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Statistical Thermodynamics Evaluation of Polymer–Polymer Miscibility

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ABSTRACT: The Simha and Somcynsky (S–S) statistical thermodynamics theory was used to compute the solubility parameters as a function of temperature and pressure [$\delta = \delta(T, P)$], for a series of polymer melts. The characteristic scaling parameters required for this task, P^* , T^* , and V^* , were extracted from the pressure–temperature–volume (PVT) data. To determine the potential polymer–polymer miscibility, the dependence of δ versus T (at ambient pressure) was computed for 17 polymers. Close proximity of the δ versus T curves for four miscible polymer pairs: PPE/PS, PS/PVME, and PC/PMMA signaled the usefulness of this approach. It is noteworthy, that the tabulated solubility parameters (derived from the solution data under ambient conditions) propounded the immiscibility of the PVC/PVAc pair. The computed values of δ also suggested miscibility for polymer pairs of unknown miscibility, namely PPE/PVC, PPE/PVAc, and PET/PSF. In recognizing the limitations of the solubility parameter approach (the omission of several thermodynamic contributions), these preliminary results are auspicious because they indicate a new route for estimating the miscibility of any polymeric material at a given temperature and pressure. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 42: 2909–2915, 2004

Keywords: cohesive energy; solubility parameter; lattice models; statistical thermodynamics; theory (Simha–Somcynsky); free volume; equation of state; corresponding states; miscibility (polymer–polymer)

INTRODUCTION

The solubility parameter (δ) is a measure of the internal energy per unit volume (U/V), also known as the cohesive energy density (CED):

$$\delta = \sqrt{U/V} = \sqrt{\text{CED}} \quad (1)$$

The experimental values of δ for polymers are estimated from the polymer behavior in solutions under ambient conditions (pressure (P) = 0.10132

MPa, temperature (T) = 25 to 35°C) with solvents of known δ -values; Grulke^{1,2} lists several determination methods for these values. As a consequence, δ -values are usually cited at $T = 25^\circ\text{C}$ and, depending on the type of solvent and the method of determination, they may vary widely³ e.g., for PVEE, $\delta = 14$ –30, for EC, $\delta = 16$ –30, for PVME, $\delta = 15$ –23, for PMMA $\delta = 18$ –26, for PEG $\delta = 18$ –30, and so on. The effects of P have been neglected.

For polymers, representation of the specific internal energy such as this is questionable because the intensive thermodynamic property of a substance should have a unique value. Furthermore, while the use of the ambient conditions for low molecular weight liquids⁴ is rea-

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sonable, this not the case for polymers; at $T = 25\text{--}35^\circ\text{C}$ most of them are not close to a liquid state.

Recently, it has been shown⁵ that δ -values for polymers, as cited in the literature,^{1,2,3} are systematically lower than those computed from the statistical thermodynamics theory of Simha and Somcynsky (S-S).⁶ To obtain numerical equivalence between these two sets of parameters, the computation of δ had to be carried out for $T \cong T_g + 300^\circ\text{C}$ rather than $T = 25^\circ\text{C}$. It is noteworthy that, in agreement with van der Waals, the S-S theory predicts that the internal energy is inversely proportional to the specific volume, $U \propto 1/V$. Furthermore, as shown in Figure 1, the reduced values of $\tilde{U}$ linearly decrease with the free volume parameter (h) with CED and δ showing even stronger dependence on h .

The polymer free volume depends on the principal independent variables (P and T), as well as on additives; it was shown⁵ that numerically, the value of h increased upon heating to $T_g + 300^\circ\text{C}$, and upon dissolution is about the same value. Thus, the values of the solubility parameters that are listed in standard tables significantly underestimate the internal energy in molten polymers. As a consequence, the δ -values computed from the PVT behavior in the melt should provide more realistic information on the internal energy, hence, on the potential polymer–polymer miscibility.

Figure 1. Isobaric ($P = 0.10132\text{ MPa}$) and isothermal ($T = 200^\circ\text{C}$) plot of the reduced internal energy, U/P^*V^* , and reduced cohesive energy density, CED/P^* , versus the free volume parameter, h , for a series of 38 molten polymers examined recently.

In the thermodynamic description of polymer blend miscibility, it has been noted that the combinatorial entropy contribution (e.g., as given by Huggins or by Flory) is vanishingly small. Several authors argued^{7–12} that miscibility depends on the noncombinatorial effects embedded in the binary interaction parameter: $\chi = \chi_h + \chi_s \leq 0$, that is; with the enthalpic and entropic contributions. Thus, minimization of the enthalpic contribution gives:⁴

$$\chi_h \cong \Delta U_m / (V\phi_i\phi_j) = (\delta_i - \delta_j)^2 \quad (2)$$

(i.e., $\delta_1 \rightarrow \delta_2$) that might provide the necessary (but not necessarily sufficient) condition for miscibility.

Hansen^{10,11} noted that all interactions may be grouped into three classes and wrote: $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, where subscripts d , p , and h refer to the dispersive, polar, and hydrogen bonding forces. Accordingly, the semi-empirical condition for miscibility is given as:

$$\Delta^2 \equiv \Delta U_m / (V\phi_i\phi_j) = (\delta_i - \delta_j)_d^2 + (\delta_i - \delta_j)_p^2 + (\delta_i - \delta_j)_h^2 \geq 0 \quad (3)$$

This approach has been highly successful for predicting the miscibility of low-molecular-weight substances as well as the miscibility of solutions such as, paints, adhesives, and so on. The approximate temperature gradients of the three contributions in eq 3 depend on the substance; Hansen expressed these in terms of the thermal expansion coefficient, $\alpha \equiv (\partial \ln V / \partial T)_P$ as:

$$\begin{aligned} (\partial \ln \delta_i / \partial T)_{P \rightarrow 0} &= -1.25\alpha; = -\alpha/2; \\ &\approx -1.85\alpha; \text{ for: } i = d, p, h \end{aligned} \quad (4)$$

The purpose of this article is to examine the applicability of the computed solubility parameters for predicting the polymer/polymer miscibility. If it is successful, the procedure would offer several advantages: (1) the computed solubility parameter (δ) represents the internal energy, unaffected by the specific interactions with different solvents; it is a true intensive thermodynamic quantity; (2) δ may be computed at any T and P of interest; (3) In contrast with a need to measure polymer solution properties in dozens of solvents, the new approach requires a single PVT test, thus, it offers substantial savings in labor and material costs; and (4) most industrial polymers

are precompounded with a host of additives that affect the internal energy, hence, the miscibility. A simple PVT test would eliminate the ambiguity of the thermodynamic behavior introduced by the unknown set of additives.

Simha-Somcynsky Equation of State and Configurational Internal Energy

The lattice-hole theory in the original formulation by S-S⁶ has proven quantitatively successful in its application to the configurational thermodynamics of single and multiconstituent melts.¹³ An important contribution of the theory is the inclusion of the volume and the temperature-dependent hole fraction [$h = h(V, T)$]; which is a measure of the free volume. In addition to entering into the thermodynamic functions, h also serves as a link to the surface tension,¹⁴ the constant stress viscosity,¹⁵ the kinetics of volume relaxation,¹⁶ and so forth. The connection of h with the results of positronium annihilation spectroscopy has also been demonstrated.¹⁷

The S-S theory is written in terms of scaled variables of state: $\tilde{P} = P / P^*$; $\tilde{T} = T / T^*$; $\tilde{V} = V / V^*$, where the characteristic scaling parameters are: $P^* = zq\epsilon^* / s\nu^*$; $T^* = zq\epsilon^* / Rc$; $V^* = \nu^* / M_o$. Here, s is the number of segments per macromolecule having $3c$ external degrees of freedom, M_o is the segmental molar mass (M/s), and ν^* and ϵ^* are the characteristic repulsion volume and the attraction energy per segment, respectively. The most frequently used form of the theory is the equation of state (eos).⁶ In addition, the theory provides an expression for the cohesive energy density⁶ and the solubility parameter:

$$\tilde{U} \equiv U/P^*V^* = - (1/2)y(y\tilde{V})^{-2}[2.409 - 1.011(y\tilde{V})^{-2}] \quad (5)$$

$$C\tilde{E}D = \tilde{U}/\tilde{V}; \text{ and } \delta^2 = CED = C\tilde{E}D \times P^*$$

To determine the scaling parameters, the experimental PVT data were fitted to the coupled eos relations⁶ using the MicroMath *Scientist*^{TM} program. Next, using the determined P^* , T^* , and V^* values, the δ of a liquid was computed from eq 5 at any desired T and P .

Calculations

The S-S theory predicts that the solubility parameter (in reduced variables), $\tilde{\delta} = \tilde{\delta}(\tilde{P}, \tilde{T})$ (see

Figure 1 in ref. ⁵) steeply decreases with the $\tilde{T}$ and mildly increases with the $\tilde{P}$. The strongest decrease of δ with T is at the lowest (i.e., ambient) pressure.¹⁸ $(\partial\delta/\partial T)_{P \rightarrow 0} \approx -0.0440$, thus, about twice as large as that calculated from eqs 3 and 4.

To compute the δ -values, the P^* , T^* , and V^* parameters were taken from Rodgers¹³ and Zoller and Walsh¹⁹ and, in addition, were determined by Utracki and Simha.⁵ The ambient pressure values of δ were computed at several temperatures and were compared to the solubility parameter values listed in the Polymer Handbook^{1,2} (see Table 1 in ref. ⁵). The δ -values from the Handbooks were found to be systematically smaller than those computed for 25 °C: $\delta_{\text{list}} \approx \delta_{25} - 8 (\pm 4 \text{ MPa}^{1/2})$. In contrast, when the internal temperature ($T_g + 300$) was used, $\delta_{\text{list}} \approx \delta_{T_g+300} \pm 2 \text{ MPa}^{1/2}$. The difference between δ_{25} and δ_{T_g+300} originates in the free volume content; heating from 25 to $T_g + 300$ °C increases the free volume by an amount comparable to that introduced by dissolution.⁵

Polymer/Polymer Miscibility

Once the polymer solubility parameters are calculated, their usefulness for miscibility examination should be tested. Since mixing/blending is carried out at a specific temperature ($T > T_g$) a new set of δ_T had to be computed for $T = 100$ to 300 °C, i.e., within the molten range for most polymers. The computed values of δ_T versus T for 17 polymers are displayed in Figure 2. Confirming expectations, the resins with δ_T that are far apart (e.g., PDMS, PTFE, or PA-66) are known to be immiscible with the other polymers, while the six encircled systems with close δ_T -values (see Table 1) are known, or expected to be miscible.²⁰ Thus, the computed values of δ_T agree qualitatively, with the experimental observations.

It is evident, however, that this simple approach neglects other contributions controlling the miscibility, for example, the eos and nonrandom mixing contributions to the free energy of mixing,²¹ thus it is unable to account for the finer miscibility effects. For example, PC/PMMA blends are miscible at $T < \text{LCST} \approx 140$ °C, and immiscible above 140°C, but Figure 2 does not suggest any phase change.

To better examine the potential miscibility of the six encircled systems, we can look at the values of δ_T at $T = 200$ °C that are listed in Table 1. Considering the small differences in the temperature gradient in Figure 2, the conclusions drawn

Figure 2. Isobaric ($P = 0.10132$ MPa) solubility parameter versus T for 17 polymers. Circles indicate the six pairs of polymers where miscibility is suspected. The polymer codes: PA-6 is poly-ε-caprolactam; PA66 is polyhexamethylene-adipamide; PDMS is polydimethylsiloxane; the others are listed in Table 1.

for $T = 200$ °C should also be applicable to other temperatures within the $T = 100$ to 300 °C range. For comparison, Table 1 also gives the δ_{list} -values from the Handbooks, as well as the differences within each of these two groups ($\Delta\delta_T$ and $\Delta\delta_{list}$). The mixtures #2, #3, and #4 are known to be miscible within a certain temperature range.

The computed difference $\Delta\delta_T \leq 0.88$ (for PPE/PS) may be taken as the necessary condition for miscibility. However, according to it, the systems PET/PSF (#1), PPE/PVC, and PPE/PVAc (#3) should also be miscible. The commercial PET/PSF blend, *Mindel B*, showed only signs of miscibility, but the PSF used in it may be chemically different from the one Zoller²² used (Union Carbide

P-1700) in the PVT tests. The other two potentially miscible blends of PPE have not been investigated because of the low thermal stability of PVC and PVAc. Similarly, information on the miscibility of mixtures #5 and #6 is missing. It is noteworthy that, whereas δ_{list} -values are significantly different from the corresponding δ_T , the differences, $\Delta\delta_{list}$ and $\Delta\delta_T$, are closer to each other. Thus, similar to $\Delta\delta_T$, the former ($\Delta\delta_{list}$) indicates miscibility for systems #2, #4, and #6, but for PVC/PVAc, it incorrectly predicts immiscibility.

It is also important to examine the validity of Hansen's approach to polymer blend miscibility. The values of δ_a , δ_p , and δ_h (see eqs 3 and 4) were

Table 1. Computed and Listed Values of the Solubility Parameter [δ (MPa^{1/2})] for the Six Groups of Polymers Predicted to be Miscible

Group # (Fig. 1)	Polymer pairs—Names and codes		δ_T (at 200°C)	$\Delta\delta_T$	δ_{list} (at 25°C)	$\Delta\delta_{list}$
1	Polyethyleneterephthalate	PET	25.41	0.13	21.54	1.28
	Polysulfone	PSF	25.28		20.26	
2	Polycarbonate	PC	23.72	0.70	19.7	0.18
	Polymethylmethacrylate	PMMA	23.02		19.98	
3	Polyvinylchloride (polyphenylene ether)	PVC (PPE)	21.45	0.06	21.42	4.42
		(21.45)				
4	Polyvinylacetate	PVAc	21.51	0.01	17	0.12
	Polystyrene	PS1301	20.57		18.62	
	Polyvinyl methyl ether	PVME	20.58		18.5	
5	Polybutadiene	PBD	19.97	0.26	17.08	1.52
	Polyethylene-vinyl acetate (40 wt% VAc)	EVAc40	19.71		18.6	
6	Polyethylene-vinyl acetate (25-wt% VAc)	EVAc25	18.79	0.31	17	0.00
	Low density polyethylene	LDPE	18.48		17	

taken from his Handbook¹¹ and the values for α from the Polymer Handbook.²³ For the miscible blends PC/PMMA and PVC/PVAc, the values of $\Delta^2 = \Delta(T)$ at $T = 100$ – 300 °C were computed as $\Delta^2 = 23$ – 20 and 30 – 27 MPa, respectively. A similar computation for PET/PSF yielded $\Delta^2 = 10.6$ – 8.1 . The relative magnitude of these parameters incorrectly predicts that these three systems are immiscible. Furthermore, better miscibility is in-

dicated for PET/PSF than for PC/PMMA or PVC/PVAc. As illustrated in Figure 3, the source of these large values of Δ^2 is the disparity between the polar contributions of the two polymers, e.g., $\delta_p = 10.52$ and 5.90 for PMMA (#66 in ref. ¹¹) and PC (#211 in ref. ¹¹), respectively. The large δ_p may be the indication of a solvent-induced dipole in some of these polymers. It is Evident that in the melt, this effect is absent.

Figure 3. Calculation of the solubility parameters difference for PC-PMMA system using Hansen's Eqs 3 and 4 and numerical values of δ_d , δ_p , and δ_h parameters from his handbook.

CONCLUSIONS

1. The solubility parameters (δ), computed from PVT data by means of the S-S eos, were used for evaluating the miscibility of molten polymer pairs. The values of $\Delta\delta_T$ computed for $T = 100$ – 300 °C correctly indicated the miscibility of several polymer pairs. Furthermore, the computed values are more consistent with observations than $\Delta\delta_{list}$ determined in solutions.
2. The results are encouraging, pointing out the usefulness of the S-S statistical thermodynamic theory for the computation of δ . The procedure is simple: (1) measure the PVT behavior of the selected materials; (2) extract the characteristic P^* , T^* , and V^* parameters; (3) compute δ -values at a P and a T of interest; and (4) compare the δ -values. Noteworthy, these δ -values reflect the bulk-average internal energy. This is important when dealing with commercial resins, which often contain up to

10 wt% of additives that are rarely mentioned in specifications.

3. Three polymer pairs: PSF/PET, PPE/PVC, and PPE/PVAc, have been identified as potentially miscible. Examination of their miscibility and performance would be of academic and industrial interest.
4. As the data in Figure 1 indicate, the cohesive energy density depends on the free volume parameter, h : $CED = 0.749 - 1.533h + 0.782h^2$. Thus, in terms of the reduced variables (corresponding states), the miscibility depends on the proximity of the free volume fractions; miscibility is favored for polymer pairs having a similar h . This conclusion could be expected from earlier publications,²⁴ but neither an explicit correlation nor a direct functional link has been formulated.
5. Evidently, an analysis that only considers the difference of the solubility parameters, neglecting other aspects (e.g., the noncombinatorial entropy, eos, and nonrandom mixing contributions), is not complete. The inadequacy is particularly important near the phase separation. However, to a large extent the solubility parameters define the polymer–polymer miscibility.
6. In a sense, the procedure proposed in this article is similar to the heat of mixing (or analog calorimetry) approach.^{7,25} Both are tools for a rapid identification of potentially miscible polymer pairs.
7. The values of δ computed from the PVT behavior in the melt better reflect the polymer cohesive energy than those deduced from the solution data, thus, the polymer–polymer miscibility predictions are more consistent than those made using the standard values of δ_{list} .
8. The induced dipole interactions change the internal energy of a polymer, making it more soluble in polar solvents. However, this effect is less important for the polymer–polymer miscibility and the use of the solution-generated sets of Hansen's parameters (δ_d , δ_p , and δ_h) to estimate polymer–polymer miscibility may lead to the wrong conclusions.

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NOMENCLATURE

Abbreviations

eos	Equation of state
EC	Ethyl cellulose
EVAc25	Polyethylene–vinyl acetate (25 wt% VAc)
EVAc40	Polyethylene–vinyl acetate (40 wt% VAc)
LCST	Lower critical solution temperature
LDPE	Low density polyethylene
PA-6	Poly- ϵ -caprolactam
PA-66	Polyhexamethylene-adipamide
PBD	Polybutadiene
PC	Polycarbonate
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PET	Polyethyleneterephthalate
PMMA	Polymethylmethacrylate
PPE	Polyphenylene ether
PS	Polystyrene
PSF	Polysulfone
PVAc	Polyvinylacetate
PVC	Polyvinylchloride
PVEE	Polyvinyl ethyl ether
PVME	Polyvinyl methyl ether
S–S	Simha and Somcynsky statistical thermodynamics theory

Symbols

$3c$	Number of the external degrees of freedom
$\delta = \delta(T, P)$	Solubility parameter as a function of temperature and pressure (in MPa ^{1/2})
$\alpha \equiv (\partial \ln V / \partial T)_P$	Thermal expansion coefficient
CED	Cohesive energy density
Δ^2	$= \Delta(T)$ Sum of squares of the Hansen's solubility parameters (see eq 3)
$h = h(V, T)$	hole fraction as a function of V and T ; a free volume parameter
M	Polymer molar mass
$M_o = M/s$	Segmental molar mass
$P; P^*$	Pressure; characteristic (scaling) pressure
R	Gas constant ($R = 8.314510$ Pa m ³ /K mol)
s	Number of statistical segment per macromolecule; $s = M/M_o$

$T; T^*$	Temperature; characteristic (scaling) temperature
T_g	Glass transition temperature
U	Internal energy
ν^*	Molar repulsion volume
$V; V^*$	Volume; characteristic (scaling) volume
$y = 1 - h$	Occupied volume fraction in S-S lattice model
$\chi = \chi_h + \chi_s$	Huggins-Flory binary interaction parameter with its enthalpic and entropic components
ΔU_m	Internal energy of mixing
$\Delta\delta_{list}$ and $\Delta\delta_T$	Difference of solubility parameters of two polymers, listed in standard tables and computed at the same temperature, T , respectively
$\delta_d, \delta_p, \delta_h$	Hansen's dispersive, polar and hydrogen bonding components of δ
δ_{25}	Computed solubility parameter at 25 °C
δ_{list}	Solubility parameter as listed in standard tables
δ_T	Computed solubility parameter at $T > T_g$
δ_{T_g+300}	Computed solubility parameter at $T = T_g + 300$ °C
ε^*	Molar attraction energy in Lennard-Jones potential
ϕ_i	Volume fraction of component "i"
$\tilde{F}$ (tilde)	Indicates reduced variables as, e.g., $\tilde{P} = P / P^*$; $\tilde{T} = T / T^*$; $\tilde{V} = V / V^*$

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