

Poly(ϵ -caprolactone)과 Chlorinated Polyethylene 블렌드의 상거동에 관한 연구. 1. MGQ 모델에 의한 해석

이 무 성 · 이 호 상 · 조 원 호
서울대학교 섬유공학과
(1990년 7월 20일 접수)

The Phase Behavior of Poly(ϵ -caprolactone) and Chlorinated Polyethylenes Blends. 1. Application of the Modified Guggenheim Quasi-Chemical(MGQ) Model

Moo Sung Lee, Ho Sang Lee, and Won Ho Jo

Department of Textile Engineering, Seoul National University, Seoul 151-741, Korea

(Received July 20, 1990)

요약 : 최근에 소개된 MGQ 모델을 이용하여 poly(ϵ -caprolactone)(PCL)과 chlorinated polyethylene(CPE) 블렌드의 상용성을 해석하였다. PCL과 상용성을 갖기위한 CPE의 최소한의 이론적인 염소 함량은 약 30wt. % 정도였고 이 값은 이미 알려진 실험결과와 잘 일치하였다. Chlorination정도가 블렌드의 상용성에 미치는 효과는 Binary Interaction(BI) 모델을 이용하여 해석하였다. CPE의 CHCl 단위와 PCL의 CH₂COO 단위 사이에는 분자간 상호작용이 존재하며 이러한 상호작용이 블렌드의 상용성에 크게 영향을 미치고 또한 각 고분자를 구성하는 구조단위 사이에 존재하는 상호반발력 역시 상용성 영역의 확대에 기여하는 것으로 해석되었다.

Abstract : The miscibility of poly(ϵ -caprolactone)(PCL) and chlorinated polyethylenes(CPEs) was studied using the MGQ model. This model predicts that the critical chlorine content in CPEs for the mixture to be miscible is near 30 wt.%. The effect of the degree of chlorination on miscibility is interpreted in terms of the segmental interaction parameters B_{ij} estimated from the binary interaction (BI) model. It was found that intermolecular interactions between CHCl units in CPE and CH₂COO units PCL are attractive and favorable for mixing of these blends. The intramolecular repulsions between the units in each polymer are also important for miscibility and thus contribute to the broadening of the miscibility boundary.

INTRODUCTION

The Flory-Huggins lattice theory predicts that a prerequisite for miscibility of polymer blends is

the negative enthalpy of mixing, since the entropy gain upon mixing is negligibly small. In general, a favorable exothermic mixing has been obtained from two basically different concepts. First, many

miscible polymer blends are considered to be the result of the occurrence of attractive intermolecular interactions between constituents, that is, hydrogen bonding,^{1~3} ion-ion^{4~6} and ion-dipole^{7,8} interactions. Secondly, for blends containing copolymers, miscibility can be caused by an intramolecular repulsion between the segments comprising copolymers. This phenomenon is well interpreted by the binary interaction(BI) model,^{9~12} which is based on the Flory-Huggins lattice theory. According to this model, the overall interaction parameter B between the two polymers can be simply expressed in terms of respective segmental interaction parameters and copolymer composition.

The evaluation of interaction parameter between two polymers is very important for predicting the phase behavior of polymer blends. Several methods for estimating such a parameter have been proposed and reviewed in many books and papers.^{13~15} Each method has offered a number of advantages and disadvantages. For example, calorimetric measurements for analog mixtures give direct information about the heat of mixing, but the improper choice of analog compounds could give an inadequate modelling of interactions between the components.¹⁶

Lai et al.¹⁷ have recently formulated a Modified Guggenheim Quasi-Chemical(MGQ) model based on a group contribution method and described the effect of structure on the heat of mixing which could lead to a priori prediction of polymer miscibility. This model has successfully predicted the miscibility of various polymer mixtures.¹⁸

It has been known that poly(ϵ -caprolactone) (PCL)/poly(vinyl chloride)(PVC) blends are miscible due to a specific interaction between the methine hydrogen in PVC and the carbonyl group in PCL. Thus it is of interest to investigate the effect of chlorine content on miscibility of PCL/chlorinated polyethylene(CPE) blends. These blend systems have been studied by other authors,^{19,20} but the critical chlorine contents for the blend to be miscible with PCL have been reported differently.

In this study, we apply the MGQ model to PCL/CPE blends and calculate the heats of mixing as a function of chlorine content and the critical chlorine content for the blends to be miscible. Also, the effect of the degree of chlorination on miscibility will be discussed in terms of the BI model.

SUMMARY OF THE MGQ MODEL

The difference in interaction energies between the contact pairs in the mixture causes a nonrandomness in the distribution of interacting pairs. Guggenheim suggested a quasi-chemical model to describe the relationship between the numbers of various contact pairs.

$$(i-i) + (j-j) \xrightarrow{2\Delta E_{ij}} 2(i-j)$$

$$\frac{N_{ij}^2}{4N_{ii}N_{jj}} = \exp\left(-\frac{2\Delta E_{ij}}{kT}\right) \quad (1)$$

where $\Delta E_{ij} = E_{ij} - 1/2(E_{ii} + E_{jj})$ is the exchange energy on mixing and N_{ij} is the number of $i-j$ contact pairs.

While the MGQ model is derived in accordance with the Guggenheim's suggestion, two principal modifications are proposed to the simple Guggenheim's model: (1) Chemical equilibrium between $i-j$ contacts is described by a change in free energy ΔF_{ij} instead of potential energy ΔE_{ij} . This consideration has the effect of adding an additional parameter, A_{ij} , corresponding to the change in entropy associated with the interaction (eq.(2)).

$$\frac{N_{ij}^2}{4N_{ii}N_{jj}} = \exp\left(-\frac{2\Delta F_{ij}}{kT}\right) = A_{ij} \exp\left(-\frac{2\Delta E_{ij}}{kT}\right) \quad (2)$$

(2) The mixing occurs between the surface fractions of the structural groups rather than between volume fractions.

The expression for the heat of mixing is expressed as eq.(3).

$$\Delta H_{\text{mix}} = z \sum_i \sum_{j>i} \left[\sum_m q_m N_m \right] \Gamma_{ij} \Delta E_{ij} \Theta_i \Theta_j - z \sum_k \sum_i \sum_{j>i} \left[\sum_m q_m N_m^{(k)} \right] \Gamma_{ij}^{(k)} \Delta E_{ij} \Theta_i^{(k)} \Theta_j^{(k)} \quad (3)$$

In eq.(3), i, j , and m are counters for the structural groups in the mixture and k is the counter for pure components in the mixture; N_m and $N_m^{(k)}$ are the number of m groups in the mixture and in molecule k , respectively; q_m is the number of coordinating neighbors per unit surface area.

A nonrandomness factor Γ_{ij} for each $i-j$ pair are introduced to account for local nonrandomness in contact sites in non-athermal mixtures. Provided that MGQ parameters (ΔE_{ij} and A_{ij}) are known, Γ_{ij} can be evaluated from eq.(4).

$$\frac{\Gamma_{ij}^2}{\Gamma_{ii}\Gamma_{jj}} = \Delta F_{ij}, \quad \sum_i \Theta_i \Gamma_{ik} = 1.0 \quad (4)$$

$$\Gamma_{ij} = \Gamma_{ji}, \quad i, j = 1, 2; \quad k = 1, 2, 3$$

RESULTS AND DISCUSSION

The chemical structures of PCL and CPE are subdivided into small interacting units for applying a group contribution method as shown in Fig. 1. It is assumed that the chlorine distribution in CPE is uniform and the other chlorinated unit, i.e., CCl_2 unit is neglected. This assumption is probably valid for solution-CPE with a low degree of chlorination.²¹ Since the ratios of CHCl and CH_2 groups in CPE's are changed with the degree of chlorination, the repeat units of CPEs are considered as $(\text{CH}_2)_x \text{CHCl}$ where x is a function of the degree of chlorination.

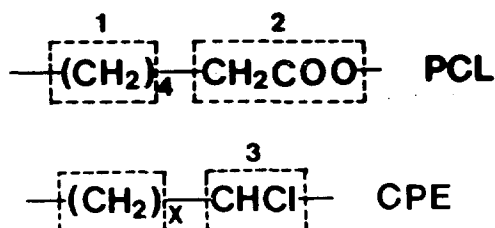


Fig. 1. Polymer repeat units and structural groups.

Tables 1 and 2 show repeat units and their molar volumes, and surface parameters of each structural group, respectively. The MGQ parameters which are estimated by fitting the MGQ models to the heat of mixing data for several liquid mixtures are listed in Table 3. The surface area fractions of each group Θ_i in the mixture, contact sites per unit volume S , and nonrandomness parameters Γ_{ij} between the $j-j$ pairs can be calculated from the given data according to eq.(4).

In Fig. 2, the heats of mixing of PCL/CPE blends with the degree of chlorination are plotted against the volume fraction of PCL. As shown in Fig. 2, the heats of mixing are changed unfavorably

Table 1. Repeat Units and Molar Volumes of Polymers Used for Calculation

Polymer Code	Repeat Unit	Molar Volume ^a cm ³ /mol
PCL	$-(\text{CH}_2)_5-\text{COO}-$	106.85
CPE25	$-(\text{CH}_2)_{6.67}-\text{CHCl}-$	137.97
CPE30	$-(\text{CH}_2)_{4.98}-\text{CHCl}-$	110.17
CPE36	$-(\text{CH}_2)_{3.57}-\text{CHCl}-$	86.98
CPE42	$-(\text{CH}_2)_{2.57}-\text{CHCl}-$	70.53
CPE48	$-(\text{CH}_2)_{1.81}-\text{CHCl}-$	58.02
PVC	$-\text{CH}_2-\text{CHCl}-$	44.70

^a reference 22

Table 2. Surface Parameters^a

Group	Surface area(Aw) cm ² /mol $\times 10^9$	q_i^b
CH_2	1.35	0.54
CH_2COO	3.55	1.42
CHCl	2.39	0.956

^a reference 23, ^b $q_i = \text{Aw}/2.5 \times 10^9$

Table 3. Summary of MGQ Parameters^a

Contact Pair	A_{ij}	ΔE_{ij} , cal/mol	ΔF_{ij}^b , cal/mol
$\text{CH}_2/\text{CH}_2\text{COO}$	1.000	137.4	0.6289
CH_2/CHCl	0.438	78.3	0.3363
$\text{CH}_2\text{COO}/\text{CHCl}$	2.14	-0.90	2.1465

^a reference 17, ^b at 298K

with decreasing the chlorine content and for CPE 30 ΔH_{mix} changes sign as the composition range is traversed. If $\Delta H_{\text{mix}}=0$ is a criterion for polymer miscibility, it is concluded that the critical chlorine content to be miscible with PCL is near 30 wt.%. This result agrees well with an experimental result¹⁹ that PCL is completely miscible with CPE's having a chlorine content higher than 30 wt.%.

The heats of mixing are used to estimate the interaction parameter B from a van Laar type expression for the heat of mixing.

$$\frac{\Delta H_{\text{mix}}}{V} = B\Phi_A\Phi_B \quad (5)$$

where Φ_A and Φ_B are volume fractions of PCL and CPE, respectively. As shown in Fig. 3, B values decrease with the increase of the chlorine

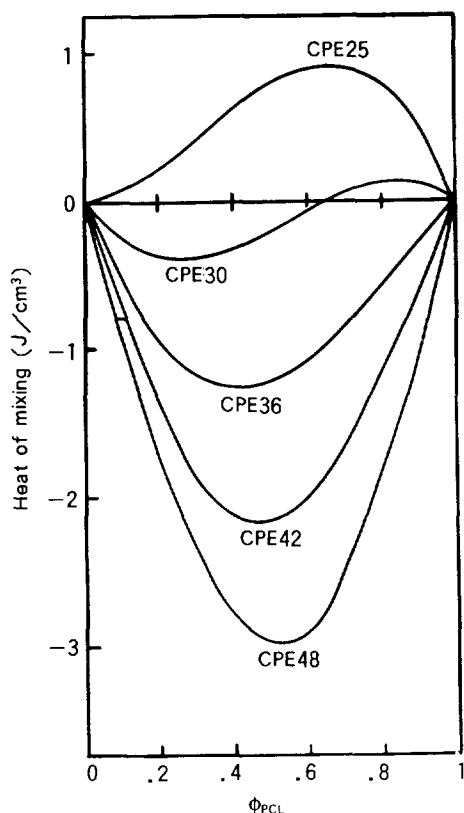


Fig. 2. Heats of mixing at 25°C for PCL/CPE blends calculated from the MGQ model.

content in CPEs. This result can be conveniently interpreted in terms of the ratio of the numbers of methylene unit to the number of CHCl unit in CPEs. PCL is miscible with CPE in which the CH_2/CHCl ratio is equal to or less than five, otherwise immiscible. It is noteworthy that the critical CH_2/CHCl ratio in CPE is almost the same as CH_2/COO ratios in PCL.

The effect of the chlorine content on miscibility can be rationalized by using the BI model. To apply the BI model for blends of two copolymers containing a common segment to the PCL/CPE blend system, the segments are identified as follows: 1= CH_2 , 2= CH_2COO , 3= CHCl . Therefore the overall B values is expressed in terms of segmental interaction parameter B_{ij} and copolymer composition (eq.(6)).

$$B = (0.384)^2 B_{12} + 0.384\phi_1(B_{23} - B_{12} - B_{13}) + \phi_1^2 B_{13} \quad (6)$$

where ϕ_1 is the volume fraction of CH_2 units in CPE, and 0.384 is the volume fraction of CH_2COO unit in PCL. Thus segmental B_{ij} values can be es-

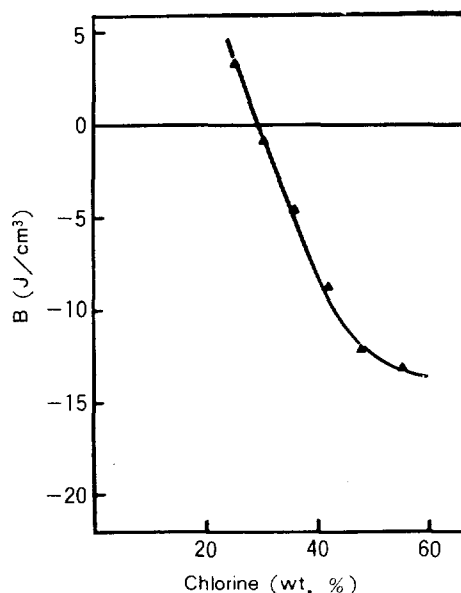


Fig. 3. Overall B parameters obtained from calculated heats of mixing data with the degree of chlorination.

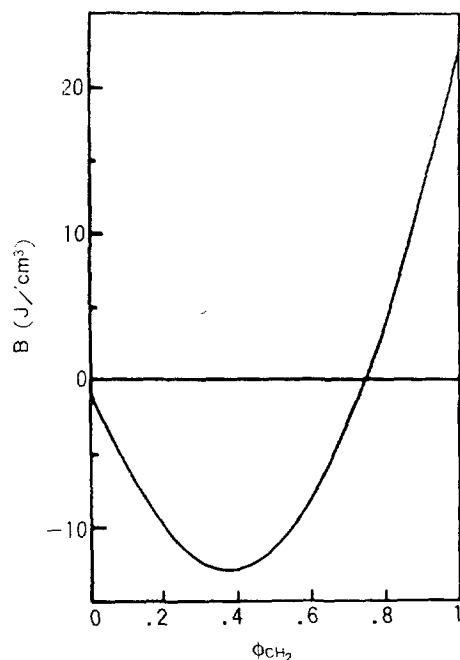


Fig. 4. Schematic representation of interaction parameter B as a function of volume fraction of CH_2 units in CPEs.

timated by fitting overall B 's into eq.(7). The obtained values are as follows :

$$\begin{aligned} B_{12} &= 156.1 \text{ J/cm}^3 \\ B_{13} &= 94.4 \text{ J/cm}^3 \\ B_{23} &= -52.8 \text{ J/cm}^3 \end{aligned}$$

Fig. 4 shows the dependence of overall B values on the volume fraction of CH_2 units in CPE, which are calculated from the obtained segmental interaction parameters. The negative B_{23} value indicates that the segmental interaction between CHCl and CH_2COO units is attractive and favorable for mixing of PCL/CPE blends.

Woo et al.²⁴ examined a series of blends of PVC and linear aliphatic polyesters having various CH_2/COO ratios in their repeat structures, which are composed of the same type interaction pairs as the PCL/CPE blends. In their study, three B_{ij} values, corresponding to CH_2/CHCl , CH_2/COO , and CHCl/COO interactions, were obtained from heats

of mixing of analogs and found to be all positive. Therefore, they concluded that there is a strong unfavorable intramolecular interaction between the CH_2 and COO units in aliphatic polyesters which is an important factor in their miscibility with PVC. On the contrary to Woo's expectation, it is clear from our result that a specific interaction between the CHCl and COO units is favorable for miscibility of the blends.

REFERENCES

1. O. Olabisi, *Macromolecules*, **8**, 316 (1975).
2. L. M. Robeson, W. F. Hale, and C. N. Merriam, *Macromolecules*, **14**, 1644 (1981).
3. E. J. Moskala, S. E. Howe, P. C. Painter, and M. M. Coleman, *Macromolecules*, **17**, 1671 (1984).
4. P. Smith and A. Eisenberg, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 223 (1983).
5. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 595 (1983).
6. M. Rutkowska and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
7. H. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
8. A. Eisenberg and M. Hara, *Polym. Eng. Sci.*, **24**, 1306 (1984).
9. R. P. Kambour, J. T. Bendler, and R. C. Bopp, *Macromolecules*, **16**, 753 (1983).
10. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
11. D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
12. T. Shiomi, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **19**, 2274 (1986).
13. O. Olabisi, L. M. Robeson, and M. T. Shaw, "Polymer-Polymer Miscibility", Academic Press, New York, 1979.
14. J. E. Harris, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **23**, 676 (1983).
15. D. J. Walsh and S. Rostami, *Adv. Polym. Sci.*, **70**, 119 (1985).
16. J. H. Kim, J. W. Barlow, and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 223 (1989).

17. C. H. Lai, D. R. Paul, and J. W. Barlow, *Macromolecules*, **21**, 2492 (1988).
18. C. H. Lai, D. R. Paul, and J. W. Barlow, *Macromolecules*, **22**, 374 (1989).
19. G. Belorgey and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 191 (1982).
20. G. Defieuw, G. Groeninckx, and H. Reynaers, *Polymer*, **30**, 595 (1989).
21. C. Zhikuan, S. Lianghe, and R. N. Sheppard, *Polymer*, **25**, 369 (1984).
22. D. W. Van Krevelen, "Properties of Polymers", Elsevier Scientific, Amsterdam, 1976.
23. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
24. E. M. Woo, J. W. Barlow, and D. R. Paul, *Polymer*, **26**, 763 (1985).