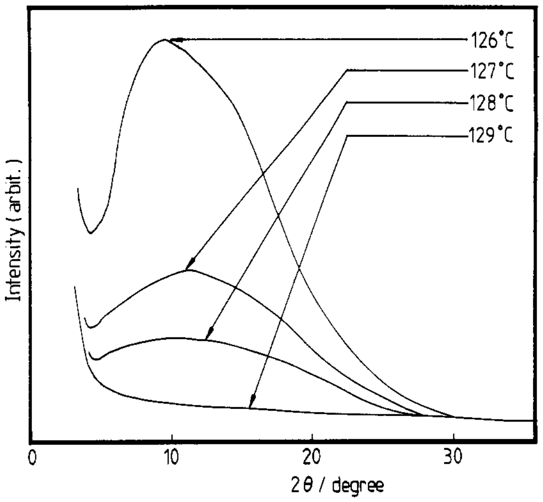

Figure 3. Light scattering profile of the PVB (54.3)/Clearon-P125 (30/70) blend in the cooling process of 0.25 °C min^{-1}. A He–Ne laser of 632.8 nm radiation wavelength was used.

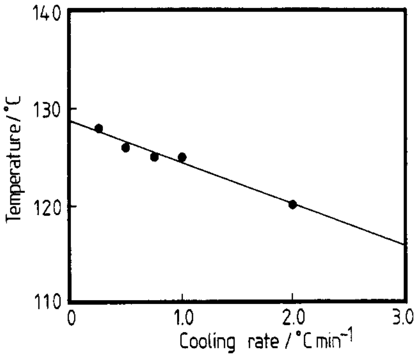

Figure 4. T_d vs cooling rate for the PVB (54.3)/Clearon-P125 blend.

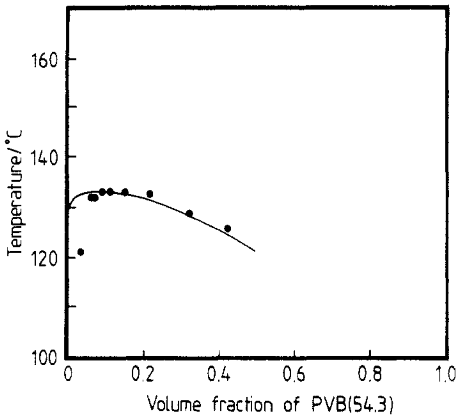

Figure 5. UCST phase diagram of PVB (54.3)/Clearon-P125 blends. The T_d's values (●) were obtained by cloud point measurements. The solid line is the binodal curve calculated by using the Flory–Huggins expression.

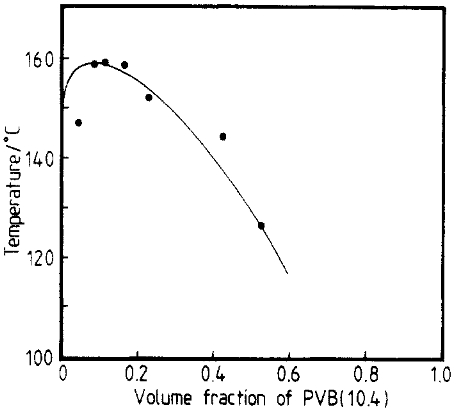

Figure 6. UCST phase diagram of PVB (10.4)/Clearon-P125 blends. The T_d's values (●) were obtained by cloud point measurements. The solid line is the binodal curve calculated by using the Flory–Huggins expression.

Table II. χ_{12} **Parameter of the PVB/Clearon-P125 Blend**

specimen	χ_{12}
PVB (10.0)/Clearon-P125	$-0.065 + 35.51/T$
PVB (24.3)/Clearon-P125	$-0.062 + 33.88/T$
PVB (32.3)/Clearon-P125	$-0.070 + 36.67/T$
PVB (47.4)/Clearon-P125	$-0.130 + 60.26/T$
PVB (54.3)/Clearon-P125	$-0.180 + 80.10/T$
PVB (60.0)/Clearon-P125	$-0.040 + 24.04/T$
PVB (70.4)/Clearon-P125	$-0.130 + 62.56/T$

diagrams, the cloud points were also fitted to the binodal curve. Consequently, the Flory–Huggins interaction parameters, χ, for all the blends can be determined. In all χ parameters, A is a negative value and B is a positive value. Both A and B varied with the 1,2-unit. If the polybutadiene were regarded as a homopolymer, then A and B would be constants. However, the copolymer effect on the miscibility of PVB/Clearon-P125 is extensive and does not vary linearly.

The phase behavior dependence on copolymer composition was secondarily investigated. The miscibility valley in a plot of UCST versus the 1,2-unit content is shown in Figure 8, where the blend composition is defined as the critical composition. The locus of experimentally obtained UCST is delineated against the 1,2-unit content as a concave curve. For the sake of the thermodynamic interpretation of the miscibility valley phenomenon, the χ parameters in Table II are utilized. According to the mean field approximation, the χ parameter of a homopolymer (A)/copolymer (BC) blend, χ_{blend}, is expressed

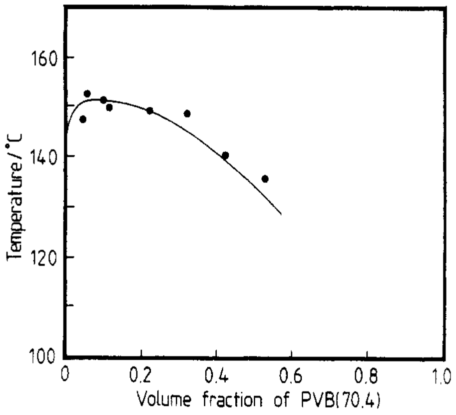

Figure 7. UCST phase diagram of PVB (70.4)/Clearon-P125 blends. The T_d's values (●) were obtained by cloud point measurements. The solid line is the binodal curve calculated by using the Flory–Huggins expression.

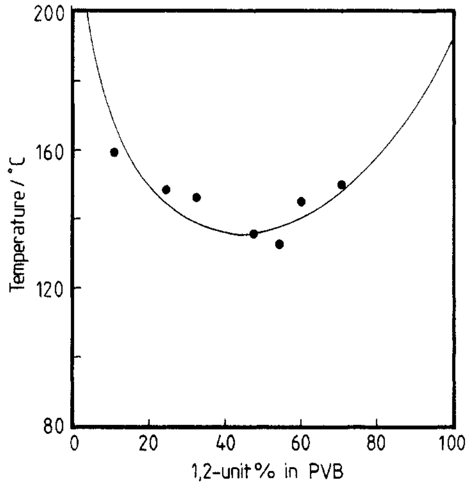

Figure 8. Locus of UCST against the 1,2-unit content (miscibility valley), where ● are obtained UCSTs.

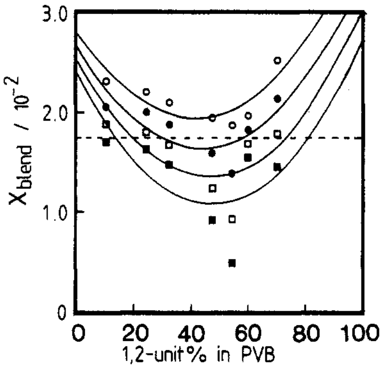

Figure 9. χ_{blend} against the 1,2-unit content: (○) 130, (●) 140, (□) 150, and (■) 160 °C, respectively.

as

$$\chi_{\text{blend}} = x\chi_{AB} + (1 - x)\chi_{AC} - x(1 - x)\chi_{BC} \qquad (1)$$

where x is the 1,2-unit content and χ_{ij} is the interaction parameter between i and j species. When eq 1 is expanded in terms of x, χ_{blend} can be represented by the following equation.

$$\chi_{\text{blend}} = \chi_{BC}x^2 + (\chi_{AB} - \chi_{AC} - \chi_{BC})x + \chi_{AC} \qquad (2)$$

Therefore χ_{blend} is represented as a second-order function of x. Since χ is proportional to $1/T$, where T is the absolute temperature, χ_{blend} is dependent upon the temperature. In Figure 9, χ_{blend} is indicated against the 1,2-unit content at each temperature. The closed circles represent exper-

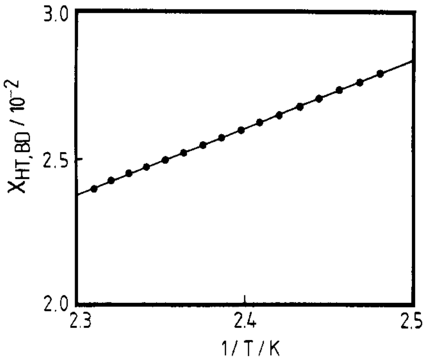

Figure 10. Temperature dependence of the $\chi_{HT,BD}$ parameter.

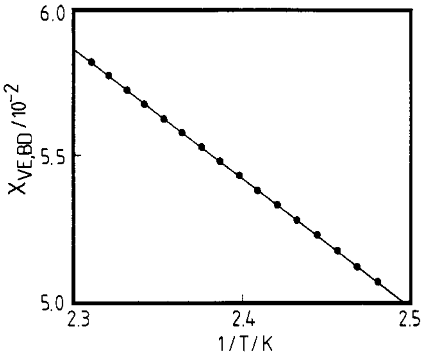

Figure 11. Temperature dependence of the $\chi_{VE,BD}$ parameter.

Table III. χ_{12} **Parameter between Blend Components**

specimen	χ_{12}
PVE/Clearon-P125	$\chi_{HT,VE} = -0.109 + 58.90/T$
PBD/Clearon-P125	$\chi_{HT,BD} = -0.030 + 23.24/T$
PVE/PBD	$\chi_{VE,BD} = 0.160 - 44.23/T$

imentally obtained χ values estimated from χ parameters in Table II. The solid curves are drawn by the second-order least squares method at each temperature. As expected from eq 2, the parabolic curve is drawn. Then, χ_{BC}, $(\chi_{AB} - \chi_{AC} - \chi_{BC})$, and χ_{AC} can be obtained. In this study, monomeric species A, B, and C are hydrogenated terpene (HT) and the 1,2-unit (VE) and 1,4-unit (BD) in polybutadiene, respectively. Using eq 2, $\chi_{HT,BD}$, $\chi_{HT,VE}$, and $\chi_{VE,BD}$ can be calculated at each temperature.

Since χ_{blend} in Figure 9 decreases with rising temperature, the temperature dependences of $\chi_{VE,BD}$, $(\chi_{HT,VE} - \chi_{HT,BD} - \chi_{VE,BD})$, and $\chi_{HT,BD}$ were investigated. Figure 10 shows the calculated $\chi_{HT,BD}$ against $1/T$. The $\chi_{HT,BD}$ at each temperature was estimated as a constant in eq 2. $\chi_{HT,BD}$ decreases with rising temperature and is proportional to $1/T$. Thus, $\chi_{HT,BD}$ is determined by the least squares approximation and listed in Table III. $\chi_{VE,BD}$ and $\chi_{HT,VE}$ were also determined in a similar manner. However, in Figure 11, $\chi_{VE,BD}$ increases as temperature rises. If the phase behavior of the blend of 1,2-polybutadiene and 1,4-polybutadiene were based upon the geometric mean rule, $\chi_{VE,BD}$ would decrease with rising temperature. Therefore, for this blend, the geometric mean rule cannot be adopted. The determined $\chi_{VE,BD}$ suggests that a LCST type phase behavior is expected in the blend of 1,2-polybutadiene and 1,4-polybutadiene. A similar χ parameter for the blend of 1,2- and 1,4-polybutadienes was estimated by Jinnai et al.,[17] using a small angle neutron scattering technique. Although the means of estimation of the χ parameter differ from each other, the LCST type phase behavior was predicted for the blend. However, the UCST type phase behavior of blends of 1,2-polybutadiene with 71% 1,2-unit content and 1,4-polybutadiene was observed by Shah and co-workers.[18] This is inconsistent with our result. A precise investigation should be carried out at higher 1,2-unit content in 1,2-polybutadiene.

Table IV. Solubility Parameter Value of Samples[a]

specimen	$\delta/(\mathrm{cal/cm^3})^{1/2}$
1,4-polybutadiene	8.39
1,2-polybutadiene	7.65
Clearon-P125	9.24

[a] Estimated from Hoy's tabulation.

Using the determined χ_{ij} parameters, the phase behavior against copolymer composition was simulated. In Figure 8, the solid curve was drawn by using eq 2. At higher temperatures, above the solid curve, miscibility of the blend is achieved. This locus of UCST against copolymer composition is the so-called "miscibility valley". In our previous study,[9] the miscibility valley of the homopolymer/copolymer blend was predicted by using eq 2 with χ_{ij} parameters, where the χ_{ij} parameters were estimated from the solubility parameters. When a copolymer consisted of two species having the largest solubility parameter and smallest one, respectively, the miscibility valley was simulated in a blend of the copolymer and homopolymer having an intermediate solubility parameter. Therefore, in this study, a similar relationship in solubility parameter is expected. Solubility parameters for three species are represented in Table IV. The solubility parameter of hydrogenated terpene resin is larger than others. According to the geometric mean rule, the miscibility valley would not be expected for the hydrogenated terpene resin/PVB blend. However, the miscibility valley is indicated in Figure 8. It is explained by the fact that the $\chi_{VE,BD}$ between 1,2-polybutadiene and 1,4-polybutadiene was determined as a χ parameter in the LCST type phase behavior. The discrepancy from the geometric mean rule can cause the miscibility valley.

Intermolecular interactions in a pair of polymers composed of carbon and hydrogen must be van der Waals dispersion forces. Although the van der Waals dispersion forces are expected between the three monomeric species in this study, the experimental evidence differs from the prediction. This implies that there is an additional interaction with van der Waals dispersion forces for the blend. This interaction will be investigated in our future work.

Conclusions

UCST type phase diagrams were drawn for seven kinds of polybutadiene blend. According to the Flory–Huggins lattice theory, Flory–Huggins interaction parameters were determined for PVB/Clearon-P125 blends. Plotting the obtained UCSTs against the 1,2-unit content in PVB, the miscibility valley type phase behavior was found, in which the locus of UCSTs was delineated against copolymer composition as a concave curve. Using the determined interaction parameters, the miscibility valley was simulated. Although the phase behavior against copolymer composition was predicted by using χ_{ij} parameters estimated from solubility parameters, this phase behavior is inconsistent with the miscibility valley. Thus, the geometric mean rule does not apply to the prediction of the miscibility valley of PVB/Clearon-P125 blends. A theoretically clear understanding for the liquid–liquid phase transition in polymer blends has not been achieved yet, even though only van der Waals dispersion forces were expected between blend components.

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