

Modified Lattice Fluid 이론에 의한 폴리염화비닐과 폴리메틸메타아크릴레이트 블렌드의 Spinodal 분해의 수치모사

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Spinodal Simulations for Poly(vinyl chloride)/Poly(methyl methacrylate) Blends by Modified Lattice Fluid Theory

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요 약 : 상용성이 있는 폴리염화비닐과 폴리메틸메타아크릴레이트 블렌드에 lattice fluid 이론과 modified lattice fluid 이론을 적용하여 spinodal 분해를 수치모사하였다. 각 구성 고분자의 특성 상수 값은 열팽창계수, 열압축계수, 밀도로부터 결정하였다. 이론적으로 예측된 spinodal 분해와 실험값의 비교로부터 modified lattice fluid 이론이 보다 예측이 잘 됨을 알 수 있었다. 이론적으로 예측되는 상분리 온도는 상호 계수 ζ_{12} 와 q_{12} 의 선택에 따라 변화하며, 폴리염화비닐과 폴리메틸메타아크릴레이트 블렌드계의 ζ_{12} 와 q_{12} 의 값이 각각 1.0013과 0.002일 때 이론값과 실험값이 가장 잘 일치하였다. 분자량의 변화에 따르는 상분리 온도의 변화를 이론적으로 예측한 결과 일반적인 경향과 잘 일치하였다.

Abstract : The spinodal curve of poly(vinyl chloride)(PVC)/poly(methyl methacrylate)(PMMA) blends was simulated using the lattice-fluid theory and the modified lattice-fluid theory. The equation-of-state parameters for pure materials were calculated from the data for the density ρ the thermal expansion coefficient α , and the thermal pressure coefficient γ or compressibility β . All data were taken from literature. When spinodals from two theories were compared with an experimental cloud point curve, it was realized that the modified lattice-fluid theory is more predictive. The best fitted spinodal curve was obtained with the value of $\zeta_{12}=1.0013$ and $q_{12}=0.002$. The dependence of lower critical solution temperature(LCST) behavior on molecular weight was successfully predicted by the theory.

INTRODUCTION

It has been observed that some polymer-polymer pairs exhibit lower critical solution tempera-

ture(LCST) behavior. One origin of the observed behavior has been found to arise from free volume effect.

Several theories have been developed to explain

the LCST behavior in polymer blend systems. Two typical theories are the Flory-Prigogine's equation of state theory¹ and the Sanchez's lattice-fluid theory.² In the Flory-Prigogine's theory,³⁻⁵ the cell character and the lack of any detailed model for the dependence of external degrees of freedom per molecular segment on external condition sometimes limit its range of applicability. The lattice-fluid theory,^{2,6} on the other hand, is able to predict vapor-liquid transition in a fundamental manner. It can, for example, be used for the prediction and correlation of the solubilities of subcritical as well as supercritical gases in polymeric liquid.⁷ It is also directly related to the classical Gibbs-DiMarzio approach⁸ to glass transition.⁹

Recently, Panayiotou¹⁰ proposed an equation of state theory which is a modification of the Sanchez's lattice-fluid theory.¹¹ Seeking an improvement of the theory, from the quantitative standpoint, without seriously sacrificing its simplicity, he considered constant number of segments per molecule in the pure state and in the mixture. Molecular shape difference was taken into account, in a direct analogy with Flory-Prigogine's equation of state theory,⁵ through the characteristic surface-to-volume-ratio of each component.

In this report, the phase behavior of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) blends is analyzed using the lattice-fluid theory and the effect of molecular weight on the phase behavior of the blend is also examined.

THEORY

Following the notation of Panayiotou,¹⁰ the equation of state of the pure components and of the mixture is given by eq. 1.

$$\frac{\hat{P}\hat{V}}{\hat{T}} = 1 - r \left[1 + \frac{\ln(1-\hat{\rho})}{\hat{\rho}} + \frac{\hat{\rho}}{\hat{T}} \right] \quad (1)$$

Where $\hat{\rho}$, \hat{P} and \hat{T} are the reduced density ($\hat{\rho} = \rho/\rho^*$), the reduced pressure ($\hat{P} = P/P^*$) and the reduced temperature ($\hat{T} = T/T^*$), respectively, and r is the number of lattice site occupied by the

molecule. In the case of high polymers ($r = \infty$) and at negligible external pressure, eq. 1 reduces to eq. 2.

$$\hat{\rho} = 1 - \exp \left[-\hat{\rho} - \frac{\hat{\rho}^2}{\hat{T}} \right] \quad (2)$$

Knowing the thermal expansion coefficient α_i and thermal pressure coefficient γ_i of the pure components, and using eqs. 3 to 7, it is possible to calculate the characteristic densities ρ_i^* , characteristic volumes v_i^* , characteristic temperatures T_i^* and characteristic pressures P_i^* for pure components.

$$\frac{1}{\alpha_i T} = \frac{-\hat{\rho}_i^2}{(1-\hat{\rho}_i)[\ln(1-\hat{\rho}_i) + \hat{\rho}_i]} - 2 \quad (3)$$

$$\hat{T}_i = \frac{-\hat{\rho}_i^2}{\ln(1-\hat{\rho}_i) + \hat{\rho}_i} \quad (4)$$

$$P_i^* = \gamma_i T_i^* \hat{v}_i^2 \quad (5)$$

$$r_i = \frac{P_i^* M_i}{RT_i^* \rho_i^*} \quad (6)$$

$$v_i^* = \frac{M_i}{\rho_i^* r_i} \quad (7)$$

where M_i is the molecular weight of pure component i . One can then calculate the characteristic parameters and number of segments of the mixture from eqs. 8 to 12:

$$T^* = \phi_1 T_1^* + \phi_2 T_2^* - \phi_1 \phi_2 T X_{12} \quad (8)$$

$$v^* = \phi_1^2 v_1^* + \phi_2^2 v_2^* + 2\phi_1 \phi_2 \left(\frac{v_1^{*\frac{1}{3}} + v_2^{*\frac{1}{3}}}{2} \right)^3 \zeta_{12} \quad (9)$$

$$P^* = \frac{RT^*}{v^*} \quad (10)$$

$$r = \frac{r_1 r_2}{\phi_1 r_2 + \phi_2 r_1} \quad (11)$$

$$X_{12} T = T_1^* + \left(\frac{s_1}{s_2} \right) T_2^* - 2 \left(\frac{s_1}{s_2} \right)^{1/2} (T_1^* T_2^*)^{1/2} \zeta_{12} \quad (12)$$

where ϕ_i and θ_i denote the volume and surface fraction of component i in close packed state, respectively, ζ_{12} is the dimensionless binary interaction parameter, X_{12} the interaction parameter, ξ_{12} the dimensionless binary parameter, and s_1/s_2 the surface area to unit volume ratio which can be obtained by a group contribution method.¹² From these values one can calculate the reduced density of the mixture $\hat{\rho}$ using eq. 1.

The chemical potential of component 1 in the mixture is given by eq. 13.¹⁰ The chemical potential for the component 2 is obtained from eq. 13 by simple interchange of subscript 1 and 2 :

$$\begin{aligned} \frac{\mu_1}{RT} = & \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + r_1 \hat{\rho} X_{12} \theta_2^2 + r_1 (\hat{v} - 1) \\ & \ln(1 - \hat{\rho}) + \ln \frac{\hat{\rho}}{w_1} - r_1 \frac{\hat{\rho}}{\hat{T}_1} + r_1 \hat{p} \frac{\hat{v}}{\hat{T}} \\ & \left(2 \frac{\phi_1 v_1^* + \phi_2 v_2^*}{v^*} - 1\right) + r_1 \theta_2^2 q_{12} \end{aligned} \quad (13)$$

where q_{12} is introduced as an entropic correction factor due to interaction.

The equation for spinodal decomposition is obtained by differentiating eq. 13 and applying spinodal condition $d(\Delta\mu)/d\phi_2 = 0$:

$$\begin{aligned} \hat{\rho} \left[2 \frac{\theta_1}{\phi_1} \left(\theta_1 \frac{s_2}{s_1} + \theta_2 \right)^2 X_{12} + \frac{\alpha}{\gamma} P^* \hat{T} \psi^2 \right] \\ + 2 q_{12} \frac{\theta_1 \theta_2}{\phi_1 \phi_2} \left(1 + \frac{\phi_1 - \theta_2}{\phi_2} \right) < \frac{1}{r_1 \phi_1} + \frac{1}{r_2 \phi_2} \end{aligned} \quad (14)$$

where

$$\psi = \hat{\rho} \lambda_{12} - \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (15)$$

and

$$\lambda_{12} = \frac{1}{\hat{T}_1} - \frac{1}{\hat{T}_2} - \left(\theta_2^2 - \theta_1 \frac{s_1}{s_2} \right) X_{12} \quad (16)$$

In eq. 14, the right hand side is the combinatorial entropy contribution, the first term of the left hand side is an energetic contribution, and second term of the left hand side is an entropic contribu-

tion from equation of state. It is significant to note that the entropic equation of state term makes an unfavorable contribution to the spinodal, i. e., its presence does not favor miscibility.

RESULTS and DISCUSSION

Binodal curves in liquid-liquid equilibria may be calculated, as usual, by equating the chemical potentials for each of the components in the coexisting phases. It is known that the shape of the binodal curves in polymer mixtures depends strongly on molecular weight distribution. However, since the effect of molecular weight distributions on spinodal curves is weak, the spinodal inequality condition (eq. 14) can be used for predicting the phase behavior of the polymer mixture whose molecular weight distributions are not specified.

The PVT data for PVC and PMMA used in this study are taken from literature¹³ (Table 1). The characteristic parameters for PVC and PMMA are calculated by the use of eqs 3-7 and the results are listed in Table 2.

The effect of the binary interaction parameter ζ_{12} on the simulation of phase separation is shown in Fig. 1. An increase in ζ_{12} makes the interchange parameter X_{12} more negative (see eq. 12), thus favoring miscibility. In other words, the LCST shifts to higher temperature as ζ_{12} increases. It is noteworthy that calculated spinodals are very sensitive

Table 1. Equation-of-State Parameters for Pure Polymers

Polymers	$\alpha(K^{-1})$	$\gamma(Jcm^3/K)$	$\rho(g/cm^3)$	\bar{M}_n
PVC	0.00050	1.1378	1.3514	36,000
PMMA	0.00058	1.1169	1.1494	38,000

Table 2. Characteristic Parameters for Pure Polymers

Polymers	$P^*(mN/m^2)$	$T^*(K)$	$\rho^*(g/cm^3)$
PVC	518.1	781	1.4547
PMMA	523.5	730	1.2522

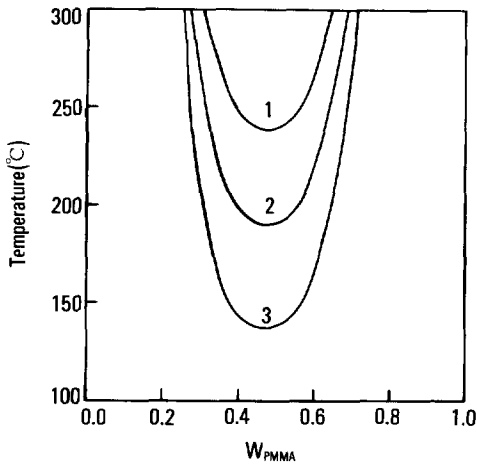


Fig. 1. Simulated spinodals for PVC/PMMA mixtures: 1, $\zeta_{12}=1.00065$; 2, $\zeta_{12}=1.00063$; 3, $\zeta_{12}=1.00058$.

to the values of ζ_{12} , as seen in Fig. 1.

Fig. 2 shows the effect of q_{12} on the phase diagram. As q_{12} increases, the curvature of the spinodal curve decreases. The interaction entropy parameter q_{12} was originally introduced into the Flory's equation-of-state theory, which resulted in the simulated spinodals being flat-bottomed. Sham and Walsh¹⁴ stated that it is not possible to fit the calculated spinodal to experimental results without using q_{12} . This is because the theory assumed that only interactions between neighboring segments contribute to X_{12} and treated X_{12} as an enthalpy parameter, while the interactions between neighbors also affect the entropy. Furthermore, for a large favorable X_{12} (strong specific interaction), a large unfavorable q_{12} is necessary and vice versa. q_{12} could be interpreted as the unfavorable entropy change associated with the formation of the specific interaction.

It is usually assumed that the cloud points are the same as the spinodals, since it is reported that the cloud points are closer to the spinodals rather than the binodals.¹⁵ Figure 3 shows the comparison of spinodals simulated by the Sanchez's lattice-fluid theory and the modified lattice-fluid theory. When simulated spinodals are compared with experimental cloud points, it is found that

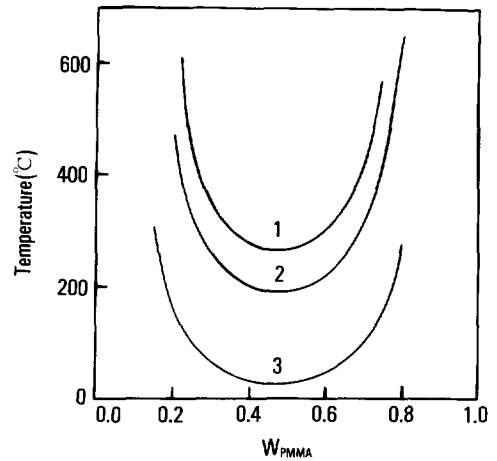


Fig. 2. The effect of q_{12} on simulated spinodal with $\zeta_{12}=1.00063$ for PVC/PMMA mixtures: 1, $q_{12}=-0.0001$; 2, $q_{12}=0.0$; 3, $q_{12}=0.0005$.

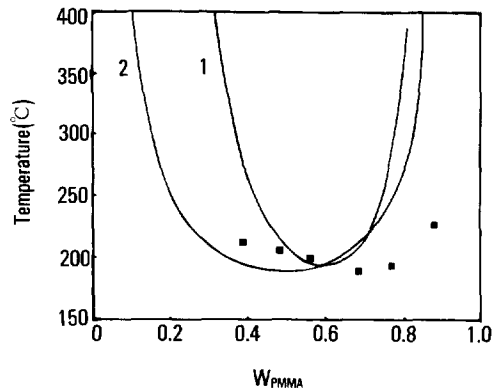


Fig. 3. Comparison between simulated spinodals with $\zeta_{12}=1.0013$ and $q_{12}=0.002$ for PVC/PMMA mixtures: 1, Sanchez's theory; 2, modified Sanchez's theory. Filled squares represents the experimental cloud points.¹³

modified lattice-fluid theory fits better than the Sanchez's lattice-fluid theory. This seems to be because the introduction of q_{12} into the lattice-fluid theory makes the spinodals flat-bottomed. The binary interaction parameter ζ_{12} and interaction entropy parameter q_{12} have been adjusted to give an adequate description of the phase behavior of the PVC/PMMA system: $\zeta_{12}=1.0013$, $q_{12}=0.002$.

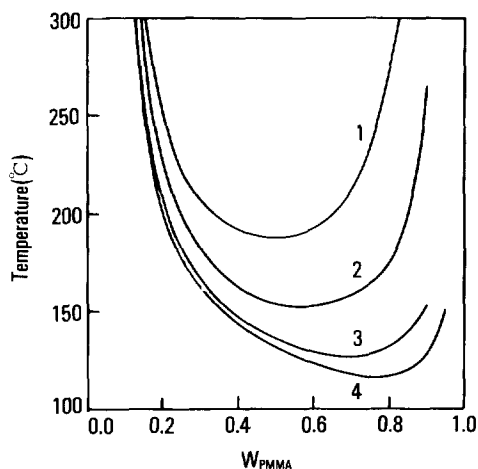


Fig. 4. Simulated spinodals for PVC/PMMA mixtures : 1, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=38,000$; 2, $\bar{M}_n(\text{PVC})=72,000$, $\bar{M}_n(\text{PMMA})=38,000$; 3, $\bar{M}_n(\text{PVC})=180,000$, $\bar{M}_n(\text{PMMA})=38,000$; 4, $\bar{M}_n(\text{PVC})=360,000$, $\bar{M}_n(\text{PMMA})=38,000$.

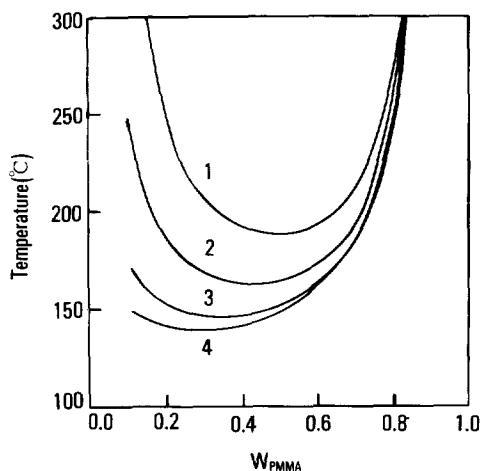


Fig. 5. Simulated spinodals for PVC/PMMA mixtures : 1, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=38,000$; 2, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=76,000$; 3, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=190,000$; 4, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=380,000$.

In Figures 4-6, the effects of molecular weight on the phase behavior are presented. The values of the binary interaction ζ_{12} and interaction entropy q_{12} used for the simulation in Figures 4-6 are

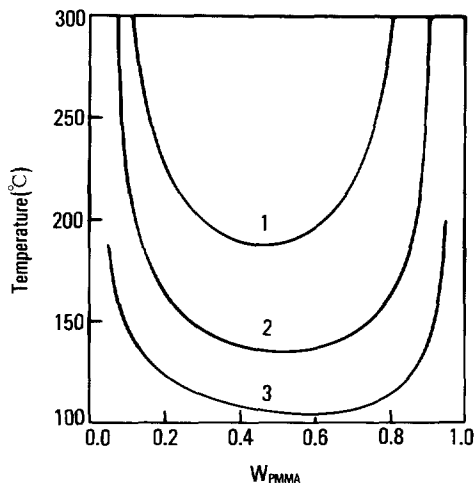


Fig. 6. Simulated spinodals for PVC/PMMA mixtures : 1, $\bar{M}_n(\text{PVC})=36,000$, $\bar{M}_n(\text{PMMA})=38,000$; 2, $\bar{M}_n(\text{PVC})=72,000$, $\bar{M}_n(\text{PMMA})=76,000$; 3, $\bar{M}_n(\text{PVC})=180,000$, $\bar{M}_n(\text{PMMA})=190,000$.

the same as the values used in Figure 3. As shown in Figure 4, as the molecular weight of PVC increases while that of PMMA remains constant, the mutual solubility of the two polymers decreases and thus the LCST shifts to lower temperature. In addition, the LCST shifts to PMMA rich compositions as the molecular weight of PVC increases, whereas the LCST occurs at middle composition when both molecular weights of PVC and PMMA are almost the same. It is known that the disparity in the sizes of the molecules of the two components is responsible for the LCST dissymmetry. Figure 5 illustrates the effect of PMMA molecular weight on the LCST behavior of the blend. As the molecular weight of PMMA increases while that of PVC remains constant, the LCST shifts to lower temperature and PVC rich compositions. In Fig. 6, as both of molecular weights of PMMA and PVC increase, the LCST shifts to lower temperature where the LCST occurs at middle composition.

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