

Poly(ϵ -caprolactone)과 Chlorinated Polyethylene 블렌드의 상거동에 관한 연구: 2. LCST의 예측

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The Phase Behavior of Poly(ϵ -caprolactone) and Chlorinated Polyethylene Blends : 2. Prediction of the Lower Critical Solution Temperature(LCST)

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요 약 : 공중합체 블렌드의 온도에 따른 상거동의 변화를 쉽게 예측할 수 있는 새로운 모델을 이용하여 poly(ϵ -caprolactone)(PCL)과 chlorinated polyethylene(CPE) 블렌드의 상분리 온도를 예측하였다. MGQ 모델로부터 계산된 혼합열이 고분자 블렌드의 혼합열과 같다는 가정하에 effective contact energy parameter X_{AB} 를 구하였는데, 염소화 정도가 증가함에 따라 이 값의 크기는 음으로 증가하였다. Binary interaction 모델로부터 구한 단량체간 상호작용에너지 밀도 B_{ij} 값과 공중합체 블렌드의 상태 방정식 이론으로부터 구한 단량체간 접촉 에너지 매개변수 X_{ij} 값의 크기가 거의 같다는 사실로부터 혼합열에 미치는 자유 부피의 기여가 작았음을 알 수 있었다. CPE내의 에틸렌 단위가 증가함에 따라 LCST는 어떤 조성에서 최대치를 보였으며 PCL/poly(vinyl chloride) 블렌드의 경우 LCST는 303°C로 예측되었다. 공중합체 블렌드의 Flory-Huggins 상호작용 매개변수 χ_{AB} 에 미치는 자유부피의 효과를 정량적으로 검토함으로써 이러한 현상을 쉽게 설명할 수 있었다.

Abstract : Using the newly developed model, which can easily quantify the effect of comonomer on the lower critical solution temperature(LCST) behavior in copolymer blends, the LCST of poly(ϵ -caprolactone)(PCL) and chlorinated polyethylene(CPE) blends was theoretically predicted. Effective contact energy parameter X_{AB} was calculated with the assumption that the heat of mixing calculated from the MGQ model is equivalent to that of the corresponding polymer blend; the X_{AB} increases favorably with increase of the chlorine content. It is found that the difference between the segmental interaction energy densities B_{ij} obtained from a binary interaction model and the segmental contact energy parameters X_{ij} obtained from the equation-of-state theory for copolymer blends is considerably small. This indicates that the free volume contribution to the heat of mixing is relatively small. As the content of ethylene unit in CPE increases, the predicted LCST first slightly increases, goes th-

rough a maximum, and then steeply decreases. By examining the free volume contribution to the Flory-Huggins interaction parameter χ_{AB} , this variation of the LCST with the chlorine content was quantitatively explained.

INTRODUCTION

In a previous paper,¹ we have discussed the effect of chlorine content on the phase behavior of poly(ϵ -caprolactone)(PCL)/chlorinated polyethylene(CPE) blends using the Modified Guggenheim Quasichemical(MGQ) model. As expected, the miscibility of these blends was such an extremely sensitive function of the chlorine content; the calculated critical chlorine content to be miscible with PCL is ca. 30 wt% of chlorine, which well agrees with experiment.² In spite of this success, more detailed understanding of the phase behavior of PCL/CPE blends requires a description of the variation of the miscibility with temperature, i. e., the variation of the lower critical solution temperature(LCST) with the chlorine content.

If we assume that the LCST reflects the interaction between components, the variation of the LCST in copolymer blends roughly corresponds to that of the Flory-Huggins interaction parameter χ_{AB} (or interaction energy density B). However, in its simplest form the Flory-Huggins theory is unsatisfactory in describing the phase behavior of polymer blends since it cannot predict the appearance of phase separation on heating. Modern thermodynamic theories³⁻⁵ introduce the equation-of-state (EOS) contribution, which is due to a mismatch of the thermal expansivities of the components, into the free energy of mixing or χ_{AB} . These are capable of predicting LCST behavior.

Very recently, according to Patterson's treatment for phase behavior of polymer blends we have proposed a simple model for copolymer blends to quantify the effect of comonomer on the LCST behavior of copolymer blends.⁶ The model explains that the repulsion within copolymers contributes to the free volume term as well as to the interactional term. Unlike its contribution to the

interactional term, the repulsion is not always favorable for the free volume term since this term depends on the difference in the characteristic temperatures of blend components: the characteristic temperature of copolymer is a function of the characteristic parameters of copolymer components and the intramolecular interaction within copolymers. We showed, using this model, that for poly(vinyl methyl ether)/styrenic copolymer blends the dependence of χ_{AB} on the copolymer composition at a given temperature was in agreement with the variation of the LCST.⁶

Although miscibility, crystallization kinetics and mechanical properties of PCL/PVC blends have been intensively studied, no experimental LCST has been reported due to the thermal decomposition of PVC at high temperatures. Nevertheless, there have been several efforts^{7,8} to simulate theoretically the spinodal of the blend. In their reports, the effects of the interaction parameter and the surface to volume ratio on the variation of the simulated spinodal have been discussed. However, the prediction of the exact LCST has been limited since the reliable interaction parameter for PVC/PCL blend could not be available.

The determination of contact energy parameter X_{AB} is a prerequisite to predict the LCST of the miscible blend from the equation of state theory. There are several ways to determine X_{AB} . For example, X_{AB} can be determined by fitting the theoretical values of the thermodynamic quantity to its experimental data of the mixtures such as inverse gas chromatography and heat of mixing measurement of low molecular weight analogues. Especially, the latter is often useful to obtain the direct information for the intermolecular interaction. Since the heat of mixing with the chlorine content is well established from the previous paper,¹ the X_{AB} values for PCL/CPE blends can be

determined as a function of chlorine content.

In this study, it is attempted to predict how the LCSTs of PCL/CPE blends vary with the chlorine content. The effect of the degree of chlorination on the LCST will be discussed more quantitatively in terms of the newly developed model.

THEORETICAL BACKGROUND

At atmospheric pressure, Flory's equation of state⁴ for chain molecules can be expressed in reduced form as

$$\hat{T} = \frac{\hat{v}^{1/3} - 1}{\hat{v}^{4/3}} \quad (1)$$

where $\hat{v} = v/v^*$ is the reduced specific volume and $\hat{T} = T/T^*$ is the reduced absolute temperature. The starred reducing quantities reflect the molecular characteristics of the chain molecule. All $\hat{v}^{1/3}$ values are found between the extremes of 1 and 4/3 due to the limit of the thermal expansion of chain molecules.

The application of this theory to mixtures of $N_A r_A$ mers and $N_B r_B$ mers is based on the mean field approximation. Each mer has to be chosen in such a way as to have equal hard core volume.¹⁷ An additional interaction parameter X_{AB} , which arises from the difference in interaction energy between like and unlike segment pairs, is introduced. The equation-of-state for two-component mixtures has a form identical with that for the pure component if the following mixing rules are made :

$$P^* = \phi_A P_A^* + \phi_B P_B^* - \phi_A \theta_B X_{AB} \quad (2)$$

$$T^* = \frac{P^*}{\phi_A P_A^*/T_A^* + \phi_B P_B^*/T_B^*} \quad (3)$$

$$\theta_B = \frac{s_B \phi_B}{s_B \phi_B + s_A \phi_A} \quad (4)$$

where ϕ_i , with $i=A, B$, denotes the segment fraction of component i , θ_B is the site fraction of component B , and s_i is the number of the contact sites per segment. The heats of mixing per unit hard

core volume is given by

$$\begin{aligned} \frac{\Delta H_m}{V^*} = & \phi_A P_A^* \left(\frac{1}{\hat{v}_A} - \frac{1}{\hat{v}} \right) + \phi_B P_B^* \left(\frac{1}{\hat{v}_B} - \frac{1}{\hat{v}} \right) \\ & + \frac{\phi_A \theta_B}{\hat{v}} X_{AB} \end{aligned} \quad (5)$$

where V^* is the total hard core volume of the mixture. The first two terms of right hand side in eq (5) represent the free volume contribution which depends on the volume change of mixing of the components.

Using the corresponding state theory and the van der Waals model, Patterson⁹ has derived an expression for the X_{AB} parameter :

$$\begin{aligned} \frac{X_{AB}}{C_A} = & \frac{\hat{V}_A^{1/3}}{\hat{V}_A^{1/3} - 1} \left[\frac{X_{AB}}{P_A^*} \right] \\ & + \frac{\hat{V}_A^{1/3}}{2(4/3 - \hat{V}_A^{1/3})} \left[1 - \frac{T_B^*}{T_B^*} \right]^2 \end{aligned} \quad (6)$$

where C_A satisfies the relation $C_A = P_A^* V_A^*/RT_A^*$ and reflects the flexibility of the molecule A . Since the reduced volume is linked with the reduced temperature by the equation-of-state(eq(1)), eq(6) is a function of temperature. The first term on the right hand of eq(6) is the interactional contribution and the second is the free volume contribution. It is helpful to note that the second depends on the ratio of the characteristic temperatures of components, which is closely related to the thermal expansion coefficient of the component. As temperature(or reduced volume) increases, the absolute value of interactional term decreases and the free volume term increases in the manner as shown in Figure 1. The free volume term is always positive and therefore tends to destabilize the mixtures at high temperature. The critical value of X_{AB} is given by

$$\frac{X_{AB, \text{crit}}}{C_A} = \frac{RT_A^*}{2P_A^*} \left[\frac{1}{V_A^{*1/2}} + \frac{1}{V_B^{*1/2}} \right]^2 \quad (7)$$

The temperature at which $X_{AB}(T) = X_{AB, \text{crit}}$ is the phase separation temperature, i.e., LCST. The system is miscible at temperatures of $X_{AB}(T) < X_{AB, \text{crit}}$

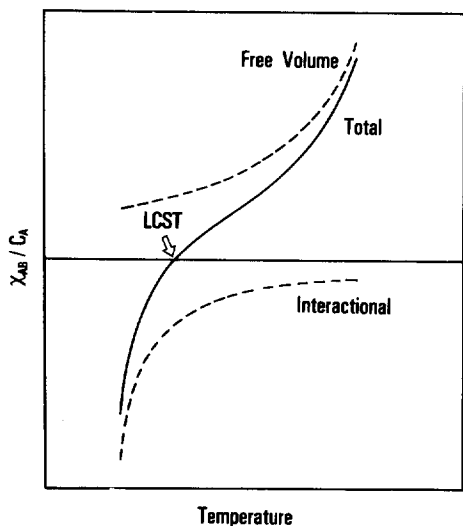


Fig. 1. Schematic illustration of the temperature dependence of χ_{AB} when the contact energy parameter χ_{AB} is negative. The dashed curves give the interactional and free volume contributions.

and immiscible at temperatures of $\chi_{AB}(T) > \chi_{AB, \text{crit}}$.

In order to apply eq(6) to copolymer blends, the effective contact energy parameter χ_{AB} and the characteristic temperatures of copolymer should be formulated in terms of segmental contact energy parameter X_{ij} , copolymer composition and the characteristic parameter of each component. According to the Flory's treatment for mixtures, we have developed the formulations for these parameters. For blends of homopolymer A of monomer 1 and copolymer B of monomers 2 and 3, X_{AB} , P_B^* and T_B^* can be expressed as follows :

$$X_{AB} = \theta_B^{(2)} X_{12} + \theta_B^{(3)} X_{13} - (s_A/s_B) \phi_B^{(2)} \theta_B^{(3)} X_{23} \quad (8)$$

$$P_B^* = \theta_B^{(2)} P_2^* + \phi_B^{(3)} P_3^* - \phi_B^{(2)} \theta_B^{(3)} X_{23} \quad (9)$$

$$T_B^* = \frac{P_B^*}{\phi_B^{(2)} P_2^*/T_2^* + \phi_B^{(3)} P_3^*/T_3^*} \quad (10)$$

where parameters with superscripts $i=2,3$ represent the copolymer composition of the component i . Eqs (9) and (10) have the form identical with those for mixtures of components 2 and 3. If it is assumed that the number of contact sites per segment

Table 1. Characteristics of CPEs Used for Calculation

Polymer Code	$\frac{\text{CH}_2\text{CH}_2}{\text{CH}_2\text{CHCl}}$	Copolymer Composition (vol. fraction of Et)
CPE 25	2.38	0.636
CPE 30	1.99	0.594
CPE 36	1.29	0.487
CPE 42	0.78	0.365
CPE 48	0.41	0.232
PVC	0	0

is the same for all segments, eq(8) can be simplified to the form identical with a binary interaction model :

$$X_{AB} = \phi_B^{(2)} X_{12} + \phi_B^{(3)} X_{13} - \phi_B^{(2)} \theta_B^{(3)} X_{23} \quad (11)$$

RESULTS AND DISCUSSION

At low chlorine content, CPE polymers can be regarded as random copolymers containing the two monomeric units, $-\text{CH}_2\text{CH}_2-(\text{Et})$ and $-\text{CH}_2\text{CHCl}-(\text{VC})$, with the assumption that the presence of other chlorinated units is negligible. Table 1 shows the ratio of Et units to VC unit and the volume fraction of VC for various CPEs. Although the repeat units of CPE are defined differently from the previous paper,¹ the heats of mixing calculated from the MGQ model are the same regardless of definition of the repeat unit, i. e., ΔH_m is only the function of the chlorine content.

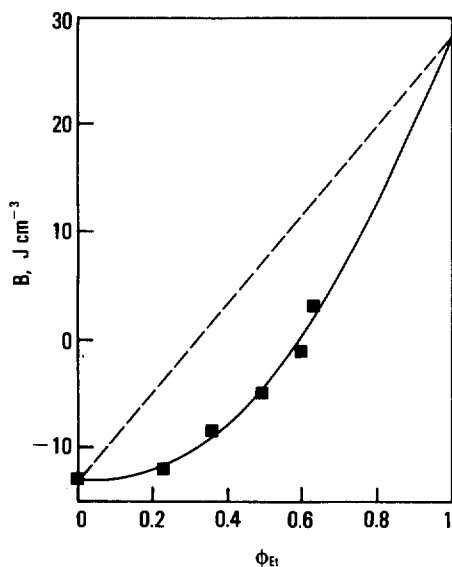
Therefore, the binary interaction model for homopolymer/copolymer blends can be applied to the PCL/CPE blends if we make the following identifications : 1 = $-(\text{CH}_2)_5\text{COO}-$, 2 = $-\text{CH}_2\text{CHCl}-$, 3 = $-\text{CH}_2\text{CH}_2-$. The net interaction energy density B is expressed as

$$B = \phi_2 B_{12} + \phi_3 B_{13} - \phi_2 \phi_3 B_{23} \quad (12)$$

where ϕ_2 is the volume fraction of VC unit in CPE. The segmental B_{ij} values can be calculated by fitting the overall B values into eq(12). The B values shown in Fig. 4 of reference 1 were used for least

Table 2. Segmental Interaction Energy Densities and Segmental Contact Energy Parameters

Segmental Pair	B_{ij} (J/cm ³)	X_{ij} (J/cm ³)
CL/VC	-12.7	-14.6
CL/Et	27.4	34.0
VC/Et	45.4	57.0

**Fig. 2.** The overall energy density parameter B as a function of the volume fraction of ethylene unit in CPE.

square curve fitting since the overall B depends only the chlorine content. The obtained B_{ij} values are listed in Table 2. Figure 2 illustrates the dependence of the overall B values on the Et volume fraction where the broken line represents the additive case in which $B_{23}=0$.

The characteristic parameters for pure components and the segmental contact energy parameters X_{ij} should be pre-determined to calculate the phase separation temperatures of PCL/CPE blends from eqs(6) and (11). The characteristic parameters of pure components are listed in Table 3. Assuming that the heats of mixing calculated from the MGQ model for PCL/CPE blends are equivalent to those of the corresponding polymer blends, the effective contact energy parameter X_{AB} at a

Table 3. Characteristic Parameters for Pure Components

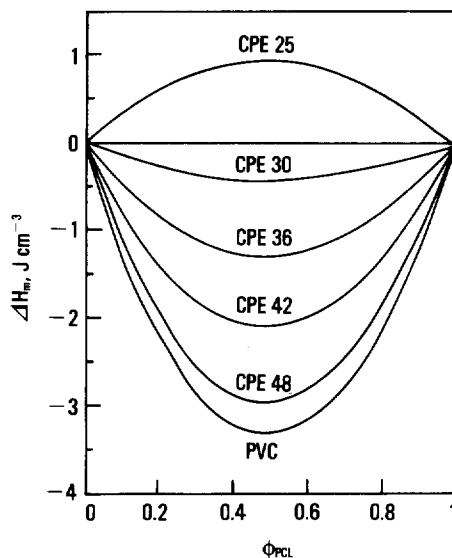
Polymer	v^* (cm ³ /g)	P^* (J/cm ³)	T^* (K)	s_i/s_{vc}^d
PCL ^a	0.769	598	6364	1.052
PVC ^b	0.625	646	8172	—
PET ^c	1.031	465	7673	1.032

^a Taken from ref. 10.

^b Determined from P-V-T data of ref. 11.

^c Determined from P-V-T data of ref. 12.

^d Determined from Bondi's table.¹³

**Fig. 3.** Heats of mixing at 25°C for PCL/CPE blends as calculated by the Flory's EOS theory.

given Et volume fraction may be calculated from eq(5). Note that eq(5) must be divided by a factor, the reduced volume of the mixture at a given temperature, to calculate the heat of mixing per unit volume at that temperature. The X_{AB} value, for which the difference between the heat of mixing from the MGQ model and that from eq(5) shows minimum, is taken as the effective contact energy parameter of a given copolymer composition at 298 K.

Figure 3 was constructed with the X_{AB} values determined in this manner. It is comparable to Fig. 2 of reference 1. Figure 4 illustrates the

dependence of X_{AB} on the Et volume fraction. As expected, X_{AB} increases with decreasing the degree of chlorination. Similarly to B_{ij} , the segmental contact energy parameter X_{ij} can be calculated from curve fitting by use of eq(8) (or eq(11)). For comparison with the binary interaction model, eq (11) was used to the least square curve fitting. The obtained values are listed in Table 2. The value of -14.7 J/cm^3 for the contact pair of CL and VC units seems reasonable when compared with the results from the inverse gas chromatography.^{7,15} As shown in Table 2, the difference between B_{ij} and X_{ij} values is surprisingly small. This means that the free volume contribution to the heat of mixing is not large. Note that X_{ij} has a similar physical meaning to B_{ij} : the net change in cohesive energy densities upon mixing at the hard core state.

Figures 5 and 6 show that the predicted values for the characteristic parameters P^* and T^* for the CPE copolymer, as calculated from eqs(9) and (10), exhibit non-additive variations with the Et volume fraction. The negative deviation from additive is the result of the repulsion within the copoly-

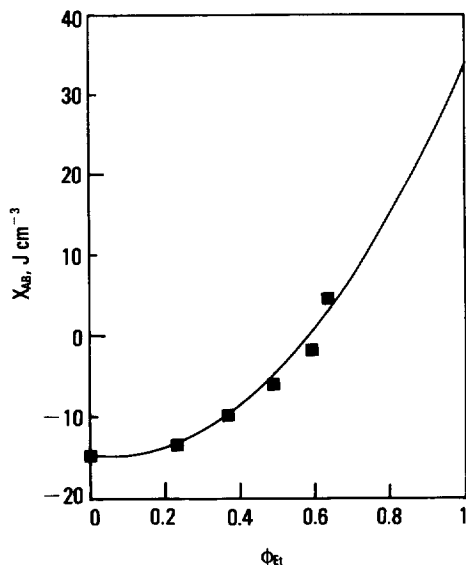


Fig. 4. The effective contact energy parameter X_{AB} as a function of the volume fraction of ethylene unit.

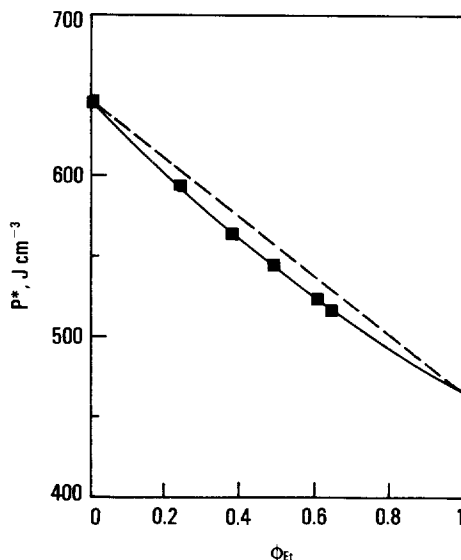


Fig. 5. Calculated characteristic pressures of CPE copolymers as a function of the volume fraction of ethylene unit. The dashed line represents the additive case.

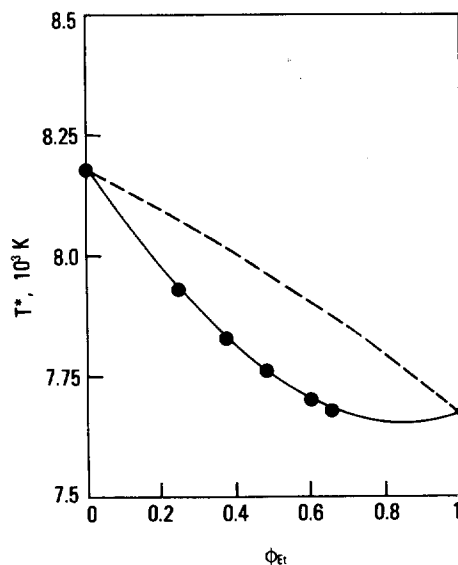


Fig. 6. Calculated characteristic temperatures of CPE copolymers as a function of the volume fraction of ethylene unit. The dashed line represents the additive case.

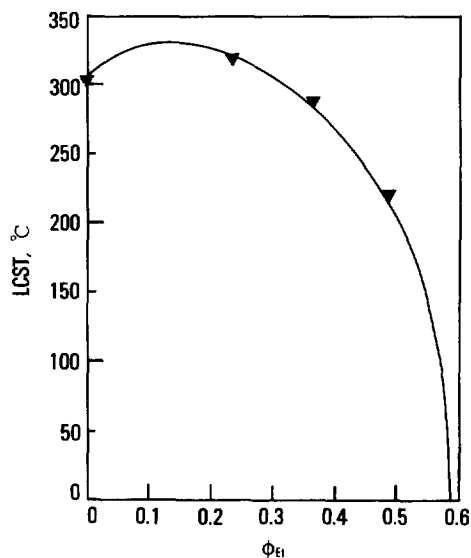


Fig. 7. Variation of the predicted LCSTs with the volume fraction of ethylene unit for PCL/CPE blends.

mer. It is noteworthy that the free volume term is proportional to the difference in the characteristic temperatures of components: the larger the difference is, the more positive the free volume term, thus, more unfavorable for mixing. Recalling that the characteristic temperature of PCL is 6364 K, it is expected that the free volume term decreases with increase of the Et units in the CPE copolymer, as shown in Figure 6. In the case of PCL/CPE blends, this effect seems to originate from both the comonomer (Et unit) having the lower characteristic temperature than that of PVC and the intramolecular repulsion between VC and Et units.

Figure 7 shows how the predicted LCST for PCL/CPE blends varies with the Et volume fraction. As the content of Et unit increases, the LCST first slightly increases, goes through a maximum, and then steeply decreases to such a low level that blends are never homogeneous. Defieuw et al.¹⁵ reported that CPE 49.1 is miscible with PCL over the entire composition and up to 180°C, while CPE 42.1 exhibits a temperature- and composition-dependent miscibility and the LCST of CPE 42.1/PCL

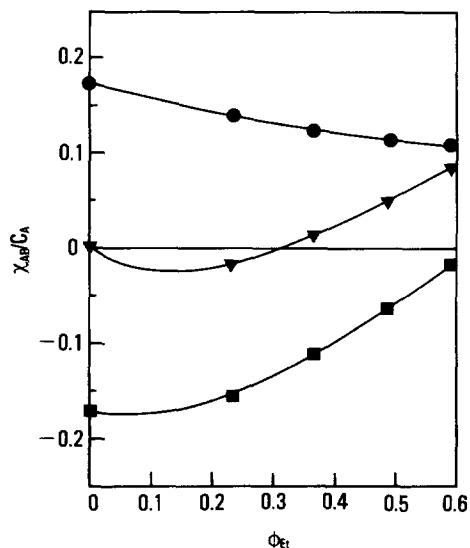


Fig. 8. Variations of the interactional(■) and free volume(●) contributions to χ_{AB} (▼) at 576K, the LCST of PCL/PVC.

blends is about 142°C. The difference of 7 wt% in the chlorine content causes a dramatic variation in the phase separation temperature. Their results agree well with the prediction of Figure 7 if one considers the assumptions involved in the calculation and the fact that the LCST may significantly vary for a small error in estimating the chlorine content. If we assume that the LCST reflects the interaction between components, an increase in the phase separation temperature upon incorporating comonomer into a component polymer of the miscible blend requires an increase in the strength of the interaction. According to the binary interaction model, this may result from the significant repulsion between the monomeric units in copolymer. However, Figure 2 does not show a minimum in the plot of copolymer composition vs. overall interaction energy density, although the LCST has a maximum at a given copolymer composition.

Figure 8 shows the dependence of χ_{AB}/C_A on the Et volume fraction at 576K (the LCST of PCL/PVC). As shown in Figure 8, the dependence of the χ_{AB}/C_A on the Et volume fraction is in good agreement with the variation of the LCST. It seems

that the interactional term is a dominant factor for controlling the phase behavior of these blends. This may result from the quadratic dependence of χ_{AB} on copolymer composition. However, although the free volume term is an adding factor, this term is important to make the χ_{AB}/C_A more negative, as compared with the case that neglects the variation of the free volume term with the copolymer composition.

CONCLUSIONS

In this work we have presented the theoretical prediction for the LCST behavior of PCL/CPE blends. It is based on the recently developed model for copolymer blends, which follows the Patterson's approach for the phase separation behavior of polymer blends. The effective contact energy parameter X_{AB} was calculated with the assumption that the heat of mixing calculated from the MGQ model is equivalent to that of the corresponding polymer blend. As expected, the magnitude of X_{AB} decreased with increasing the degree of chlorination.

One must consider the following aspects, which may affect the prediction of the LCST behavior : (a) In the calculation we have assumed X_{AB} to be temperature independent but experimental evidence shows that X_{AB} is more often dependent upon temperature.¹⁶ Therefore, the determination of X_{AB} from the heat of mixing measurement at a given temperature may not be the same as X_{AB} at relatively high temperatures near LCST. (b) We have neglected an entropic correction parameter due to interaction. However, when X_{AB} from the heats of mixing of oligomeric mixtures is used to predict the experimental spinodal, an entropic correction factor Q_{AB} should be introduced into the spinodal equation. This parameter does not affect the heat of mixing but the spinodal of polymer mixture is very sensitive to the variation of Q_{AB} . In

the presence of specific interactions between polymers, Q_{AB} should be negative, corresponding to an ordering of the component molecules by the interaction. As a result, both the effective X_{AB} and the LCST decrease.

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