Estimation of miscibility of polymer blends using the solubility parameter concept

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(Received 23 September 1991; revised 27 November 1991; accepted 20 January 1992)

A number of approaches for the prediction of polymer–polymer miscibility have been reviewed. Much work, reported in the literature, has been directed towards understanding the behaviour of polymer and copolymer mixtures using polymer interaction parameters based on empirical or semi-empirical values. These values often require extensive experimental data for their calculation and tend to lack general applicability. A new concept is presented here that is based upon the utilization of the individual component contributions to the solubility parameter. The development of a 'miscibility parameter', which describes the interaction of polymer repeat units, provides semi-quantitative values which relate the three basic interactive forces, i.e. dispersive, polar and hydrogen bonding. This results in a generalized scheme applicable to large classes of systems. The validity of the miscibility parameter is tested against other methods described in the literature with good results.

(Keywords: miscibility; polymer miscibility; solubility parameters; miscibility parameters)

INTRODUCTION

Polymer blends have been of great interest particularly in the last 10 years. The forces that have fuelled this interest are the costs and time associated with the development of new polymers and the ability to tailor properties by blending, which may result in new, desirable, and in some cases, unexpected synergistic effects on properties. It is not surprising then that polymer–polymer miscibility and the factors that control miscibility have been studied and discussed extensively[1].

When two polymers are blended, there is always a trace of one in the other and for most polymer pairs this solubility limit is very low and the polymers are classified as incompatible. However, it has been found that for more polymer mixtures than was previously suspected, regions of miscibility may exist. It is further recognized from theoretical and experimental studies that miscible blends result when there are exothermic interactions, such as those resulting from hydrogen bond formation between unlike blend components[1–10]. Consequently, there have been a number of studies of these molecular interactions that involve hydrogen bonds[11–19].

Traditionally, the Hildebrand solubility parameter concept[20] has been used to estimate the miscibility of two materials. The idea is simply that two materials that have matched solubility parameters will have balanced forces and therefore will be miscible. Techniques for estimating solubility parameters have been reported by Small[21], Hoy[22] and van Krevelen[23]. A general relationship is:

$$F = \sum n_i F_i \qquad (1)$$

where F is a molar property, n_i is the number of contributing components of type i, and F_i is the numerical contribution. In the case of solubility parameter determination of a compound, the following relationship is used:

$$\delta = \sum F_i / V \qquad (2)$$

where F_i is the molar attraction constant and V is the molar volume. From the solubility parameters, the polymer–polymer interaction parameter χ can be calculated according to[1,24]:

$$\chi = \frac{V_r}{RT}(\delta_A - \delta_B)^2 \qquad (3)$$

where V_r is the molar volume of the rubbery phase of the repeat unit, and δ_A, δ_B are the solubility parameters of the two polymers. Therefore, molecular mixing of two high molecular weight polymers can occur only when χ is very close to zero. This approach suffers from two distinct and important limitations: it requires that χ is always zero or positive and it imposes the condition that the solubility parameter is accurately calculated (or known) in order to determine the magnitude of this difference. The critical value of χ which sets the upper limit on miscibility is[25]:

$$\chi_{crit} = 1/2[1/N_A^{1/2} + 1/N_B^{1/2}]^2 \qquad (4)$$

where N_A and N_B are the degrees of polymerization. N_A and N_B are normally assumed to be ≈ 1000 and V_r to be 100 cm^3. The effect of these parameters is to require that the solubility parameter difference is less than 0.1 cal$^{1/2}$ cm$^{3/2}$ which necessitates that $\chi_{crit} \approx 0.002$. This means that the solubility parameters of the polymers in question must be known to an accuracy of better than 0.05 cal$^{1/2}$ cm$^{3/2}$.

As a consequence of these limitations, much work has been invested in the study of copolymer miscibility as a function of copolymer composition with the extraction

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of interaction energy values. In a recent paper, it was demonstrated that an interaction density database was useful in searching for miscible polymer blends[26].

The basis for a subsequent study utilized the interaction density or parameter B, of which the critical value for miscibility must be less than an expression similar to equation (3) and B is related to the heat of mixing[27]:

$$\Delta H_{\mathrm{m}} = B\phi_{\mathrm{A}}\phi_{\mathrm{B}} \qquad (5)$$

For the mixing of a copolymer of monomers 1 and 2 with a copolymer containing two separate and distinct monomers from the first case, a binary interaction model has been developed[28]. A plot from the interaction parameter values (B), showed that B went through a minimum at compositions where mixing occurred for the case of blends of polystyrene/poly(styrene–acrylonitrile) and poly(cyclohexyl methacrylate)/methyl methacrylate.

This method utilizes the free energy of mixing of two polymers:

$$\Delta G_{\mathrm{mix}} = RT\left[\frac{\phi_{\mathrm{A}}\ln\phi_{\mathrm{A}}}{V_{\mathrm{A}}} + \frac{\phi_{\mathrm{B}}\ln\phi_{\mathrm{B}}}{V_{\mathrm{B}}}\right] + B\phi_{\mathrm{A}}\phi_{\mathrm{B}} \qquad (6)$$

where

$$B_{\mathrm{crit}} = (RT/2)\left[\frac{1}{V_{\mathrm{A}}^{1/2}} + \frac{1}{V_{\mathrm{B}}^{1/2}}\right]^2 \qquad (7)$$

and ϕ_i = volume fraction and V_i = molar volume. From equations (4) and (7), it can be seen that:

$$\chi_{\mathrm{crit}}RT = B_{\mathrm{crit}}k \qquad (8)$$

For the mixing of two copolymers of monomers 1 and 2 with a copolymer of monomers 3 and 4, the individual interaction energy density parameter is:

$$\begin{aligned} B = {} & (B_{13}\phi_1 + B_{23}\phi_2)\phi_3 + (B_{14}\phi_1 + B_{24}\phi_2)\phi_4 \\ & - B_{12}\phi_1\phi_2 - B_{34}\phi_3\phi_4 \end{aligned} \qquad (9)$$

This requires knowledge of the B_{ij} values, which must be gathered from various literature sources or must be determined for the pair in question. In a recent work[29], Coleman *et al.* added to the equation for the free energy of mixing a term which accounts for favourable intermolecular interactions. This interaction is commonly due to hydrogen bond interactions but is not limited exclusively to them. Thus:

$$\frac{\Delta G^{\mathrm{M}}}{RT} = \frac{\phi_{\mathrm{A}}}{V_{\mathrm{A}}}\ln\phi_{\mathrm{A}} + \frac{\phi_{\mathrm{B}}}{V_{\mathrm{B}}}\ln\phi_{\mathrm{B}} + \phi_{\mathrm{A}}\phi_{\mathrm{B}}\chi + \frac{\Delta G_{\mathrm{H}}}{RT} \qquad (10)$$

In the absence of favourable intermolecular interactions, mixing can occur only when χ is very close to zero, as indicated in equation (3).

This approach again relies on accurate estimates of the solubility parameter, since the ultimate criterion is that described in equation (3). The modification introduced here[29] is that the requirement for a χ value, i.e. χ_{crit}, is adjusted upwards depending upon the favourable interactions expected and the use of non-hydrogen bonded solubility parameters for those polymers that strongly associate such as poly(vinyl alcohol) and poly(4-vinyl phenol), among others.

Because of the above requirements imposed by these approaches, we investigated the possibility of minimizing restrictions necessary to estimate polymer blend compatibility. In addition, we wished to examine a more generalized approach that could be applied to large classes of systems that are simple blends wherein miscibility is not obtained by functionalization or reaction of system components *in situ* during blending.

MISCIBILITY PARAMETER METHOD

The original solubility parameter concept introduced by Hildebrand and Scott[20] was only applicable to molecules that are dispersive in nature, i.e. $\Delta H_{\mathrm{m}} \geqslant 0$, and was relegated to simple liquids. Even though attempts to relate the concept to other systems that involve interactions such as hydrogen bonding[30] have not been very successful, the attraction of using the solubility parameter concept and the ability to characterize a system using only component properties is indeed appealing.

Our approach was to investigate the use of solubility parameters for evaluating trends in approaching a χ_{crit} value. This would obviate the need for an accurate knowledge of the absolute solubility parameter values, assuming the same database was used for all calculations.

Since there is extensive literature available on the underlying theory of the solubility parameter concept[20–23,31–34] and its application to polymers[1,23], we start with the solubility parameters of two materials, of unknown or questionable miscibility, and their relationship to the enthalpy of mixing:

$$\Delta h_{\mathrm{m}} = \phi_1\phi_2(\delta_1 - \delta_2)^2 \qquad (11)$$

where Δh_{m} = enthalpy of mixing per unit volume, ϕ_1 and ϕ_2 = volume fractions of components 1 and 2 and δ_1 and δ_2 = solubility parameters of components 1 and 2. The comparison of the solubility parameters necessitated that the contributions of each solubility parameter were examined. We therefore needed to examine the individual contributions to the total solubility parameter which is given by:

$$\delta^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2 \qquad (12)$$

where δ_{d} = contribution of dispersion forces, δ_{p} = contribution of polar forces and δ_{h} = contribution of hydrogen bonding forces.

Van Krevelen[23] has pointed out that the equivalent of equation (11) is:

$$\begin{aligned} \Delta h_{\mathrm{m}} = \phi_1\phi_2[(\delta_{\mathrm{d}_1} - \delta_{\mathrm{d}_2})^2 + (\delta_{\mathrm{p}_1} - \delta_{\mathrm{p}_2})^2 \\ + (\delta_{\mathrm{h}_1} - \delta_{\mathrm{h}_2})^2] \end{aligned} \qquad (13)$$

If $\Delta h_{\mathrm{m}} = 0$, then the Gibbs free energy of mixing is negative, and χ will be at or below χ_{crit} and miscibility will occur. It should be appreciated that equation (13) is not mathematically and therefore not numerically equal to equation (11). The quantity

$$(\delta_{\mathrm{d}_1} - \delta_{\mathrm{d}_2})^2 + (\delta_{\mathrm{p}_1} - \delta_{\mathrm{p}_2})^2 + (\delta_{\mathrm{h}_1} - \delta_{\mathrm{h}_2})^2$$

is a vector quantity whose magnitude $|\vec{d}|$, is indicative of the difference between components in three-dimensional space.

For purposes of evaluation, we utilized a materials properties spreadsheet[35] which calculates the individual solubility parameter contributions based on van Krevelen's work[23]. A similar technique has been used recently[36] where the total solubility parameter has been separated into its component parts. However, this approach differs from the present one in that the volume fraction was calculated that minimized the heat of mixing with respect to the second component and this value was subsequently used in the calculation of a total solubility parameter that represented a single criterion for miscibility.

Based upon the absolute values of the blend solubility parameters reported, it appears to be difficult to determine whether or not blends are miscible, since the blend solubility parameters are not at all close to zero. Our method differs considerably from the technique of Huang and Wang[36] as will be appreciated from the following. Further, rather than treat the solubility parameter of a copolymer as a single lumped parameter whose average value may not be too meaningful, we calculated the solubility parameter for each repeat unit or block. For monomers 1 and 2 of polymer A, we have:

$$(\delta_1^{\mathrm{P}})^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2 \tag{14}$$

$$(\delta_2^{\mathrm{P}})^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2 \tag{15}$$

Weight fractions of monomer units, ϕ', were multiplied by their selected respective individual solubility parameter contributions to give a single solubility parameter characterizing the polymer. We would like to point out here that the dispersive, polar, and hydrogen bonding solubility parameter components are not utilized in every case. In some instances, only two of the three are utilized in appropirate combinations, as will be made clear in subsequent sections.

$$\delta_{\mathrm{A}}^{\mathrm{P}} = \delta_1^{\mathrm{P}}\phi_1' + \delta_2^{\mathrm{P}}\phi_2' \tag{16}$$

Similarly for a second polymer B, we have:

$$\delta_{\mathrm{B}}^{\mathrm{P}} = \delta_3^{\mathrm{P}}\phi_3' + \delta_4^{\mathrm{P}}\phi_4' \tag{17}$$

where ϕ_3' and ϕ_4' are the weight fractions. These values were then used to calculate a miscibility parameter (MP) which is defined as

$$\mathrm{MP} = (\delta_{\mathrm{A}}^{\mathrm{P}} - \delta_{\mathrm{B}}^{\mathrm{P}})^2 \tag{18}$$

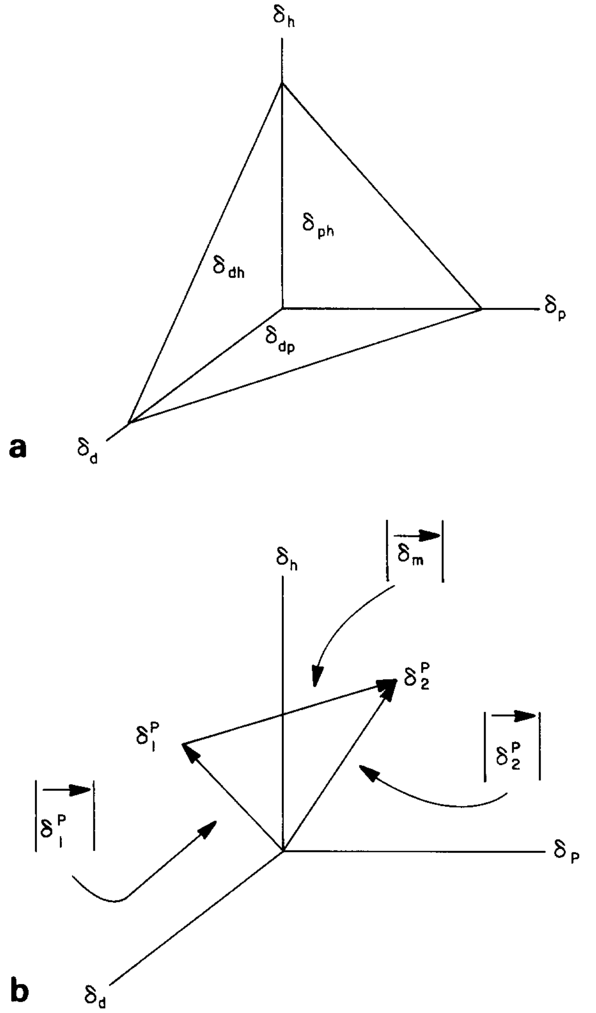
We then plotted MP as a function of the weight fraction composition of one of the components in the copolymer to see if trends and/or regions of miscibility might be indicated.

The use of equations (14) and (15) is different from that employed by Huang and Wang[36]. They utilized the quantity

$$\delta_{\mathrm{m}}^2 = (\delta_{\mathrm{d}_1} - \delta_{\mathrm{d}_2})^2 + (\delta_{\mathrm{p}_1} - \delta_{\mathrm{p}_2})^2 + (\delta_{\mathrm{h}_1} - \delta_{\mathrm{h}_2})^2$$

which measures the difference in solubility parameters in three-dimensional space, i.e. $|\overrightarrow{\delta_1^{\mathrm{P}}\delta_2^{\mathrm{P}}}|$, whereas equations (14) and (15) measure the magnitude of the solubility parameters from the origin in three-dimensional space, i.e. $|\overrightarrow{\delta_1^{\mathrm{P}}}|$ and $|\overrightarrow{\delta_2^{\mathrm{P}}}|$. These quantities are adjusted for their weight fraction contributions (equations (16) and (17)), and are then subtracted to establish the extent of their dissimilarity (equation (18)). In the case where only two of the three solubility parameter components are utilized, the magnitude of δ_1^{P} and δ_2^{P} and all possible solutions of equation (18) are confined to a single plane of the coordinate system δ_{d}, δ_{p}, δ_{h}. However, their differences in magnitude, measured from the origin, are again compared as opposed to the vector difference between their locations. These points are illustrated in *Figure 1*.

The key reason for separating the solubility parameter into its component contributions is the underlying concept that blends of copolymers essentially interact through their blocks or individual functional groups. This implies that while the total solubility parameter might be useful, it is an average value and, as such, may be misleading. It may therefore be useful to examine the solubility parameter components individually and in *appropriate* combinations in order to estimate regions of miscibility. It is important to point out that it may not always be simple to distinguish which solubility parameter combinations are appropriate, but the guide is to keep in mind that non-reactive polymer blends are thought to interact via their individual blocks or functional groups and therefore examination of the solubility parameter components must be carried out with critical appraisal of values which are similar and those that are not. These will be the blocks or groups which interact or do not interact favourably and affect miscibility.



$$|\overrightarrow{\delta m}| = [(\delta_{d_1} - \delta_{d_2})^2 + (\delta_{p_1} - \delta_{p_2})^2 + (\delta_{h_1} - \delta_{h_2})^2]^{1/2}$$

$$|\overrightarrow{\delta_1^{P}}| = [\delta_d^2 + \delta_p^2 + \delta_h^2]^{1/2}$$

$$|\overrightarrow{\delta_2^{P}}| = [\delta_d^2 + \delta_p^2 + \delta_h^2]^{1/2}$$

Figure 1 (a) Solubility parameter coordinate axis system; (b) illustration of solubility parameter vector quantities

RESULTS AND DISCUSSION

The considerations described above were applied by first calculating the dispersive (d), polar (p) and hydrogen bonding (h) contributions to the total solubility parameter for a polymer blend system that has very weak or non-existent favourable intermolecular interactions. This is a good 'test case' system since this category of polymer blend requires χ_{crit} to be at a value very close to zero.

A good blend for evaluation is the butadiene-*co*-acrylonitrile (BDAN)/polystyrene (PS) system since their solubility parameters span a wide range ($\delta \approx 8.1-13.8$), depending upon the AN content since both BD and styrene have essentially dispersive forces while AN contributes both polar and hydrogen bonding forces. The dispersive, polar and hydrogen bonding components of the solubility parameter were calculated as described previously[35]. These are listed in *Table 1*.

At this point a calculation of MP combinations was made and plotted graphically (*Figure 2*). Inspection reveals distinct minima for the (dph), (dp), (dh) and (ph) combinations. The miscibility trend curves involving hydrogen bonding are not relevant, however, since BD and styrene repeat units are incapable of hydrogen bonding. This leaves only MP(dp) to suggest a possible miscibility window. A recent publication[29] using averaged copolymer solubility parameters and imposing a low χ_{crit} (<0.002) gives a range of miscibility of 30–34%. At MP(dp) ≈ 0.012 or the equivalent $\chi_{crit} \approx 0.002$, the regions of miscibility are about 11–15% AN. These calculations indicate a potentially very narrow region of miscibility at low AN content, but in this work we have imposed no criteria for accuracy on the solubility parameters or for a minimum in the solubility parameter differences. We are only looking for trends in the MPs and we use the numerical value of 0.05 for weakly interacting systems only as a guide for the miscibility window. It should be noted that BDAN copolymers are not miscible with PS[31]. The same reasoning that led us to eliminate the hydrogen bonding interaction could very reasonably be applied to the polar forces. The result is a MP using just dispersive interactions. This calculation is significantly greater than 0.05 across the entire range of AN content, which supports immiscibility.

We include a number of examples to illustrate this approach along with an example of a new polymer blend application which we are currently investigating. In most cases, V_g was used in place of V_r for the solubility parameter calculations. This was done for those polymers that were glassy at ambient temperatures even though they are rubbery at the temperatures of mixing. Although no substantial change in miscibility was found, in general a slightly better agreement with literature ranges of miscibility was observed. This observation is consistent with the decreased volume change that will accompany blending of two miscible polymers.

As an example of the application of the MP to the relatively weak favourable intermolecular interactions blend[29], we chose the poly(vinyl chloride)/styrene acrylonitrile (PVC/SAN) polymer blend. The relevant solubility parameter component values are also shown in *Table 1*. An examination of *Table 1* leads to the conclusion that the best estimate for regions of miscibility will be given by the MP calculated using only the dispersive and polar solubility parameter components. The results are illustrated in *Figure 3*.

The (dph) and (dp) plots both show a similar miscibility range with a minimum between 25 and 30% AN in SAN. The minimum is shifted to ~46% for the (ph) combination. This result might also infer that miscibility is influenced most strongly by the contribution of the polar forces. The (dph) and (dp) plots are also similar to that recently reported by Coleman *et al.*[29]. The (dh) plot may indicate a trend towards immiscibility as AN content increases, although no distinct minimum is evident. Thus the (dh) curve should not be interpreted as being contrary to the other combinations and previously reported experimental evidence[38].

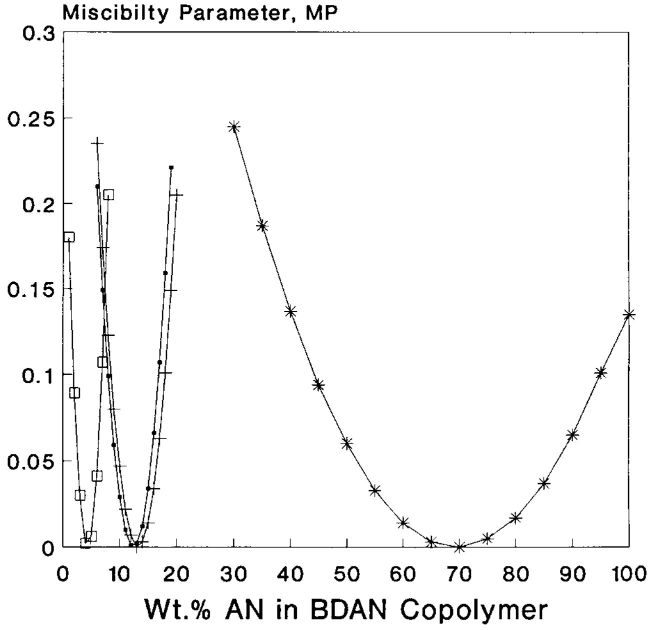


Figure 2 BDAN/styrene miscibility parameter: •, (dph); +, (dp); ∗, (dh); □, (ph)

Table 1 Solubility parameter components for those polymers used in evaluating regions of miscibility

Polymer repeat unit	Abbreviation	δ_d	δ_p	δ_h
Butadiene	BD	8.01	0	0
Styrene	PS	8.88	0.55	0
Acrylonitrile	AN	8.51	12.00	3.65
Vinyl chloride	VC	8.65	5.95	1.45
Vinyl butyral	VB	7.72	2.90	3.26
Vinyl alcohol	VA	7.62	6.80	11.54
Methylene bis-4,4′-dicyclohexyl diisocyanate based diurethane	MBDCI	8.90	2.16	4.00
Methylene bis-4,4′-diphenyl diisocyanate based diurethane	MBDPI	9.64	2.60	4.33
Tetramethylene ether glycol	PTMEG	7.76	2.63	3.11

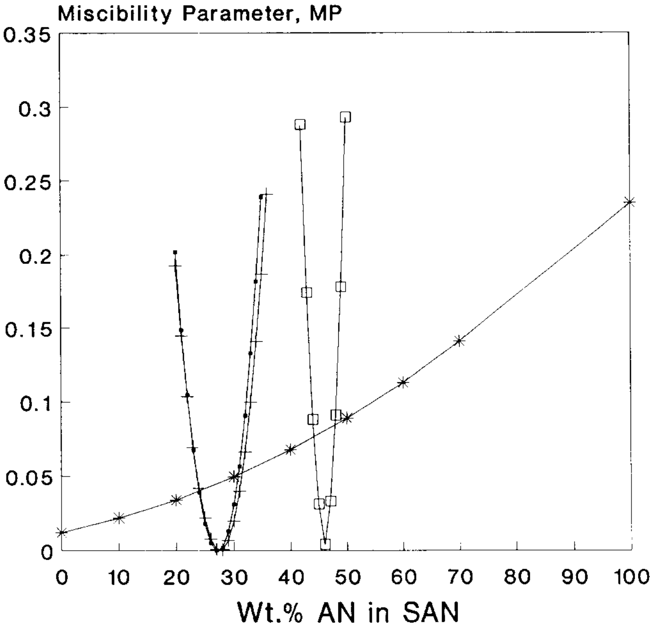


Figure 3 PVC/SAN miscibility parameter: •, (dph); +, (dp); ∗, (dh); □, (ph)

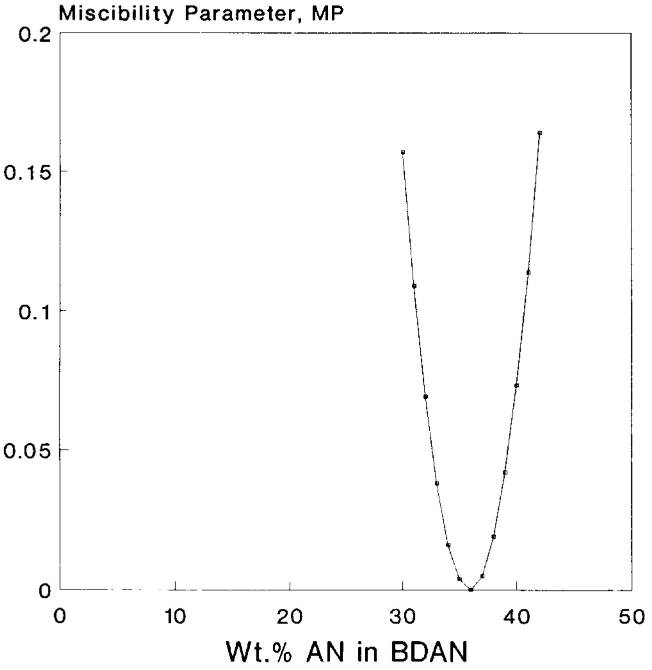


Figure 4 PVC/BDAN miscibility parameters: • , (dp)

Coleman *et al.*[29] showed a minimum which occurred at ~10–11% AN in SAN while Kim *et al.*[38] reported miscibility of PVC with SAN copolymers that contained 11.5–26% AN. It appears that an MP value an order of magnitude greater, i.e. ≈0.12, is appropriate for weakly favourable molecular interactions[29,36], and it can be seen from *Figure 3* that an MP ≈0.12 shows a window of miscibility from ~21 to 33% AN, which includes a large portion of the reported ranges of miscibility.

The third example is for the PVC/BDAN blend system. Using the same reasoning as before, the dispersive and polar MPs are expected to provide the best estimate of regions of miscibility. The plot in *Figure 4* has a similar shape and minimum to that reported by Coleman *et al.*[29] for the expected miscibility range (27–48% AN) and it acts as a valuable guide to exploring the blend ranges that should be investigated.

Another example addresses blends containing the polyhydroxy ether of bisphenol A and various aliphatic polyesters. This system has been studied by Harris *et al.*[37]; it differs from the previous system in that there are strong favourable molecular interactions, since all of the miscible blends were reported to exhibit characteristics indicative of the presence of exothermic interactions between binary components[37].

In *Table 2*, all data associated with the polymers studied by Harris *et al.*[37] are included, together with individual component solubility parameters, and various combinations of these that were used to calculate the MPs. Since these blends are expected to provide strong, favourable molecular interactions, with some competing endothermic interactions between immiscible blend components, we choose to plot the MP calculated from a combination of the hydrogen bonding and polar solubility parameter components. These MPs are plotted in *Figure 5* as a function of the CH_x/COO ratio. This curve matches that previously reported[37] and also shows a minimum at an optimum value of 4 and miscibility of all blends below MP = 1.0.

The previous study and subsequent plot was constructed using the interaction parameter χ_{12} observed from studies of melting point depression. The only two blend systems that would be judged to be immiscible from the present approach, namely PES and PHS, were also found to be immiscible by Harris *et al.*[37], thus providing an excellent check of the overall strategy.

We examined the behaviour of the MPs in polyamide systems reported recently by Ellis[39], since these systems are also strongly interacting but perhaps less so than those in the last blends considered. Ellis pointed out that a much overlooked factor of intramolecular repulsive interactions may be a key contributor to polymer blend phase behaviour. This statement is consistent with our

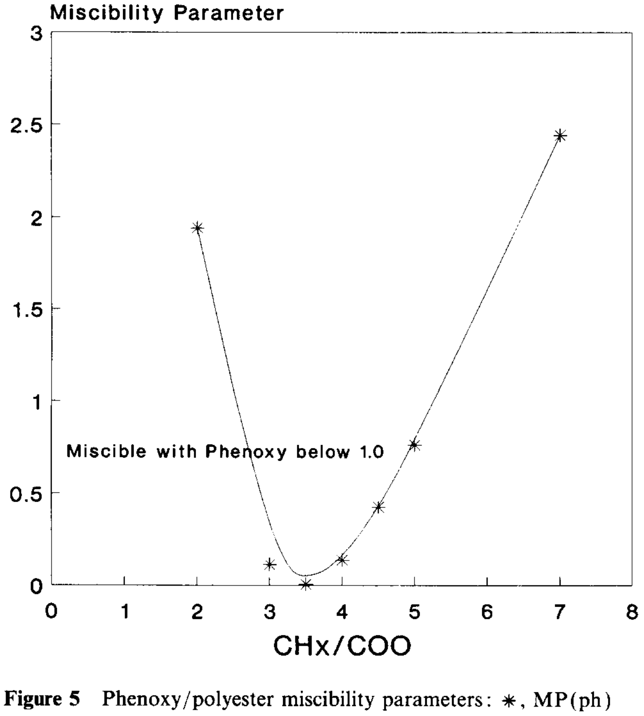


Figure 5 Phenoxy/polyester miscibility parameters: ∗, MP(ph)

Table 2 Solubility and miscibility parameter data for binary blends containing polyhydroxy ether of bisphenol A and aliphatic polyesters

Polymer[a]	δ_d	δ_p	δ_h	MP (dph)	MP (dp)	MP (dh)	MP (ph)	CH_x/COO	Miscibility[b]
Phenoxy	8.74	1.95	5.06						
PES	7.91	4.17	5.39	0.024	0.002	0.278	1.938	2	I
PEA	7.93	3.24	4.76	0.236	0.151	0.723	0.112	3	M
PBA	7.95	2.65	4.30	0.751	0.330	1.125	0.138	4	M
PCL	7.96	2.24	3.96	1.248	0.470	1.460	0.762	5	M
PHS	7.97	1.71	3.46	2.046	0.646	1.989	2.444	7	I
PDPS	7.77	2.90	4.50	0.723	0.437	1.254	0.005	3.5	M
PDPA	7.81	2.42	4.11	1.287	0.606	1.622	0.427	4.5	M
PCDS	8.02	2.39	4.08	0.951	0.343	1.212	0.482	5	M

[a] Phenoxy, polyhydroxyether of bisphenol A; PES, poly(ethylene succinate); PEA, poly(ethylene adipate); PBA, poly(1,4-butylene adipate); PCL, poly(ε-caprolactone); PHS, poly(hexamethylene sebacate); PDPS, poly(2,2-dimethyl-1,3-propylene succinate); PDPA, poly(2,2-dimethyl-1,3-propylene adipate); PCDS, poly(1,4-cyclohexane-dimethanol succinate)
[b] I, immiscible; M, miscible

interpretation that in cases where there is extremely strong intra-hydrogen bonding of groups, such as alcohols, these groups would self-associate and therefore could be viewed as repulsive interactions. Ellis used the binary interaction model, mentioned above, and determined regions of miscibility for blends of aromatic and aliphatic nylons. We found that the present scheme compares very favourably with that of Ellis but does not require previous knowledge of the concentrations where $\chi_{blend} = 0$ or an estimate of χ_{blend}. Direct comparisons of the results of Ellis' data and the present work are shown in *Figure 6*.

Table 3 compares the results of an experimental study of poly(styrene-*co*-maleic anhydride) (SMA) blends with three polymethacrylate homopolymers in which miscibility windows were determined[40] as a function of wt% MA. We have included an estimate of the miscibility window using the dispersive/hydrogen bonding miscibility parameter, MP(dh), and a value of ~0.1 as the upper limit of miscibility. As noted before the value of 0.1 is arbitrary and can be expected to change depending on the strength of segmental interactions. The MP(dh) calculation is in good agreement with the experimental results except for the lower limit in the SMA/PMMA blend.

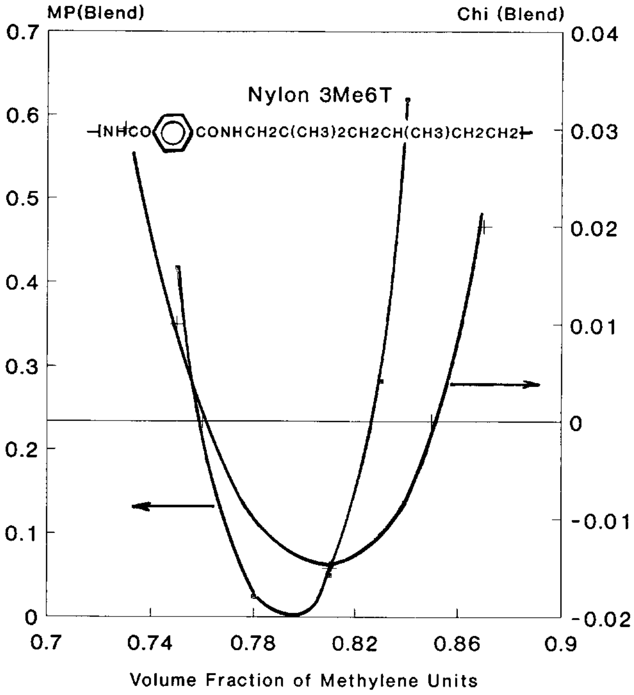


Figure 6 Miscibility parameter and χ *versus* volume fraction of methylene units: •, MP(dph); +, χ

Table 3 Miscibility windows for SMA with polymethacrylates (data from ref. 40)

Polymethacrylate	Lower limit wt% MA (MP (dh))	Upper limit wt% MA (MP (dh))
Poly (methyl methacrylate)	6–8 (0)	33–47 (38)
Poly (ethyl methacrylate)	0 (0)	33–47 (30)
Poly (n-propyl methacrylate)	0 (0)	18–25 (24)

Cimmino *et al.*[41] recently reported the failure of group contribution and solubility parameter theory in predicting the miscibility of poly(ethylene oxide)/poly(ethylene-*co*-vinyl acetate) (PEO/EVAC) blends. These authors also state that there is no optical evidence (haze?) of incompatibility in blends containing EVAC with 56 mol% or more VAC, which suggests a lower miscibility limit. *Figure 7* is a plot of mol% VAC in EVAC *versus* MP(dph). Using the MP value of 0.1 a range of VAC content from 59 to 100 mol% indicates miscible blends with PEO, which once again agrees with the experimental evidence.

Coleman *et al.*[42] have extensively studied polymer blends that self-associate and interact through hydrogen bonds. They determined that the poly(4-vinyl phenol)/poly(styrene-*co*-methyl acrylate) (PVPH/PSMA) system was miscible at 150°C up to about 65 wt% styrene in PSMA. Earlier studies showed that poly(methyl acrylate) homopolymer was miscible with PVPH, but immiscible with polystyrene. The MP calculation for this blend as a function of wt% styrene was very interesting in that the only MP that was close to the arbitrary 0.1 upper limit was MP (dp). *Figure 8* is a plot of MP(dp) *versus* wt% styrene. We conclude from these results that PSMA copolymers become immiscible with PVPH at 80–85 wt% styrene and that poly(methyl acrylate) is miscible with PVPH and immiscible with PS.

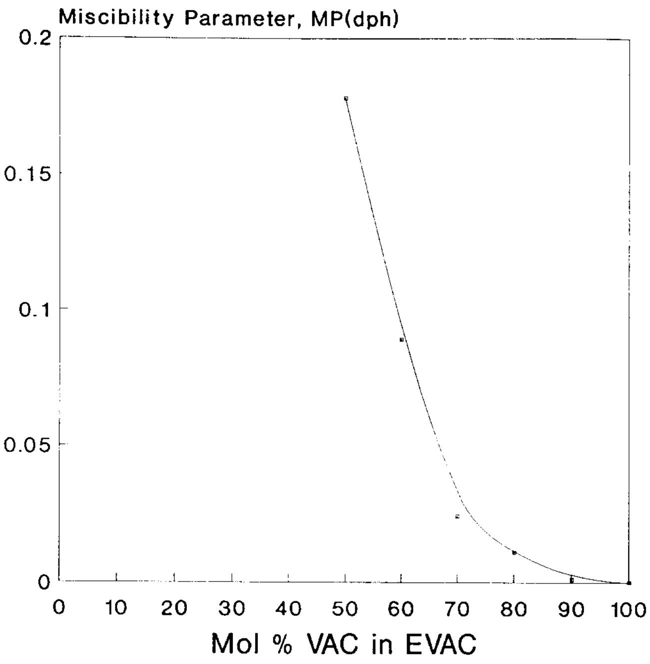


Figure 7 MP(dph) for PEO/EVAC blends

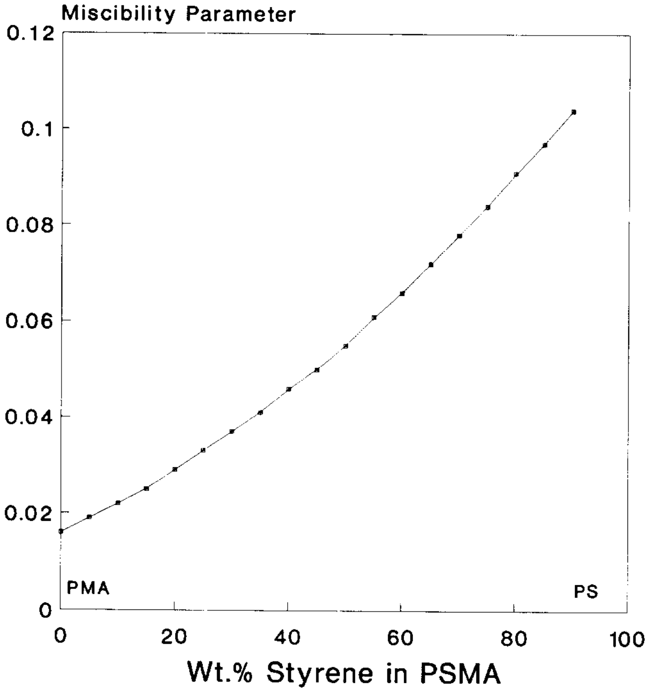


Figure 8 MP(dp) for poly(vinyl phenol)/poly(styrene-*co*-methyl acrylate)

We are directly interested in the miscibility of a polymer blend of poly(vinyl butyral) (PVB) and linear polyurethane (PU) elastomers. PUs can be prepared from a number of different starting materials; for linear urethane elastomers, the main isocyanate is methylene bis-4,4′-cyclohexyl diisocyanate (MBDCI) or methylene bis-4,4′-diphenyl diisocyanate (MBDPI) and the major soft segments are incorporated as a result of reactions with either polyethers or polyesters. The PU reported here was prepared from poly(tetramethylene ether glycol) (PTMEG) and MBDPI or MBDCI. Since the PUs were to be blended with various amounts of PVB containing different amounts of residual PVA, we felt it would be useful to develop techniques for estimating regions of compatibility which would aid in preparing miscible blends.

This polymer blending application is excellent for evaluation of this technique since it has been reported previously by Kraus[25] that PUs are not miscible with PVB. In addition, Coleman *et al.*[29] have pointed out that for materials capable of hydrogen bonding, particularly for hydroxyl-containing polymers, the *non-hydrogen bonded* solubility parameter must be used. This number is derived from essentially unassociated model compounds or hypothetical analogues that are missing the hydroxyl portion by employing the ether group contributions.

Using the approach outlined earlier – inspection of the solubility parameter contributions for the urethane components – one can see that the δ_h of VA (*Table 1*) is very much greater than the hydrogen bonding component for any of the urethane components as well as VB. Remembering the premise that copolymers interact between functional blocks, we eliminate the use of δ_h for PVA since the VA groups will tend to interact between themselves. It should be pointed out that this treatment of the block PVB segments is entirely consistent with experimental observations of hydrogen bonding of hydroxyls as judged from infra-red measurements and hydroxyl associations based on small angle neutron scattering (SANS) experiments. The favourable interactions in this blend will therefore be dominated by the polar solubility parameter component, but in conjunction with the dispersive component.

The MPs were calculated from the proper weighted combination of the polar and dispersive solubility parameter components. *Figures 9* and *10* show expected regions of miscibility for blends of PVB/PU prepared from MBDCI or MBDPI at various levels of residual VA. The problem encountered was that no molar volume listing for the NH group is given by van Krevelen[23]. Consequently, we utilized our best estimate of this molar volume group contribution, based on other NH-

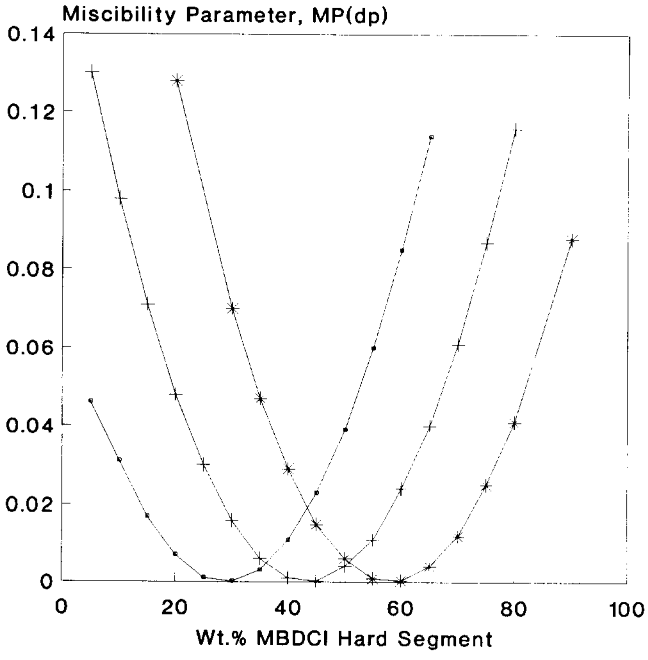


Figure 9 Miscibility parameters for PVB/MBDCI. PVOH (wt%): •, 11; +, 18; ∗, 25

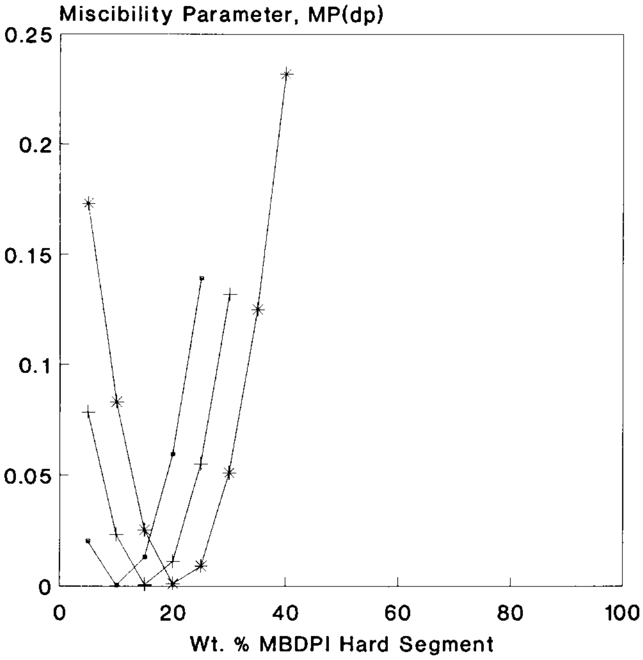


Figure 10 Miscibility parameters for PVB/MBDPI. PVOH (wt%): •, 11; +, 18; *, 25

containing compounds and a compound that conformed to the 'glassy' volume consistent with our experimental observations.

The blend containing the urethane based on MBDCI shows broader regions of miscibility at a given VA hydroxyl level. Miscibility at higher hydroxyl levels requires a higher concentration of hard segments. The same trends are evident for the urethanes prepared from MBDPI except in this case the regions of miscibility are quite narrow and occur at lower concentrations of hard segments. These results precisely parallel our experience. To illustrate this, the haze data are listed in *Table 4*; these were measured on blends of PVB and thermoplastic PU (TPU) at the indicated blend concentrations. These results are adequately supported by the curves in *Figures 9* and *10* and illustrate the power of the miscibility parameter, which uses a relatively simple, straightforward technique utilizing readily obtainable literature values. In a subsequent paper we will present experimental evidence (other than haze) for the miscibility of the PVB/PU blends in the regions of compatibility.

The MPs of the MBDPI and MBDCI hard segments indicated immiscibility with VA. As expected miscibility of the VA segment of the polymer and the PTMEG was not indicated. It will also be observed that the MP(dp)s dominate the miscibility of these blends (*Table 5*) and clearly indicate that the hard segments of the MBDCI are miscible while the MBDPI hard segments are not. This illustrates the importance of examining the influence of individual block constituents, some of which at first glance may not appear to be key factors in determining compatibility of copolymer blends.

The blend of PVB/PU is a good example that shows the value of examining various combinations of solubility parameters, since in this instance none of the other MP combinations, including MP(dph) indicate miscibility that conforms to experimental results (*Table 4*). *Figure 11* illustrates this for the PVB/MBDCI blend with PVB containing 11% PVOH.

Plots of the MP(dp)s as a function of PVOH concentration in PVB for each type of urethane hard segment show that the MBDCI is miscible in the range of ~11–20% PVOH using this MP as the criterion whereas the MBDPI is immiscible in this range of PVOH or the range used for blending (*Figures 12* and *13*).

Table 4 Haze data for PVB/TPU blends

PVOH in PVB (wt%)	TPU type	Ratio PVB/TPU (wt%)	Hard segment (wt%)	Haze (%) at 0.762 mm thickness
19.9	Aliphatic	80/20	35	2.7
		60/40		7.8
	Aliphatic	80/20	52	2.7
		60/40		3.4
	Aromatic	80/20		77
		60/40		91
18.2	Aliphatic	80/20	35	1.2
		60/40		2.0
	Aliphatic	80/20	52	1.7
		60/40		1.6
	Aromatic	80/20		24
11.7	Aliphatic	80/20	35	1.3
		60/40		1.8
	Aliphatic	80/20	52	36
		60/40		61
	Aromatic	80/20		60
		60/40		97

Table 5 Summary of PVB/TPU individual component miscibility parameters

Components	Ratio	MP(dp)
VB/PTMEG	1:1	0.003
VA/PTMEG	1:1	4.008
VB/MBDCI, hard segments	1:1	0.054
VB/MBDPI, hard segments	1:1	2.405
VA/MBDCI, hard segments	1:1	3.005
VA/MBDPI, hard segments	1:1	0.172

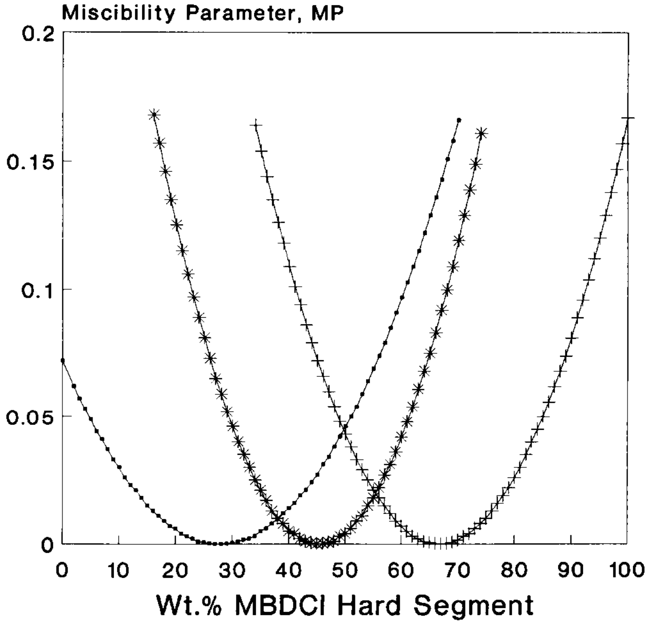


Figure 11 Miscibility parameters for MBDCI hard segment and 11% PVOH in PVB: •, (dp); +, (dph); *, (dh)

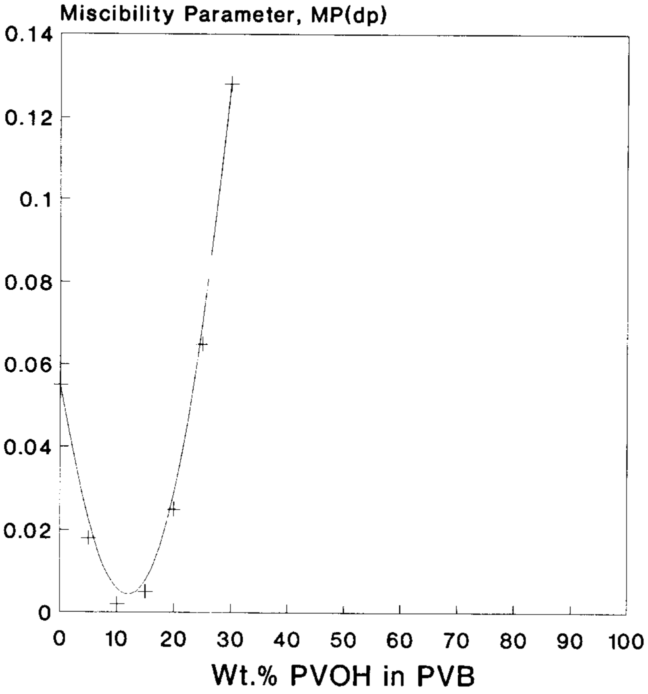


Figure 12 MP(dp) for MBDCI *versus* wt% PVOH

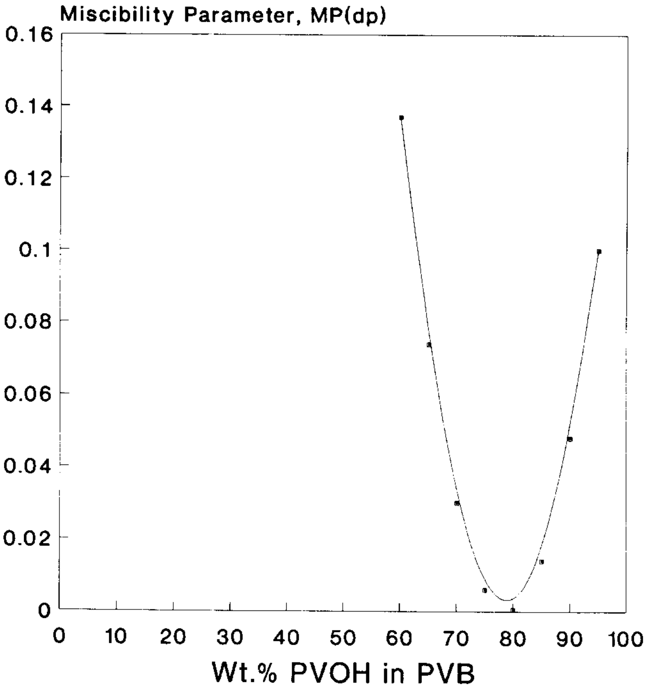


Figure 13 MP(dp) for MBDPI *versus* wt% PVOH

Molecular weight is not an overriding consideration, on the one hand because of the idea of functional block interactions, but on the other hand we would expect some instances of blend mixing where only weak favourable interactions are present, in which case this model may not be useful. Molecular weight may also influence miscibility in the ability of a certain size of miscible polymer/copolymer chain to be accommodated in the microphases of a second polymer/copolymer. However, it is encouraging that an examination of several additional blends[43] indicated that miscibility of these blends would be no surprise even though miscibility was not expected at the outset by the investigators. Nevertheless, situations may arise where combinatorial entropy for low molecular weight systems and the enthalpy of mixing are such that the weak favourable interactions do not allow miscibility to be estimated.

CONCLUSIONS

Our purpose was to investigate the use of the individual solubility parameter components in estimating polymer blend miscibilities in place of the conventional total solubility parameter. We believe the results show that this is a very useful technique that can simply and easily estimate miscibility and regions of miscibility, and is highly applicable to wide ranges of blends of industrial interest.

This approach eliminates the need for extremely accurate solubility parameter values since the same set of matrix values is used to make comparisons and detect trends because absolute values are not being tracked. Judgement of the absolute level of χ_{crit} acceptability need not be made. Also eliminated is the need to estimate non-hydrogen bonded solution parameters for highly associated materials. For any polymer blend system there are four possible MPs: MP(dph), MP(dp), MP(dh) and MP(ph). The choice of which one most accurately predicts miscibility and miscibility ranges seems formidable. In fact, the use of common sense can simplify the selection process and quickly reduce the possibilities. We have found the following guidelines useful.

1. When blend components each have significant dispersive, polar and hydrogen bonding solubility parameters, the total MP(dph) most often predicts actual behaviour. In these cases the minimum in the MP(dph) is usually closely associated with one or two other MPs in a plot of MP *versus* composition.
2. The miscibility of polymer blends with groups that show strong polar and particularly hydrogen bonding tendencies can often be determined based on the 'donor–acceptor' criterion. In other words, one can eliminate all hydrogen bonding MP combinations if one or other of the components in the blend is incapable of hydrogen bonding.
3. In the event of strong hydrogen bond formation, the use of the remaining interactions, dispersive and polar, has been used succcessfully to predict miscibility and miscibility ranges.
4. The window of miscibility has often been found to be delineated by the MP value of approximately 0.1. It is expected that the type and magnitude of blend component interactions will raise or lower this value.

The real value of the technique is that it serves to guide the industrial researcher to look for windows of compatibility in those regions of blend composition where MP approaches zero, using the numerical criteria described above.

The present work reinforces the work of Coleman *et al.*[29] and presents an alternative which uses easily obtainable literature values used in proper combination. This shows the value of utilizing conventional solubility parameters for miscibility estimations as an alternative to the more rigorous approaches developed in the past. Future effort would probably be well placed in refining the accuracy of the individual solubility parameter components as listed by van Krevelen[23], which would allow an even more accurate appraisal of miscibility and regions of miscibility.

ACKNOWLEDGEMENT

We wish to acknowledge the meaningful contributions of Professor Ashok Misra of IIT, New Delhi, India. Professor Misra first introduced us to the value of utilizing the solubility parameter concept and provided many suggestions during our collaborative efforts of past years. We are particularly indebted to him for his valuable comments during the preparation of this manuscript.

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