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Interaction-structure-property relationships in amorphous polymer blends

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Summary

Miscibility, structure and property relationships were studied by different techniques for various polymer pairs. Four blends of polystyrene (PS), styrene-acrylonitrile copolymer (SAN), polycarbonate (PC) and polyphenylene oxide (PPO) [PS/PPO, PS/PC, PS/SAN and PPO/SAN] were investigated in the entire composition range. Glass transition temperatures were measured by DSC, mechanical properties were characterized by tensile test, methanol absorption was determined at 50 °C. The Flory-Huggins interaction parameter (χ) was derived from Hildebrand solubility parameters, and compared to χ-related quantities calculated from the experimental results. Good correlation was obtained between parameters derived from different methods used for the characterization of polymer/polymer interaction.

1. Introduction

The properties of polymer blends are controlled primarily by the microstructure of the system, which depends upon the miscibility of the components in the first place. Thermodinamical miscibility means mixing of the components on molecular level resulting in a homogeneous structure. The free energy of mixing must be negative for the formation of a homogeneous system. In contrast to small molecules, the change of entropy is small when polymers of high molecular masses are mixed, therefore a large negative enthalpy of mixing is required for miscibility. This condition is fulfilled by polymer pairs showing strong specific interactions. In the case of moderate or weak interactions, a temperature and composition dependent miscibility window may exist, as both thermodynamical parameters (ΔH and ΔS) depend on these variables. In the absence of favorable intermolecular interactions the solubility parameters of polymers must match in order to find miscible pairs [1].

Partial miscibility results in a heterogeneous, two-phase structure, in which only a limited amount of the other component is dissolved in both phases. In such blends the balance of properties may satisfy certain requirements, they are often termed as compatible blends. The degree of miscibility or compatibility of polymers can be studied by different methods [2-6]. A number of theoretical and empirical equations are available for the characterization of structure on the basis of property changes. Some of these methods yield the Flory-Huggins interaction parameter (χ) [7] or a number related to it. The goal of this study was comparing χ parameters and related quantities which were derived from measured properties of blends by various methods.

2. Experimental

2.1. Materials and experimental methods

The polymers used for the experiments and their characteristics are listed in Table 1. PS/PPO, PS/SAN, PS/PC and PPO/SAN blends were prepared in the entire composition range by extrusion and subsequent compression molding. Extrusion was carried out at 50 min^{-1}. The temperatures of the zones were set to 265 - 270 - 275 - 280 °C for PS/PC and PS/SAN blends, while to 280 - 290 - 295 - 300 °C for PS/PPO and PPO/SAN.

The glass transition temperature (T_g) of the polymers and the blends was measured by differential scanning calorimetry (DSC; DSC-30 Cell of Mettler TA 4000 Thermal Analysis System) under nitrogen at a heating rate of 20 °C/min (SD: 0.5 °C). Mechanical properties were characterized by tensile test at ambient temperature using a cross-head speed of 5 mm/min (SD: 10-15 %). Methanol absorption of sheets of about 1 mm was measured at 50 °C as a function of time. The diffusion coefficient (*D*) and the equilibrium solubility of the solvent were determined by mathematical methods (SD: 10%).

2.2. Evaluation methods

The Flory-Huggins interaction parameter (χ_{12}) can be calculated from the Hildebrand solubility parameter (δ) of the components by the following equation [8]:

$$\chi_{12} = \left(\frac{V_r}{RT}\right)\left(\delta_1 - \delta_2\right)^2 \tag{1}$$

where subscripts 1 and 2 refer to the two polymers, V_r is a reference volume (for polymers 100 cm^3/mole can be used; see Krause in [4]), *R*, the universal gas constant, *T*, the absolute temperature.

From the degree of polymerization (*N*) a critical value of the interaction parameter, $(\chi_{12})_{cr}$, can be calculated [9, 10]:

$$\left(\chi_{12}\right)_{cr} = 0.5\left(N_1^{-1/2} + N_2^{-1/2}\right)^2 \tag{2}$$

If $\chi_{12} < (\chi_{12})_{cr}$, the blend can be considered miscible. With increasing difference between the two values the composition dependent miscibility window becomes wider.

The measurement of glass transition temperature is frequently used for the estimation of compatibility. Heterogeneous blends of a polymer pair exhibit two glass transitions at temperatures around those of the components. Partial miscibility results in a shift of the glass transition temperature as a function of composition. The ratio of T_g shift is related to the degree of component mixing [11]. Miscible polymer blends reveal single intermediate glass transitions, though a single T_g is not an efficient proof of thermodynamical miscibility [6,12]. The changes in the glass transition temperature of a miscible blend can be described by the Fox equation (3) [13].

Table 1 Polymers studied

Polymer	Abbre-viation	Commercial name	Density [g/cm^3]	T_g [°C]	M_n	M_w
Polystyrene	PS	Edistir N 1381	1.05	104	99,190	211,900
Polyethylene oxide	PPO	experim. product	1.06	215	66,330	159,100
Styrene-acrylo-nitrile copolymer	SAN	Luran 358	1.08	109	27,510	105,800
Polycarbonate	PC	Macrolon 2800	1.20	147	14,560	86,710

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{3}$$

where w_1 and w_2 are the mass fraction, while T_{g1} and T_{g2}, the glass transition temperature of polymer 1 and 2, respectively.

In a heterogeneous blend the extent of component mixing can be calculated also from the Fox equation [11]. The mass fraction of polymer 1 in the phase rich in polymer 1 can be given by Eq. (4a), and a similar expression applies for polymer 2 Eq. (4b):

$$w_1' = \frac{T_{g1}\left(T_{g1,b} - T_{g2}\right)}{T_{g1,b}\left(T_{g1} - T_{g2}\right)} \qquad w_2'' = \frac{T_{g2}\left(T_{g2,b} - T_{g1}\right)}{T_{g2,b}\left(T_{g2} - T_{g1}\right)} \tag{4a-b}$$

where $T_{g1,b}$ and $T_{g2,b}$ are the glass transition temperatures of polymer 1 and 2 in the blend.

Apparent volume fractions (ϕ) can be derived from the apparent mass fractions, than the χ parameters can be calculated by the equations of Kim and Burns [11]:

$$\chi_{12} = \frac{\ln\left(\phi_1''/\phi_1'\right) + \left(1 - m_1/m_2\right)\left(\phi_2'' - \phi_2'\right)}{m_1\left(\phi_2'^2 - \phi_2''^2\right)} \qquad \chi_{21} = \frac{\ln\left(\phi_2''/\phi_2'\right) + \left(1 - m_2/m_1\right)\left(\phi_1'' - \phi_1'\right)}{m_2\left(\phi_1'^2 - \phi_1''^2\right)} \tag{5a-b}$$

where the two conjugate phases are denoted by single and double primes; *m* is essentially the degree of polymerization, relating the molar volumes to a fictitious molar volume of one submolecule of the polymer (lattice site volume). Within the experimental error Eqs. (5a) and (5b) should yield the same solubility parameter values. Although the use of Eqs 5a an 5b assumes thermodynamic equilibrium what is obviously not achieved under the conditions of extrusion, they were successfully employed for the calculation of χ before [14,15].

Polymer/polymer miscibility may be deduced also from solvent absorption experiments [4,6]. In the case of Fickian diffusion, diffusion coefficient and equilibrium solvent uptake can be determined by the numerical solution of Fick's equation [16,17]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[-\frac{D(2m+1)^2\pi^2 t}{l^2}\right] \tag{6}$$

where D is the diffusion coefficient, M_t, the amount of diffusant taken up by the film of thickness, l, at time, t; M_∞ is the equilibrium sorption attained after infinite time.

The equilibrium solvent uptake of polymer blends depends on the strength of solvent/polymer, as well as polymer/polymer interactions. If the solvent/polymer interaction parameter (χ_{si}) is independent from the equilibrium solvent uptake (ϕ_s) in the binary systems, the activity (α_s) of the solvent sorbed into a homogeneous blend of polymers 1 and 2 can be given as follows [4]

$$\ln a_s = 0 = \ln\phi_s + \left(1 - \phi_s\right) + \left(\chi_{s1}\phi_1 + \chi_{s2}\phi_2\right)\left(1 - \phi_s\right) - \chi'_{12}\,\phi_1\phi_2 \tag{7}$$

where ϕ_i is the volume fraction of the corresponding component in the ternary system. The polymer/polymer interaction parameter, χ'_{12}, is related to the Flory-Huggins interaction parameter by

$$\chi'_{12} = \left(V_s/V_1\right)\chi_{12} = \left(V_s/V_2\right)\chi_{21} \tag{8}$$

where V_s, V_1 and V_2 are the corresponding molar volumes.

A semi-empirical model was developed earlier for the determination of polymer/polymer compatibility from the tensile properties of blends [18-20]. According to the model the tensile strength of a two-component system is determined by the true tensile strength of the matrix polymer (σ_{T0}), the volume fraction of the dispersed phase (ϕ_d) and a parameter, *B*, which reflects the effect of interaction:

$$\sigma_{Tred} = \frac{\sigma_T}{\lambda^n}\frac{1+2.5\phi_d}{1-\phi_d} = \sigma_{T0}\exp\left(B\phi_d\right) \tag{9}$$

where σ_T is the true, σ_{Tred}, the reduced tensile strength of the blend, respectively; λ is the relative elongation ($\lambda = L/L_0$); *n* is a parameter characterizing the strain hardening tendency of the matrix and it can be determined by the stress vs strain correlation of the neat, matrix polymer [21]. Parameter *B* indicates the relative load bearing capacity of the components:

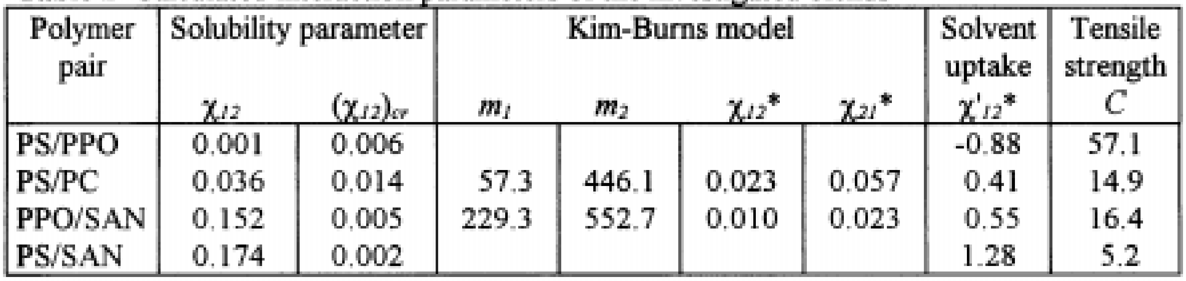
$$B = \ln\left(\frac{C\sigma_d}{\sigma_0}\right) \tag{10}$$

where σ_d and σ_0 are the tensile strengths of the dispersed phase and the matrix, respectively. *C* is a proportionality constant related to the stress transfer, and so, reciprocally to the Flory-Huggins interaction parameter [18,19].

Results and discussion

According to the results the studied blends can be classified into three groups: miscible, partially miscible and immiscible (incompatible) blends. PPO and PS are miscible polymers. Although early experiments indicated that mixing does not occur at the segmental level [22,23], from the later results molecular mixing was deduced, which was attributed to phenyl-group coupling [24]. The Flory-Huggins interaction parameter calculated from the solubility parameters of the two components is small, less than the critical value (Table 2). PS/PPO blends give single intermediate glass transitions, the temperatures of which are lower than calculated by the Fox equation. The values are close to those derived by the Couchman equation [24]. Tensile strengths are higher than calculated by the additivity rule, and go through a maximum at around 0.4 PS volume fraction (Fig. 1). The proportionality constant, *C*, calculated from the tensile strength is high (Table 2). The diffusion constant calculated from methanol absorption goes through a minimum as a function of composition (Fig. 2) indicating that the free-volume of the blends is lower than the additive volume due to specific interaction of the components [25]. This deduction is confirmed also by the restricted maximum solvent uptake (Fig. 3). Though the interaction parameters, χ'_{12}, calculated from the solubility uptake show composition dependence (Fig. 4),

Table 2 Calculated interaction parameters of the investigated blends



Polymer pair	Solubility parameter		Kim-Burns model				Solvent uptake	Tensile strength
	χ_{12}	$(\chi_{12})_{cr}$	m_1	m_2	χ_{12}*	χ_{21}*	χ'_{12}*	*C*
PS/PPO	0.001	0.006					-0.88	57.1
PS/PC	0.036	0.014	57.3	446.1	0.023	0.057	0.41	14.9
PPO/SAN	0.152	0.005	229.3	552.7	0.010	0.023	0.55	16.4
PS/SAN	0.174	0.002					1.28	5.2

* Average values

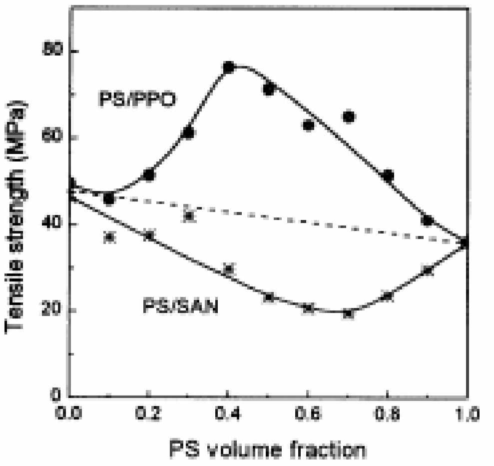


Figure 1 *Composition dependence of tensile strength for PS/PPO and PS/SAN blends*

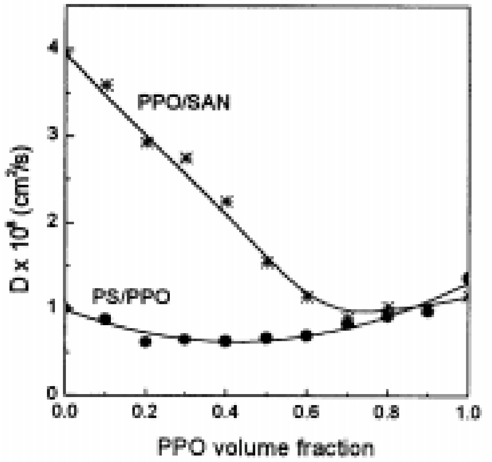


Figure 2 *Composition dependence of the diffusion coefficient of methanol at 50 °C*

each of them is negative. All results indicate the miscibility of PS/PPO blends.

Contrary to the above polymer pair, PS/SAN blends are incompatible at each composition. χ_{12} calculated from the solubility parameters is the highest among the blends investigated, and exceeds considerably the critical value (Table 2). The glass transition temperatures of these polymers differ only with 5 °C (Table 1), therefore compatibility can not be deduced from the thermal properties. The mechanical properties reveal strong incompatibility: the tensile strength of the blends shows considerable negative deviation from additivity, and goes through a minimum at 0.7 PS volume fraction as a function of composition (Fig. 1). The proportionality constant, *C*, is ten times lower than that of PS/PPO blends (Table 2). The diffusion coefficient plotted as a function of composition indicates phase inversion between 0.2 and 0.5 PS volume fraction (Fig. 5). This result does not agree with the composition range of phase inversion deduced from the mechanical proper-

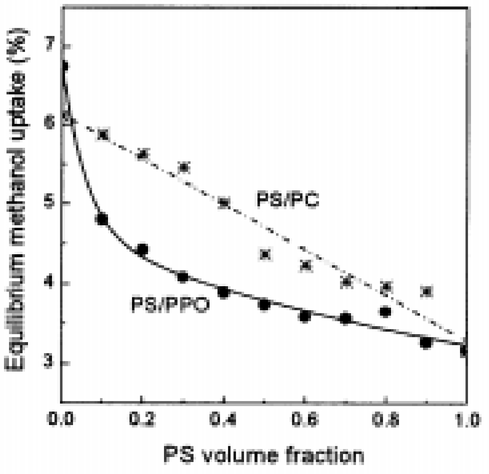


Figure 3 *Composition dependence of equilibrium methanol uptake at 50 °C*

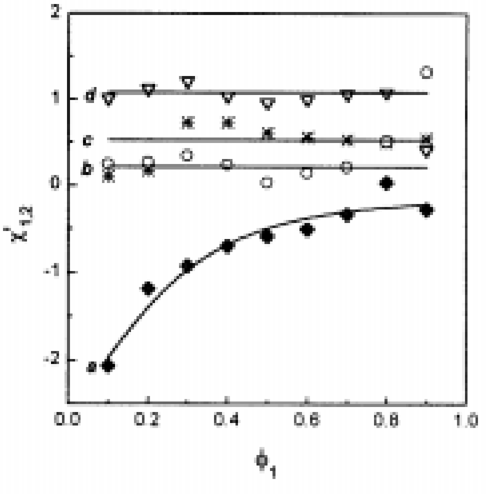


Figure 4 *Interaction parameter derived from methanol absorption of a: PS/PPO; b: PS/PC c: PPO/SAN; d: PS/SAN;*

ties. The dissimilarity can be explained by the strong incompatibility of the two polymers. Most probably the phase inversion is at around 1/1 component ratio. At 0.5 and higher PS volume fractions the rate of solvent diffusion is controlled mainly by the characteristics of the matrix polymer. On the other hand, the mechanical properties are determined not only by the characteristics of the matrix, but also by the strength of interaction. The equilibrium methanol uptake of PS/SAN is a linear function of composition, and changes between 3 (for PS) and 24 w/w% (for SAN). The interaction parameters, χ'_{12}, determined from methanol uptake are positive, and the highest among the four systems investigated (Fig. 4). The results of the different methods harmonize well also for this polymer pair.

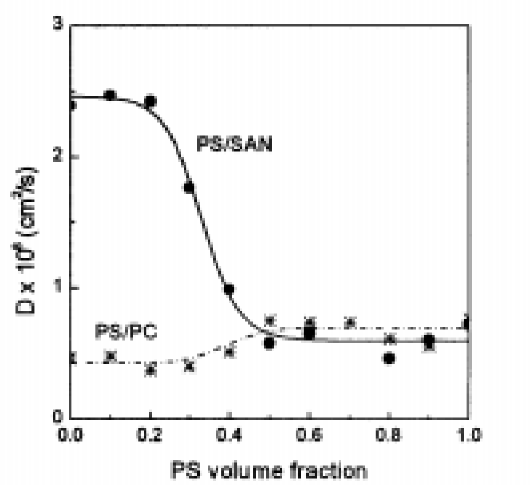


Figure 5 *Composition dependence of the diffusion coefficient of methanol at 50 °C*

The compatibility of PS/PC and PPO/SAN blends lies between the two extremes discussed above. The χ_{12} values calculated from the solubility parameters are higher than $(\chi_{12})_{cr}$ indicating that only partial miscibility can be expected for these systems. Compatibility of the PS/PC blends seems to be better than that of PPO/SAN. Both polymer pairs exhibit two glass transition temperatures in the entire composition range which show some shift with composition. In the case of PS/PC blends the T_g of the PS phase changes about 3 °C, while that of the PC phase varies within 5 °C. In PPO/SAN blends the shift of the T_g values is even smaller, it does not exceed 2-3 °C. From the shift of the glass transition temperatures interaction parameters were calculated by the equations of Kim and Burns (5a-b). Although the average of χ_{12} and χ_{21} is 0.04 for the PS/PC blends (Table 2), which agrees well with the value of 0.044 determined by Kim and Burns for 1/1 component ratio of this polymer pair [14], the deviation between the two parameters is higher than expected. Moreover, χ_{21} shows strong composition dependence (Fig. 6), and at low PC volume fractions χ_{21} is about four times higher than χ_{12}. The same trend was observed for PPO/SAN blends: χ_{12} is practically independent of composition; χ_{21} is higher than χ_{12}, and changes with composition. The average of the interaction parameters is 0.017 for PPO/SAN, which suggests higher compatibility than for PS/PC blends. However, the opposite conclusion can be drawn from the interaction parameters derived from the solubility parameters (Table 2). Model calculations revealed that the selected lattice site volume affects strongly the interaction parameters calculated by Eqs. (5a-b). The mechanical properties of these

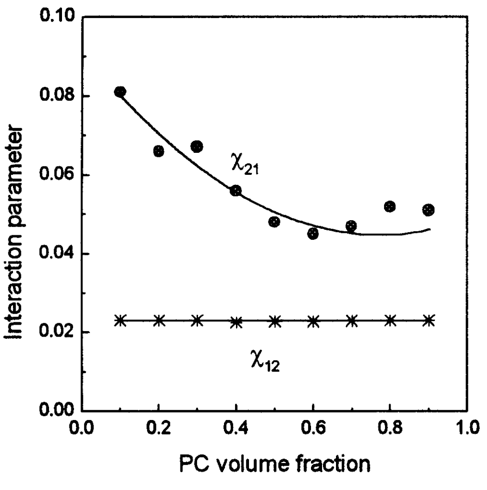


Figure 6 *Interaction parameter determined by Eqs (5a-b) for PS/PC blends*

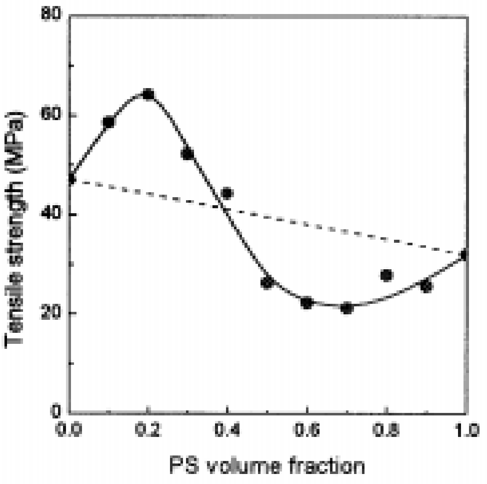


Figure 7 *Composition dependence of the tensile strength of PS/PC blends*

polymer pairs are between those of PS/PPO and PS/SAN blends. The tensile strength of PPO/SAN blends corresponds to additivity, while that of PS/PC goes through a maximum and a minimum as a function of composition (Fig. 7). The calculated proportionality constants, *C*, are similar for these systems (Table 2), and lie between those of PS/PPO and PS/SAN. The rate of methanol diffusion in PS/PC is controlled essentially by the characteristics of the matrix polymer (Fig. 5), and a change indicates phase inversion between 0.3 and 0.5 PS volume fractions. In PPO/SAN blends the diffusion rate of methanol is determined by matrix properties above 0.5 PPO content (Fig. 2). On the other side of the composition range *D* decreases linearly with increasing PPO volume fractions, which suggests limited mixing of the polymer components. The equilibrium solvent uptake changes according to the composition of PS/PC (Fig. 3) and PPO/SAN blends. The calculated interaction parameters, χ'_{12} are similar (Table 2) and suggest somewhat better compatibility in PS/PC than in PPO/SAN. From these results we can conclude that the strength of interaction is similar in PS/PC and PPO/SAN blends, and the differences in the derived parameters are in the range of experimental error.

The study presented in this paper reveals that the combination of several experimental methods offers proper insight into the interaction-structure-property relationships of amorphous polymer blends. Furthermore, correlations can be established between the interaction parameters from different characteristics of the blends. Fig. 8 shows the relationship between χ'_{12} calculated from methanol absorption and parameter *C* derived from the tensile strength of the polymer blends.

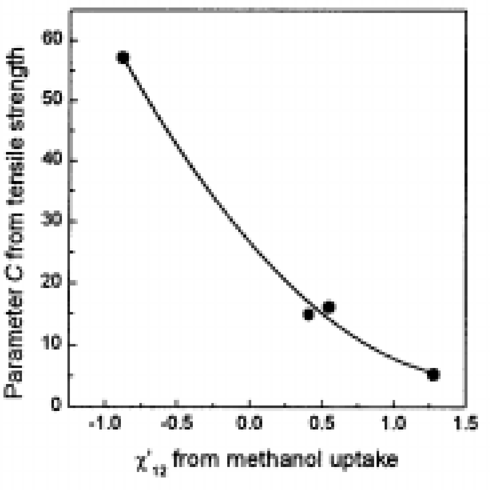


Figure 8 *Relationship between quantities related to Flory-Huggins interaction parameter determined by different methods*

Conclusions

Interaction-structure-property relationships were studied by different methods in PS/ PPO, PS/PC, PPO/SAN and PS/SAN blends in the entire composition range. These polymer pairs cover the whole scale from miscible to immiscible blends. The following conclusions were drawn from the results of the different methods:

- Different experimental techniques must be used for a reliable determination of component interaction in polymer blends.
- The interaction-related parameters derived from variable characteristics of blends in this study correlate well and

characterize the compatibility of the components.

- The expressions deduced by Kim and Burns [11] for the calculation of polymer/polymer interaction in partially miscible blends yield results which depend strongly on the selected lattice site volume.
- Quantitative correlation was found between the proportionality constant derived from tensile strength and the equilibrium solvent uptake of the blends.

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