

ASPECTS OF THERMODYNAMICS OF POLYMER MIXTURES

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ABSTRACT

In this brief review article some aspects of the thermodynamics of polymer mixtures are discussed, mainly based on the author's research. The studies of poly (methyl methacrylate)/chlorinated polyethylene (CPE), poly (butyl acrylate)/CPE and CPE/CPE (different chlorine content) mixture verify the "dissimilarity" and "similarity" principles for predicting miscibility of polymer mixtures. The sign of heat of mixing of oligomeric analogues is not sufficient in predicting the miscibility. The Flory equation of state theory has been applied to simulate the phase boundaries of polymer mixtures. The empirical entropy parameter Q_{12} plays an important role in the calculation, this reduces the usefulness of the theory. With energy parameter $X_{12} \neq 0$ and $Q_{12} \neq 0$ the spinodals so calculated are reasonable compared to experiments. A hole model was suggested for the statistics of polymer mixtures. The new hole theory combines the features of both the Flory equation of state theory and the Sanchez lattice fluid theory and can be reduced to them under some conditions.

The study of thermodynamics of polymer-polymer mixtures is one of the most important fields for polymer blends. This study mainly deals with polymer miscibility in the molecular state of dispersion. It tells why the polymer could be mixed and under which conditions the polyblends are stable. It also predicts how the thermodynamic properties of blends change upon mixing. The knowledge from this study helps us to clarify some problems such as the morphology of two phase mixtures, the adhesion between phases, etc., which are of significance in technology. Therefore, the study lays a foundation for understanding the correlation among structure-property-application of polyblends and composites.

In this paper some aspects concerning the origin of miscibility, the application of the Flory equation of state theory and a hole model for polymer mixtures are discussed. It is a brief review of the author's research in recent years.

ORIGIN OF POLYMER MISCIBILITY

The origin of polymer miscibility is a question of considerable interest^[1-3]. Because of very small combinatory entropy (ΔS_{comb}), the principal factor normally operative in promoting mixing of small molecules is diminished. The remaining factors are the equation of state contribution and the interactions between components. Only when these two factors have a proper combination which results in not only a negative free energy of mixing but also a positive derivative of the chemical potential versus composition, the polymer mixtures are homogeneous and stable. These statements could be written as the following formulas:

$$\Delta G_m = \Delta H_m - T\Delta S_m = \Delta H_m - T(\Delta S_{comb} + \Delta S_{eq}) \cong \Delta H_m - T\Delta S_{eq} < 0 \quad (1)$$

$$(\partial\Delta\mu_1/\partial\varphi_1)_{T,P} > 0 \quad 2)$$

In Eq. 1 we should emphasize that the contribution of equation of state is not confined to the entropy $T\Delta S_{eq}$, through the reduced volume it also influences ΔH_m . ΔH_m is mainly due to the interactions in mixture.

It is generally recognized that specific interactions play a major role in determining the miscibility of polymer mixtures. As seen from Eq. 1, ΔH_m will usually be negative at this situation. But this does not mean that in some cases the equation of state contribution may not play an important role in miscibility behavior. The problem is how to find the condition under which the usually less important equation of state contribution becomes important. From Eq. 1 we see that if ΔH_m is near zero, $T\Delta S_{eq}$ is important in determining sign and magnitude of ΔG_m . We may meet this case when dispersion forces dominate in mixtures.

In practice the analysis leads to the so-called "similarity" and "dissimilarity" principles for choosing compatible polymer pairs. According to the "similarity" principle the matched polymer pair should have similar chemical structures, their interactions should be small and the equation of state properties should be similar, i.e. the pair should have nearly same thermal expansion coefficients. The "dissimilarity" principle argues for rather different chemical structures which allow the formation of specific interactions through the functional groups on the matched molecules. Since even weak positive dispersion force interactions are large enough to bring about phase separation, the "dissimilarity" principle should give the opportunity to identify a wider range of compatible polymer pairs.

We have, therefore, studied two groups of polyblends. One is poly (methyl methacrylate) (PMMA)/CPE^[4] and poly (butyl acrylate) (PBA)/CPE mixtures^[5], which are believed to have specific interactions between some functional groups; the others are the mixtures of CPEs with different chlorine content^[6], which should have no specific interactions. The low molecular weight analogues are also studied on purpose.

Investigation of the effect of chlorine content on the heats of mixing of oligomeric PMMA and chlorinated octadecane (COD) shows that there are two kinds of interactions in the mixtures. As

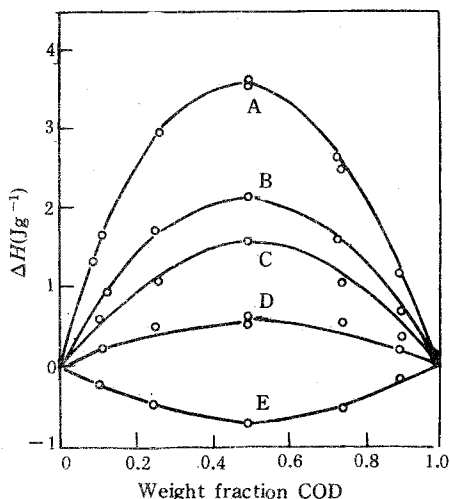


Fig. 1 Heats of mixing for oligomeric PMMA with COD plotted against weight fraction of COD

A = COD2(24.6%Cl), B = COD3(33.7%Cl), C = COD3A(34.9%Cl), D = COD4(43.2%Cl), E = COD5(52.9%Cl)

shown in Fig.1, with increasing chlorine content of COD the heats of mixing gradually decrease and change from endothermic to exothermic. The interaction energy parameter X_{12} so calculated were plotted in Fig. 2. X_{12} can be separated into two terms as discussed by Paul^[7].

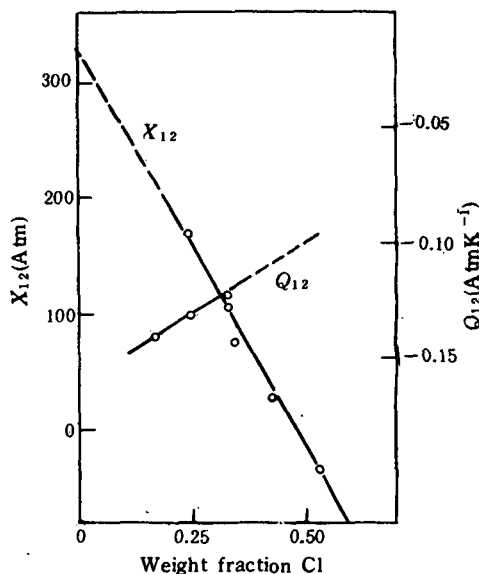


Fig. 2 Values of the interaction energy parameter X_{12} and the interaction entropy parameter Q_{12} for mixtures of oligomeric PMMA with COD against the percentage chlorine in COD

$$X_{12} = X_{12,dis} + w_{cl} X_{12,sp} \quad 3)$$

The second term is the specific interaction which is proportional to the chlorine content of COD, the first term is the dispersion force which is from the remaining parts of the structure. This analysis could be applied to the high molecular analogues, since they have the same structure of the repeat units. It is believed that the two kinds of interactions also exist in PMMA/CPE and PBA/CPE systems. It is found that only when the chlorine content of CPE reaches a certain value, where the specific interactions dominate in the mixture, is the miscibility possible. This value, obtained from observations of a series of mixtures with CPE containing 16.5-62.1 wt% of chlorine, is around 50 wt% of chlorine for PMMA/CPE system. Fig. 3 is a typical phase diagram of miscible pairs.

In the CPE/CPE system only the dispersion forces exist, because the heat of mixing of CODs is endothermic and only proportional to the difference of chlorine content between them. Their miscibility is determined by similarity of the equation of state properties of the pure components. In Fig. 4 the diagram is divided into four regions. In regions A and B the pairs of plastic/plastic and rubber/rubber (with similar expansion coefficient) are miscible. In region C the plastic does not mix with the rubber, while in region D two rubbers are not miscible because the difference in their thermal expansion coefficients or the dispersion force is too large. Fig. 5 shows the dynamic mechanical measurements for the blends of a miscible pair in region A, the pair has the largest difference of chlorine content in the region. Fig. 6 is the thermal expansion coefficients of CPEs. It is interesting to see that CPE4 and 8 have nearly equal thermal expansion coefficients, $-T\Delta S_{eq}$ so calculated is negative (-0.176J/g) which is favorable to mixing. But the moderate dispersion

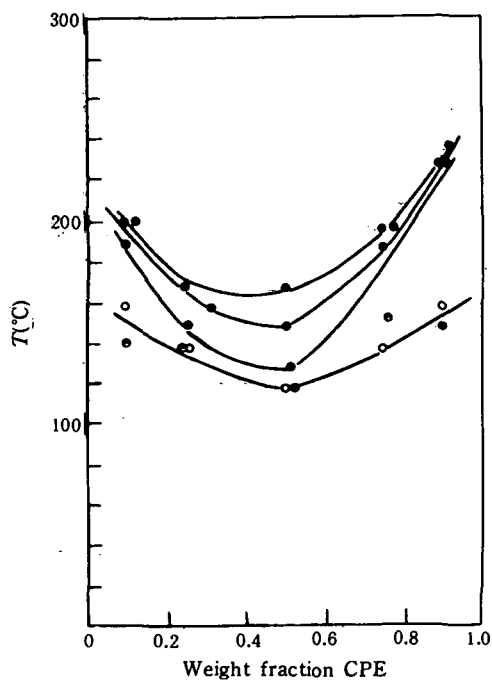


Fig. 3 Experimental phase boundaries for mixtures CPE16/PMMA

The molecular weight of PMMA: $\ominus$ 1.44×10^4 , $\oplus$ 4.88×10^4 , $\ominus$ 8.38×10^4 , $\odot$ 14.0×10^4 and $\bullet$ 26.4×10^4

62.1	49.8	48.0	45.6	44.7	44.1	36.9	35.7	27.4	24.5	22.4	21.0	16.5	W_{cl}
20	17	3	18	15	19	1	4	2	5	11	12	8	CPE(%)
-			-	-	-	+	+		+	+	+	+	20 62.1
	-		A		-	+	+		+				17 49.8
		-			-	+	+		+		C		3 48.0
			-	-	-	+	+			+	+	+	18 45.6
				-	-	+	+			+	+	+	15 44.7
					-	+	+	+	+	+	+	+	19 44.1
						-	-	+	+	+	+		1 36.9
							-	-	-	-	+	D	4 35.7
								-	B	-	-	+	2 27.4
									-	-	-	+	5 24.5
										-	-	+	11 22.4
											-	+	12 21.0
												-	8 16.5

Fig. 4 Compatibility among CPEs: - miscible, + immiscible

forces result in a ΔH_m of $+0.803\text{J/g}$. The resultant ΔG_m ($+0.627\text{J/g}$) leads to immiscibility of the pair.

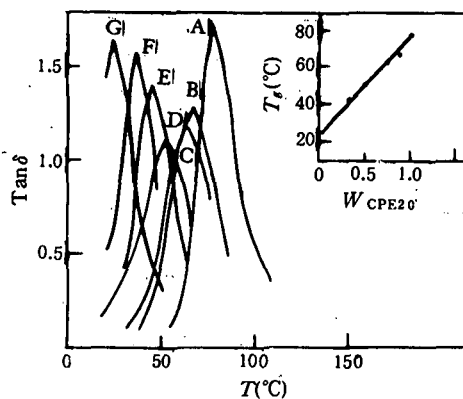


Fig. 5 Dynamic mechanical measurements for CPEs 19/20 blends

Curve A, CPE20; curves B-F, weight fractions of CPE 19: B, 0.1227, C, 0.2646, D, 0.5025, E, 0.7445, F, 0.8911; curve G, CPE19

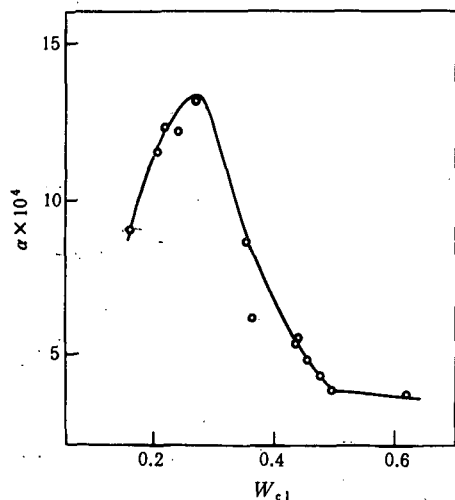


Fig. 6. The thermal expansion coefficient α as a function of chlorine content in CPE

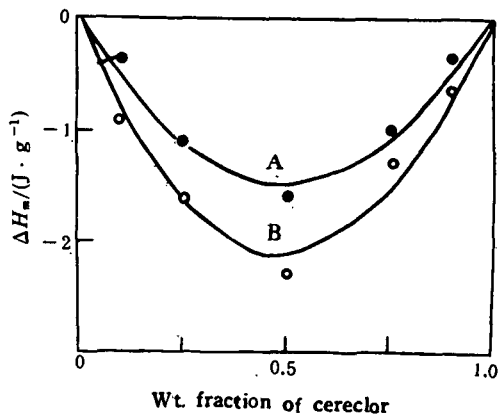


Fig. 7 Heats of mixing for PBA/cereclor at 70°C.

A, cereclor45, B, cereclor52

A strong exothermic heat of mixing of the oligomeric analogues usually predicts miscibility for the polymer mixture, but this is not always true. Similarly, a positive heat of mixing does not always result in immiscibility for polymer mixtures. As shown in Fig. 7, PBA/cereclor45 (45.7wt% Cl) has a negative heat of mixing whereas the corresponding PBA/CPE3 (48.0wt% Cl) is immiscible. Cereclor is a commercial product of chlorinated paraffin. All the COD/COD pairs have positive heat of mixing, but we still find two regions among the CPE/CPE blends in which all the polymer pairs are miscible.

APPLICATION OF THE FLORY EQUATION OF STATE THEORY

The Flory equation of state theory was first applied to the thermodynamics of polymer solutions. The analysis has been quite successful. Solution properties such as the excess volume,

the lower critical solution temperature (LCST) in some solutions, the interaction parameter χ in athermal solutions and the χ dependence on concentration could be derived directly from the theory. These properties could not be predicted by the Flory-Huggins lattice model theory.

The theory was adapted to the study of the miscibility of polymer mixtures. The thermodynamic mixing functions were calculated. The LCST behavior was predicted to be a common phenomenon in polymer blends. The dependence of phase boundaries on the molecular weight, the equation of state parameters, the interaction parameter and pressure, etc., were predicted.

There were some works^[8,9] discussing the irregular asymmetry when the Flory theory was used to simulate the phase boundaries of practical systems. The irregular asymmetry is a phenomenon where the miscibility gap including the upper critical solution temperature (UCST) and LCST is not located in the low molecular weight component-rich region. It is an opposite phenomenon to the regular asymmetry, which is a result of the contribution of the combinatory entropy of mixing. When (1) $X_{12} < 0$ and $s_1/s_2 < 1$ or (2) $c_{12} > 0$ and $m_1/m_2 < 1$ we could find the irregular asymmetry, where X_{12} is the interaction energy parameter, s_i is the surface area per unit volume of segment, c_{12} is used to revise c from the additive rule: the number of external degrees of freedom per segment in the mixture, $3c$, is determined by

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \phi_2 c_{12} \quad (4)$$

where c_i is the same parameter of component, and m_i is the mass per segment of component.

We have applied the Flory theory to simulate the phase boundaries of polymer and oligomer mixtures^[4-6,10]. The interaction energy parameter X_{12} obtained from the measured heat of mixing of oligomer pairs are used for polymers. By adjusting the interaction entropy parameter Q_{12} the spinodals are calculated to fit the experimental data.

It is found that Q_{12} plays an important role in the calculation. In the systems where there are the specific interactions, Q_{12} is negative which means that some ordered structure may exist in the mixture. In the systems where the dispersion forces dominate, Q_{12} is positive which indicates that some ordered structure may exist in the pure components or the mixture has a more random structure. Fig. 8 is the calculated spinodals for mixtures of CPE16 (51.6 wt% Cl)/PMMA. The parameters used in calculation are listed in Table 1. A negative value of Q_{12} decreases miscibility of the mixtures. Fig. 9 shows free energy of mixing ΔG_m vs. difference in chlorine content of mixed CPE polymers. Without introducing the positive empirical parameter Q_{12} , the Flory theory cannot generate a negative ΔG_m and hence fails to predict the observed miscibility of CPE/CPE mixtures. Although Q_{12} gives quite right physical meaning, the usefulness of the theory is reduced since Q_{12} as an empirical parameter was set arbitrarily. The similar conclusions about ordered structure were also reported for polymer solutions^[11].

Table 1 Parameters of CPE16/PMMA blend

	M_w	$d(\text{g}/\text{cm}^3)$ 30°C	α ($\times 10^4/\text{K}$)	γ (atm/K)	s_1/s_2	X_{12} (atm)	Q_{12} (atm/K)
1. CPE16	19.8×10^4	1.400	5.45	10.00	0.94	-30	-0.06
2. PMMA	*	1.200	5.74	11.56			

* M_w of PMMA are A. 1.44×10^4 , B. 4.88×10^4 , and C. 26.4×10^4 , respectively.

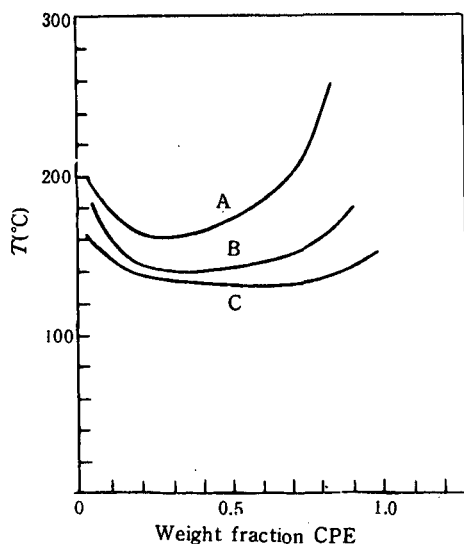


Fig. 8 Simulated spinodals for mixtures of CPE16/PMMA

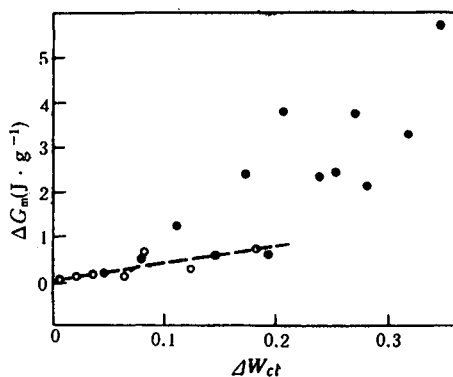


Fig. 9 ΔG_m vs. difference in chlorine contents of mixed CPE polymers ● immiscible, ○ miscible

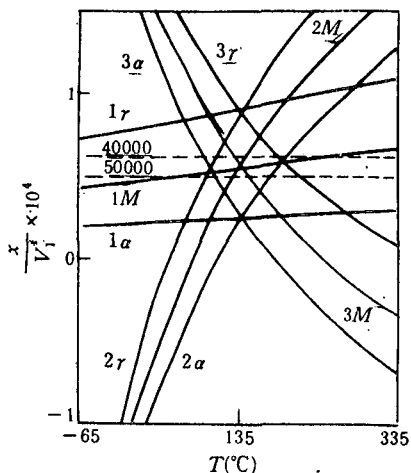


Fig. 10 Temperature dependence of the interaction parameter χ .

The dotted lines are the critical values when both components having the same molecular weight as denoted

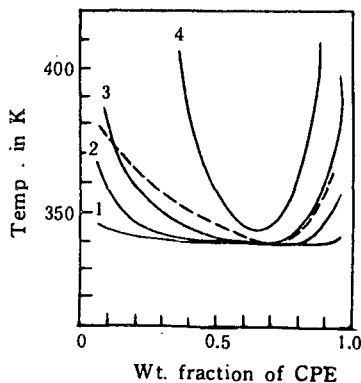


Fig. 11 Spinodals calculated using different values of X_{12} and Q_{12} for PBA/CPE17 blends
1, $X_{12} = -94$, $Q_{12} = -0.235$; 2, $X_{12} = -30$, $Q_{12} = -0.076$; 3, $X_{12} = -10$, $Q_{12} = -0.026$; 4, $X_{12} = -1$, $Q_{12} = -0.0034$ (X_{12} in atm, Q_{12} in atm/K). The dashed line follows the experimental results.

The previous work^[2] exaggerated the influence of molecular weight and the equation of state parameters upon phase diagram and predicted a narrow concentration region for phase separation on the assumption that $X_{12} = 0$ and $Q_{12} = 0$. For practical systems $X_{12} \neq 0$ and $Q_{12} \neq 0$, the influence of these factors upon phase diagram and the shape of phase diagram will be predicted to be reasonable as compared with experiment^[12]. Fig. 10 shows the temperature dependence of

Flory-Huggins' parameter χ . The dotted line is the critical value χ_c . The cross point of χ with χ_c is the critical point, above which phase separation appears. We can see that at $X_{12} = 0$ and $Q_{12} = 0$ a little change of the thermal expansion coefficient (difference of two components from 10% to 7%) or the thermal pressure coefficient (from 0 to 50%) moves curve 1 from 1M to 1 α or 1 γ . This will change miscibility greatly. Changing the molecular weights of the pair from 5×10^4 to 4×10^4 will move LCST up at about 200°C. At $X_{12} \neq 0$ and $Q_{12} \neq 0$ curves 2 and 3 have much larger slopes, which result in a little influence of α , γ and M_w upon miscibility. Fig. 11 is the spinodals calculated using different values of X_{12} and Q_{12} . We see that although various combinations of X_{12} and Q_{12} give a proper LCST, but the shape of spinodal is quite different. With large negative values of X_{12} and Q_{12} the spinodals are flat-bottomed, while with small negative X_{12} and Q_{12} the spinodals have more curvature. At $X_{12} = 0$ and $Q_{12} = 0$ the spinodal is located at very narrow concentration region. With a proper combination of X_{12} and Q_{12} the calculated spinodal will have a reasonable fit with experiment.

A HOLE MODEL OF POLYMER MIXTURES

Up to now the three most important theories of statistical thermodynamics of polymer mixtures (including solutions and blends) are the Flory-Huggins theory, the Flory equation of state theory and the Sanchez lattice fluid theory. The Flory-Huggins theory is based on a lattice model^[13]. It explained the extraordinary large entropy of mixing of polymeric molecules with solvent firstly in history and, therefore, laid the foundation of science of polymer solutions. The Flory equation of state theory is mainly based on a cell model^[14]. The appearance of the theory is a breakthrough. We have talked its applications at the beginning of the above paragraph. In 1974 Sanchez began to develop a theory which is based on a lattice fluid model^[15]. Besides polymer miscibility, the Sanchez theory successfully described liquid-vapour phase transitions of mixtures of low molecular weight compounds. The later two theories can be reduced to the Flory-Huggins theory under some conditions.

Inspecting the models used in the above theories reminds us of the hole model, which is also widely used in the statistics of liquids. The features of the four models are concisely shown in Fig. 12. In a lattice model a small molecule or a segment of a high molecule occupies a whole site of the

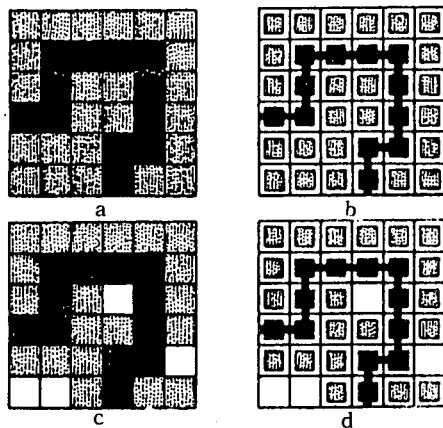


Fig. 12 Models for polymer mixtures

a, lattice model; b, cell model; c, lattice fluid; and d, hole model

lattice, the liquid is incompressible, its volume obeys an additive rule during mixing. Although linked together, the segments of a high molecule have innumerable configurations, this gives the chain molecule flexibility. In a cell model a small molecule or a segment does not occupy a whole site but forms a core in it. The site is now called as the cell. The core can move freely in the cell. The space where the center of gravity of core reaches is defined as free volume. Owing to existence of the free volume liquids no longer obey the additive rule for the total volume of mixture. By introducing vacant sites (holes) into the above two models we obtain the lattice fluid and the hole model. The holes do not only make liquid compressible but also increase its entropy. Through increasing number of holes the transition from liquid to vapour phase becomes continuous. Obviously, the cell and the lattice fluid models are the developments of the lattice model, and the hole model combines some features of both developed models.

The hole model was already introduced into polymer science by Simha,^[16] Nose^[17] for discussing the thermal and glass transition properties of pure polymers. We have used this model to deal with the thermodynamics of polymer mixtures. Based on the analysis of features of models the relation among the new hole theory, the Flory equation of state theory and the Sanchez lattice fluid theory was explored.

In the hole model the configurational partition function of a pure polymeric liquid could be written as^[18]

$$Z(T, P) = \text{const}(1/f_0)^{N_0} (\omega/f)^N (v_f^{\frac{1}{3}})^{3crN} \exp[-(E + PV)/kT] \quad (5)$$

If the first two terms are omitted the remaining parts are the partition function of the Flory theory. If the v_f term is omitted we have Sanchez' partition function. It is assumed that a lattice is occupied by N r-mers and N_0 vacant sites.

$$f_0 = N_0/(N_0 + rN), f = rN/(N_0 + rN) \quad (6)$$

ω is the number of configurations available to a r-mer in the close-packed pure state. v_f is the free volume. c , introduced by Prigogine,^[19] was defined in Eq. 4. $0 < c \leq 1$. E , P , V , T are energy, pressure, volume and temperature of the system. k is the Boltzmann constant.

In the hole model the reduced volume $\bar{v}$ is a function of the reduced cell volume $\bar{w}$ and the fraction of empty sites f_0 .

$$\bar{v} = v/v^* = \bar{w}/f = 1/\bar{\rho}, \quad \bar{w} = w/v^* \quad (7)$$

where v is the specific volume, v^* the core volume and w the cell volume. Because we do not know the functional relation between $\bar{w}$ and f , when discussing the volume change we used to assume one of $\bar{w}$ and f constant.

In this way we have the following two sets of equation of state:

(1) At constant f_0 , when the change of volume $\bar{v}$ is due to the change of the size of cell $\bar{w}$, the equation of state is

$$\bar{\rho}^2 + \bar{P} - \bar{T}f/(\bar{w} - f\bar{w}^2) = 0 \quad (8)$$

where $\bar{P}$ and $\bar{T}$ are the reduced pressure and temperature. $\bar{P} = P/P^*$, $\bar{T} = T/T^*$. $P^* = \varepsilon^*/v^*$ and $T^* = \varepsilon^*/ck$. $-\varepsilon^*$ is the interaction energy of a segment when surrounded by the nearest neighbour segments in the close-packed configuration.

At $f_0 = 0$ Eq. 8 becomes

$$\bar{\rho}^2 + \bar{P} - \bar{T}/(\bar{v} - \bar{v}^3) = 0 \quad (9)$$

Eq. 9 is Flory's equation of state.

(2) At constant $\bar{w}$, when the change of volume is due to the change of the number of holes f_0 , the equation of state is

$$\bar{\rho}^2 + \bar{P} + (\bar{T}/c)[(1/\bar{w})\ln f_0 + \bar{\rho}(1 - 1/r)] - 3\bar{T}\bar{\rho}f/(\bar{w}^3 - f) = 0 \quad (10)$$

At $\bar{w} = 0$, $\bar{T} \ll 1$, and after redefining a characteristic parameter $T^* = \epsilon^*/k$, Eq. 10 becomes

$$\bar{\rho}^2 + \bar{P} + \bar{T}[\ln f_0 + \bar{\rho}(1 - 1/r)] = 0 \quad (11)$$

Eq. 11 is the Sanchez equation of state.

For a binary mixture one more term $(\omega_i/f_i)^{N_i}$ is put in Eq. 5, the partition function of pure component. Assume $v_1^* = v_2^* = v^*$ for simplifying derivation, the chemical potential could be derived as

$$\begin{aligned} \mu_1 = kT[\ln \varphi_1 + (1 - r_1/r_2)\varphi_2 + r_1\bar{\rho}\chi\varphi_2^2] \\ + r_1\epsilon_{11}^*\{-\bar{\rho} + \bar{P}_1\bar{v} + (\bar{T}_1/c_1)[(f_0/f)\ln f_0 + (1/r_1)\ln(f/\omega_1)] - 3\bar{T}_1\ln(\bar{w}^3 - fv^{\frac{1}{3}})\} \end{aligned} \quad (12)$$

where φ_i is the segment fraction. Let $\varphi_1 = 1$, μ_1^0 results from Eq. 12. At $f_0 = 0$, we have

$$\begin{aligned} \mu_1 - \mu_1^0 = kT[\ln \varphi_1 + (1 - r_1/r_2)\varphi_2 + r_1\bar{\rho}\chi\varphi_2^2] \\ + r_1\epsilon_{11}^*\{\bar{\rho}_1 - \bar{\rho} + \bar{P}_1(\bar{v} - \bar{v}_1) + 3\bar{T}_1\ln[(\bar{v}_1^{\frac{1}{3}} - 1)/(\bar{v}^{\frac{1}{3}} - 1)]\} \end{aligned} \quad (13)$$

Eq. 13 is the chemical potential of the Flory theory. At $\bar{w} = 1$, $\bar{T}_1 \ll 1$, and redefine $T^* = \epsilon^*/k$, Eq. 12 can be rewritten as

$$\begin{aligned} \mu_1 = kT[\ln \varphi_1 + (1 - r_1/r_2)\varphi_2 + r_1\bar{\rho}\chi\varphi_2^2] \\ + r_1kT_1^*\{-\bar{\rho} + \bar{P}_1\bar{v} + \bar{T}_1[(\bar{v} - 1)\ln(1 - \bar{\rho}) + (1/r_1)\ln(\bar{\rho}/\omega_1)]\} \end{aligned} \quad (14)$$

Eq. 14 is the formula of the Sanchez theory.

From the chemical potential we obtain the spinodal as

$$(1/r_1\varphi_1) + (1/r_2\varphi_2) = \bar{\rho}(2\chi + \bar{T}\psi^2 P^*\beta/c) \quad (15)$$

where β is the isothermal compressibility of the mixture,

$$\beta = -(1/V)(\partial V/\partial P)_T = (\partial \ln \bar{v}/\partial P)_T \quad (16)$$

Since the equation of state is used in the derivation, we have to express ψ and β according to the two simplified conditions as we did before.

(1) If the mixture keeps a constant f_0 when $\bar{v}$ changes,

$$\psi = -\bar{\rho}\lambda_{12} + (c_1 - c_2)\bar{w}^{\frac{1}{3}}/(\bar{w}^3 - f) \quad (17)$$

$$P^*\beta = \{- (2/\bar{v}^2) + 2\bar{T}\bar{w}^{\frac{1}{3}}/[3\bar{v}(\bar{w}^3 - f)] + \bar{T}\bar{w}^{\frac{2}{3}}/[3\bar{v}(\bar{w}^3 - f)^2]\}^{-1} \quad (18)$$

where

$$\lambda_{12} = \partial(\epsilon^*/kT)/\partial \varphi_1 = (1/\bar{T}_1) - (1/\bar{T}_2) + (\varphi_1 - \varphi_2)\chi \quad (19)$$

At $f_0 = 0$ the two equations become

$$\psi = -\bar{\rho}\lambda_{12} + (c_1 - c_2)/(1 - \bar{\rho}^{\frac{1}{3}}) \quad (20)$$

$$P^*\beta = \{-(2/\bar{v}^2) + 2\bar{T}/[3\bar{v}(1 - \bar{\rho}^{1/3})] + \bar{T}/[3\bar{v}(1 - \bar{\rho}^{1/3})^2]\}^{-1} \quad (21)$$

This is the result of the Flory theory.

(2) If the mixture has a constant $\bar{w}$ when $\bar{v}$ changes,

$$\psi = (1/r_1 - 1/r_2) - \bar{\rho}\lambda_{12} + 3(c_1 - c_2)f/(\bar{w}^{1/3} - f) \quad (22)$$

$$P^*\beta = \{-(2/\bar{v}^2) + (\bar{T}/c)[1/(f_0\bar{v}) - (1 - 1/r)/\bar{v}] + 3\bar{T}f/[\bar{v}(\bar{w}^{1/3} - f)] + 3\bar{T}\bar{w}^{4/3}/[\bar{v}^2(\bar{w}^{1/3} - f)^2]\}^{-1} \quad (23)$$

At $\bar{w} = 1$, $\bar{T} \ll 1$ and redefine $T^* = \epsilon^*/k$,

$$\psi = (1/r_1 - 1/r_2) - \bar{\rho}\lambda_{12} \quad (24)$$

$$P^*\beta = \{-(2/\bar{v}^2) + (\bar{T}/\bar{v})[1/(\bar{v} - 1) + 1/r]\}^{-1} \quad (25)$$

Eqs. 24 and 25 are Sanchez' formulas.

The effect of equation of state to stability of mixture is confirmed. This means that the Flory and Sanchez theories make different estimations for miscibility of polymer blends is understandable^[20]. The practical blends are more complicated, their miscibility should be in between the predictions of the two theories.

Keywords:

Thermodynamics; Polymer mixtures; Equation of state theory; Hole theory

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