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Self-association *versus* interassociation in hydrogen bonded polymer blends:
2. Comparison of theoretical and experimental miscibility windows for poly(2,6-dialkyl-4-vinyl phenol) blends

George J. Pehlert, Xiaoming Yang, Paul C. Painter and Michael M. Coleman*
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
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Self-association and interassociation equilibrium constants determined from i.r. studies of miscible poly(2,6-dimethyl-4-vinyl phenol) (PDMVPh) and poly(2,6-diisopropyl-4-vinyl phenol) (PDIPVPh) blends with poly(n-butyl methacrylate) and an ethylene-*co*-vinyl acetate (EVA) copolymer are used to calculate theoretical miscibility windows for the homologous series of poly(n-alkyl methacrylate)s and the entire copolymer composition range of EVA copolymers. Miscibility gaps are predicted to increase significantly for analogous blend systems in the series PDIPVPh > PDMVPh > poly(4-vinyl phenol). One factor contributing to this trend is the steric hindrance of the 2,6-dialkyl substituents, which serve to reduce the relative strength of self-association *versus* interassociation. Experimental i.r. studies of these blend systems corroborate the overall shape and size of the single phase region of the predicted miscibility windows. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer blends; hydrogen bonding; phase behaviour)

INTRODUCTION

In the preceding paper[1] we discussed the results obtained from i.r. studies of miscible poly(2,6-dimethyl-4-vinyl phenol) (PDMVPh) and poly(2,6-diisopropyl-4-vinyl phenol) (PDIPVPh) blends with poly(n-butyl methacrylate) (PBMA) and an ethylene-*co*-vinyl acetate (EVA) copolymer containing 70 wt% vinyl acetate (EVA[70]). Equilibrium constants that describe the stoichiometry of miscible hydrogen bonded PDMVPh and PDIPVPh blends with (co)polymers containing acetoxy and methacrylate carbonyl groups were determined and we emphasized the accentuation of interassociation over self-association caused by the size (steric hindrance) of the 2,6-dialkyl substituents. This factor is predicted to favour miscibility. We can now employ these equilibrium constants to calculate the fraction of hydrogen bonded carbonyl groups, $f_{\mathrm{HB}}^{\mathrm{C=O}}$, that would be present in single phase mixtures for the entire range of EVA copolymers and the homologous series of poly(n-alkyl methacrylate) homopolymers, as a function of blend composition. By comparing experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ data obtained from such blends with the theoretical values for single phase systems, we can ascertain whether or not a particular blend composition is single phase and prepare an experimental miscibility window[2–6].

The free energy of mixing of hydrogen bonded polymer blends may be calculated from the equation:

$$\frac{\Delta G_m}{RT} = \left\{\frac{\Phi_A}{M_A}\ln\Phi_A + \frac{\Phi_B}{M_B}\ln\Phi_B\right\} + \Phi_A\Phi_B\chi + \frac{\Delta G_H}{RT} \quad (1)$$

where Φ_A and Φ_B, and M_A and M_B, are the volume fractions and degrees of polymerization of polymers A and B, respectively. This equation is discussed in the introduction to the preceding paper[1] and described in detail in refs 2 and 3. A computer program that accompanies our 1991 monograph[2] calculates the free energy, phase diagrams and miscibility windows and maps. The parameters required for the calculations include values of the equilibrium constants, enthalpies of hydrogen bond formation and segment information; molar volumes, molecular weights and solubility parameters. Since we now have, or can make informed estimates, of the values of all the parameters required to theoretically calculate miscibility windows for PDMVPh and PDIPVPh blends with EVA copolymers and the homologous series of poly(n-alkyl methacrylate) homopolymers, we can use the experimental miscibility windows to assess the predictive capabilities of our model.

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* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), toluene and methylisobutylketone (MIBK) were purchased from Aldrich Chemical Co. Inc., Milwaukee, WI. The poly(n-alkyl methacrylate)s (PAMA); poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PPMA), poly(n-butyl methacrylate) (PBMA), poly(n-hexyl methacrylate) (PHMA), poly(n-octyl methacrylate) (POMA), poly(n-decyl methacrylate) (PDMA), poly(n-lauryl methacrylate) (PLMA) and poly(n-hexadecyl methacrylate) (PHDMA); poly(vinyl acetate) (PVAc) and the ethylene-*co*-vinyl acetate (EVA) copolymers containing 70, 45, 25, 18 and 14 wt% vinyl acetate, denoted EVA[70], EVA[45] etc., have been used and described in previous blend studies[2,4-9]. An additional (EVA) copolymer containing 33 wt% vinyl acetate (EVA[33]) was purchased from Scientific Polymer Products, Inc., Ontario. It has a reported weight average molecular weight of 155 000.

Sample preparation and instrumentation

I.r. spectroscopic measurements were recorded on a Digilab model FTS60 Fourier transform i.r. (*FT*i.r.) spectrometer at a resolution of 2 cm^{-1}. All *FT*i.r. samples were sufficiently thin to be within the absorption range where the Beer–Lambert law is obeyed. Polymer blend films for transmission *FT*i.r. were cast on KBr windows from ≈2% solutions of THF in the case of the EVA blends and MIBK for the PAMA blends. Care was taken to ensure that uniform films were obtained that resulted in high quality infra-red spectra with essentially linear baselines. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 h, followed by 2 h at a temperature of 120°C for the EVA blends and 150°C for the PAMA blends, to remove residual solvent completely.

RESULTS AND DISCUSSION

The fraction of hydrogen bonded carbonyl groups and the determination of phase behavior

We commence this discussion by describing two sets of room temperature i.r. spectra (*Figures 1* and *2*) recorded in the carbonyl stretching region from films of PDMVPh and PDIPVPh blends with EVA[33], respectively. Pure EVA[33] has a non-hydrogen bonded carbonyl stretching frequency at ≈1739 cm^{-1}. The hydrogen bonded carbonyl band, on the other hand, is observed some 21 cm^{-1} lower at ≈1718 cm^{-1}. The main purpose of showing these spectra is to make the point that although there is a major contribution from hydrogen bonded carbonyl groups in both blends, one cannot simply pronounce these systems miscible. Actually, both these polymer blends are immiscible under the strict definition of miscibility, which requires a single phase over the entire composition range at a particular temperature. A two phase blend system can still exhibit a large fraction of hydrogen bonded carbonyl groups, however. For example, as we will show later, the 80/20 blend compositions of both the PDMVPh and PDIPVPh blends with EVA[33] are two phase materials.

From our monograph and recent review[2,3], it is clear that if we have a knowledge of the molar volumes of the (co)polymer segments of the two components of the blend, plus appropriate values of the dimensionless self-association and interassociation equilibrium constants, we can readily calculate the fraction of hydrogen bonded carbonyl groups as a function of the composition of the blend, *assuming that the blend is miscible* (i.e. a single phase across the entire composition). Equilibrium constants that describe the stoichiometry of miscible hydrogen bonded PDMVPh and PDIPVPh blends with (co)polymers containing acetoxy and methacrylate carbonyl groups are given in *Table 1*, and the molar volumes

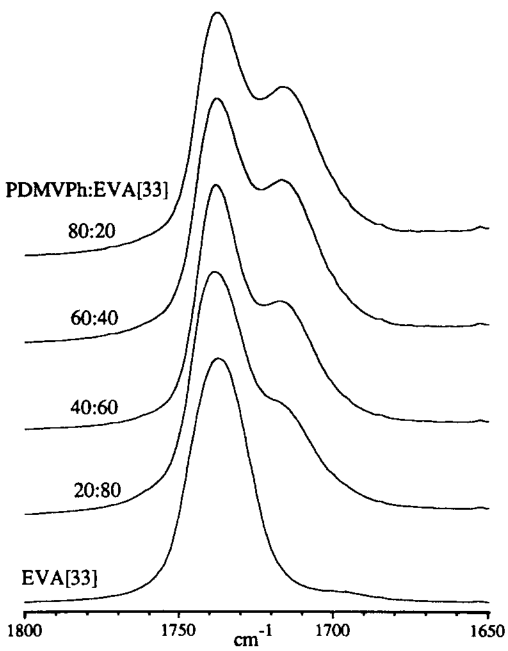


Figure 1 I.r. spectra recorded at room temperature in the carbonyl stretching region (1650–1800 cm^{-1}) of films of pure EVA[33] and PDMVPh blends containing 80, 60, 40 and 20 wt% EVA[33]

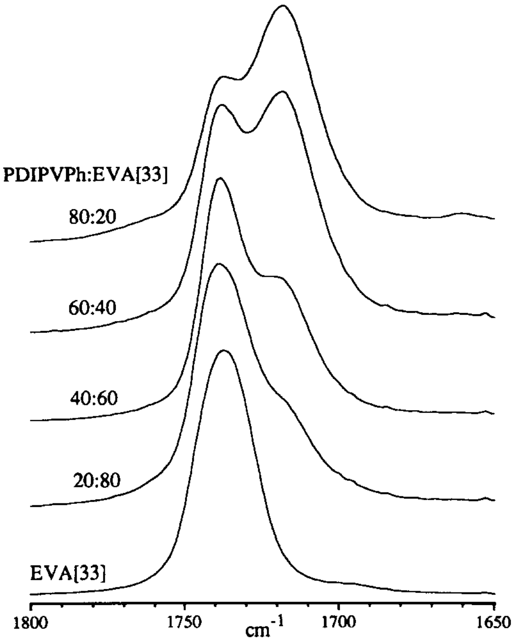


Figure 2 I.r. spectra recorded at room temperature in the carbonyl stretching region (1650–1800 cm^{-1}) of films of pure EVA[33] and PDIPVPh blends containing 80, 60, 40 and 20 wt% EVA[33]

of the phenolic polymers and carbonyl containing (co)polymers in *Tables 1* and *2*.

The least squares curve fitting methodology used to determine quantitatively the fraction of hydrogen bonded carbonyl groups $f_{\mathrm{HB}}^{\mathrm{C=O}}$, from the carbonyl stretching region of the infra-red spectrum of the PDMVPh and PDIPVPh blends with the series of PAMA homopolymers and EVA copolymers, is identical to that described in detail for the PBMA and EVA[70] blends in the previous paper[1]. In the interest of brevity, we will therefore forego the spectroscopic details and present only the $f_{\mathrm{HB}}^{\mathrm{C=O}}$ data calculated from the i.r. spectra of the individual blend compositions.

PDMVPh blends with the homologous series of poly(n-alkyl methacrylate)s. *Table 3* shows a comparison of experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ data to the theoretical values calculated from equilibrium constant values of $K_2 = 4.8$, $K_B = 17.4$ and $K_A = 24.3$ and the appropriate segment molar volumes given in *Tables 1* and *2*. As we discussed in the previous paper[1], we have most confidence in experimental results that are in the range of $f_{\mathrm{HB}}^{\mathrm{C=O}} = 0.40$–$0.70$ (estimated standard error ≈ 0.03). Values outside this range are subject to greater error because of the assumptions and vagaries of curve fitting overlapping and poorly resolved i.r. bands. It should also be recognized that if the equilibrium constants and stoichiometric equations are essentially correct, experimental values that exceed those calculated are not possible and most likely attributed to errors (because less than the maximum number of hydrogen bonds are inevitably formed if there is more than one phase). With these factors in

Table 1 Dimensionless self- and interassociation equilibrium constants

		Self-association		Interassociation	
Polymer	Molar volume ($\mathrm{cm^3\,mol^{-1}}$)	Dimer formation K_2	Multimer formation K_B	Acetoxy carbonyls K_A	Methacrylate carbonyls K_A
PVPh	100	21.0	66.8	58.0	37.8
PDMVPh	139	4.8	17.4	29.6	24.3
PDIPVPh	207	1.1	2.7	11.4	7.2

Table 2 Parameters for carbonyl containing polymers

Polymer segment	Molar volume ($\mathrm{cm^3\,mol^{-1}}$)	Solubility parameter ($\mathrm{cal\,cm^{-3}}$)$^{0.5}$	Polymer segment	Molar volume ($\mathrm{cm^3\,mol^{-1}}$)	Solubility parameter ($\mathrm{cal\,cm^{-3}}$)$^{0.5}$
PEMA	101	8.9	PVAc	69.8	9.6
PPMA	118	8.8	EVA[70]	113	9.0
PBMA	134	8.7	EVA[45]	194	8.6
PHMA	167	8.5	EVA[33]	275	8.4
POMA	200	8.4	EVA[25]	374	8.3
PDMA	233	8.4	EVA[18]	531	8.2
PLMA	266	8.3	EVA[14]	692	8.2
PHDMA	332	8.3			

Table 3 Fraction of hydrogen bonded carbonyl groups at 25°C for PDMVPh–PAMA blends

Blend composition (wt%)	Expt	Theory[a]	Blend composition (wt%)	Expt	Theory[a]
PDMVPh–PEMA			PDMVPh–PPMA		
20/80	0.19	0.18	20/80	0.20	0.19
40/60	0.38	0.38	40/60	0.40	0.41
50/50	0.48	0.48	50/50	0.49	0.50
60/40	0.55	0.55	60/40	0.56	0.57
80/20	0.65	0.68	80/20	0.68	0.69
PDMVPh–PHMA			PDMVPh–POMA		
20/80	0.28	0.22	20/80	0.28	0.26
40/60	0.46	0.45	40/60	0.37	0.49
50/50	0.53	0.53	50/50	0.32	0.56
60/40	0.59	0.59	60/40	0.40	0.61
80/20	0.75	0.70	80/20	0.48	0.71
PDMVPh–PDMA					
20/80	0.18	0.29			
50/50	0.24	0.58			
80/20	0.36	0.72			

[a] Calculated using equilibrium constant values of $K_2 = 4.8$, $K_B = 17.4$ and $K_A = 24.3$

mind, we conclude that PDMVPh is miscible with PEMA, PPMA and PHMA, because the experimental and theoretical $f_{HB}^{C=O}$ data are, within error, the same. This is depicted graphically in *Figure 3*, where the experimental $f_{HB}^{C=O}$ data for these three blends are superimposed upon the theoretical single phase curve. PDMVPh blends with POMA and PDMA, however, are obviously immiscible. Only the 20/80 PDMVPh/POMA composition has an experimental $f_{HB}^{C=O}$ value that is close to that of the theoretical.

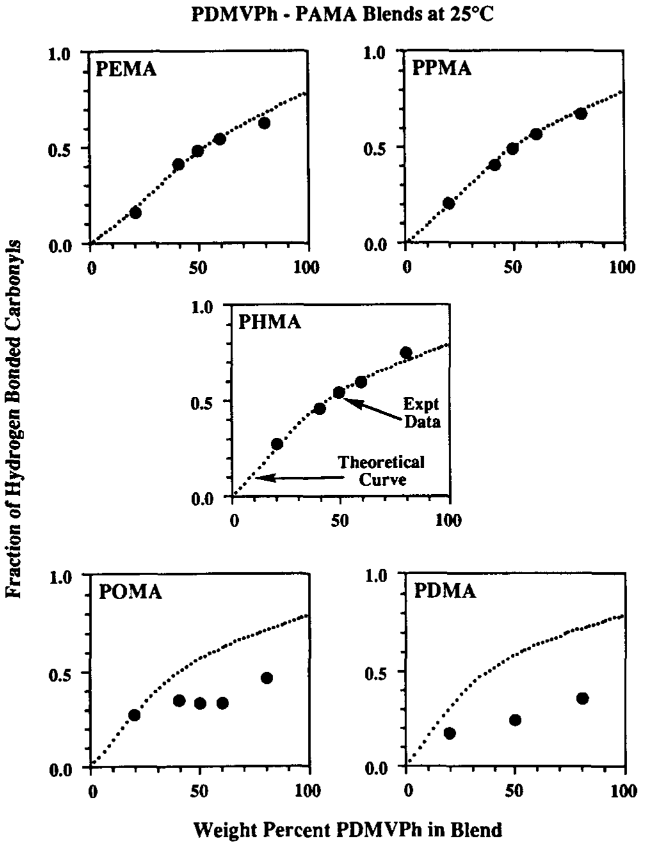


Figure 3 Comparison of experimental data (●) to the theoretical single phase curve of the fraction of hydrogen bonded carbonyl groups as a function of blend composition at 25°C for PDMVPh blends with PEMA, PPMA, PHMA, POMA and PDMA

In summary, PDMVPh forms miscible blends with the homologous series of PAMA homopolymers up to PHMA. It is interesting to note in passing that PVPh is immiscible with PHMA[2].

*PDMVPh blends with ethylene-*co*-vinyl acetate copolymers.* The corresponding data for PDMVPh blends with PVAc, EVA[45], EVA[33], EVA[25] and EVA[14] copolymers are present in *Table 4* and compared graphically in *Figure 4*. Theoretical values $f_{HB}^{C=O}$ were calculated from the set of equilibrium constants $K_2 = 4.8$, $K_B = 17.4$ and $K_A = 29.6$, together with the appropriate molar volumes (*Tables 1* and *2*). The data for the PVAc, EVA[70][1] and EVA[45] blends closely matches that calculated theoretically and these systems can confidently be identified as miscible. On the other hand, although there is a large fraction of hydrogen bonded carbonyl groups present in the EVA[33] blend compositions of >20% PDMVPh, the experimental $f_{HB}^{C=O}$ data do not match, within error, the theoretical values. The PDMVPh/EVA[33] blend system is thus immiscible at ambient temperature. Only the 20/80 PDMVPh/EVA[33] blend composition has an experimental $f_{HB}^{C=O}$ that matches that of the theoretical calculation and is thus consistent with a single phase system. In the case of the EVA[25] and EVA[14] blends there is no correspondence between the experimental and theoretical $f_{HB}^{C=O}$ values at any blend composition and these blend systems are grossly phase separated.

To summarize, PDMVPh forms miscible blends with EVA copolymers containing greater than approximately 40 wt% vinyl acetate. Below about 35 wt% vinyl acetate, PDMVPh forms two phase systems with EVA copolymers. Again, it is interesting to note that

Table 4 Fraction of hydrogen bonded carbonyl groups at 25°C for PDMVPh–EVA blends

Blend composition (wt%)	Expt	Theory[a]	Blend composition (wt%)	Expt	Theory[a]
PDMVPh–PVAc			PDMVPh–EVA[45]		
20/80	0.15	0.14	20/80	0.29	0.27
40/60	0.31	0.33	40/60	0.53	0.52
50/50	0.45	0.44	50/50	0.60	0.60
60/40	0.54	0.53	60/40	0.63	0.65
80/20	0.72	0.69	80/20	0.72	0.74
PDMVPh–EVA[33]			PDMVPh–EVA[25]		
20/80	0.37	0.34	20/80	0.09	0.40
40/60	0.44	0.57	40/60	0.19	0.61
50/50	0.49	0.64	50/50	0.22	0.66
60/40	0.51	0.68	60/40	0.25	0.70
80/20	0.53	0.76	80/20	0.35	0.77
PDMVPh–EVA[14]					
20/80	0.20	0.52			
40/60	0.34	0.66			
50/50	0.37	0.70			
60/40	0.40	0.73			
80/20	0.43	0.78			

[a] Calculated using equilibrium constant values of $K_2 = 4.8$, $K_B = 17.4$ and $K_A = 29.6$

PDMVPh blends are miscible with EVA[45] while PVPh blends are not[2].

PDIPVPh blends with the homologous series of poly(n-alkyl methacrylate)s. In the same manner as that described above, *Table 5* and *Figure 5* compare the experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ data to the theoretical values calculated from the set of equilibrium constants $K_2 = 1.07$, $K_B = 2.71$ and $K_A = 7.20$. Here we conclude that PDIPVPh is miscible with PEMA, PHMA and POMA, because the experimental and theoretical $f_{\mathrm{HB}}^{\mathrm{C=O}}$ data are, within error, the same. PDIPVPh blends with PLMA and PHDMA are obviously immiscible. As far as we can tell the PDIPVPh/PDMA blend system is right on the 'edge of miscibility'. We have repeated i.r. studies of this blend system many times, especially for those compositions rich in PDIPVPh, taking into account possible $\Delta\chi$ effects by changing solvents and thermal histories, and have consistently found that the blend compositions of >80% PDIPVPh have experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ values that fall below those predicted by theory.

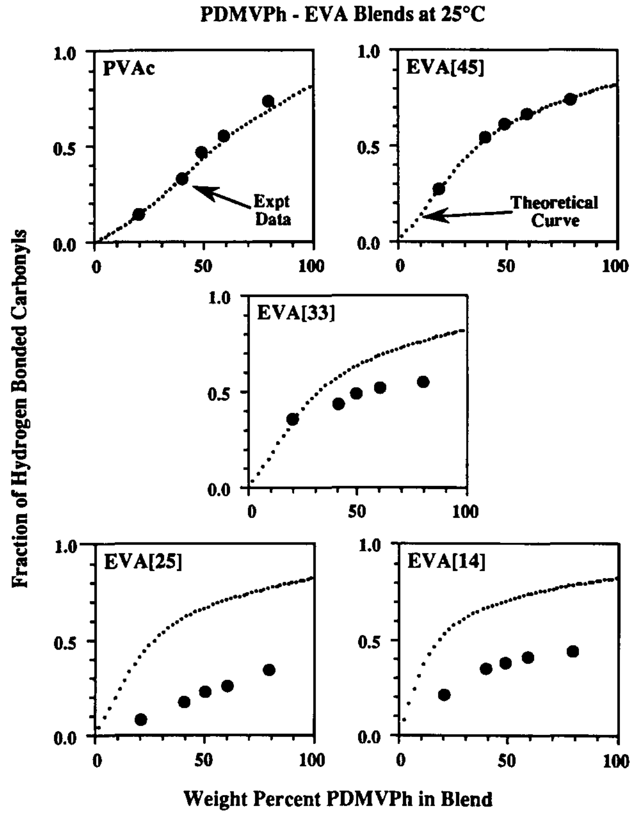


Figure 4 Comparison of experimental data (●) to the theoretical phase curve of the fraction of hydrogen bonded carbonyl groups as a function of blend composition at 25°C for PDMVPh blends with PVAc, EVA[45], EVA[33], EVA[25] and EVA[14]

In summary, PDIPVPh forms miscible blends with the homologous series of PAMA homopolymers to at least POMA, with PDMA being on the very 'edge of miscibility'. For comparison purposes, PVPh is immiscible with PHMA and higher homologues[2] and PDMVPh is immiscible with POMA and higher homologues.

*PDIPVPh blends with ethylene-*co*-vinyl acetate copolymers.* Finally, data pertaining to PDIPVPh blends with PVA, EVA[45], EVA[33], EVA[25] and EVA[18] copolymers are presented in *Table 6* and *Figure 6*. Theoretical values of $f_{\mathrm{HB}}^{\mathrm{C=O}}$ were calculated from the set of equilibrium constants, $K_2 = 1.07$, $K_B = 2.71$ and $K_A = 11.4$. The data for the PVAc, EVA[70][1] and EVA[45] blends closely match that calculated theoretically and these systems can confidently be identified as miscible. In common with the PDIPVPh–PDMA system discussed above, PDIPVPh–EVA[33] blends appear to be on the 'edge of miscibility'. The $f_{\mathrm{HB}}^{\mathrm{C=O}}$ values for compositions of $\leq 50\%$ PDIPVPh parallel those theoretically calculated and are consistent with single phase mixtures, but

Table 5 Fraction of hydrogen bonded carbonyl groups at 25°C for PDIPVPh–PAMA blends

Blend composition (wt%)	Expt	Theory[a]	Blend composition (wt%)	Expt	Theory[a]
PDIPVPh–PEMA			PDIPVPh–PHMA		
20/80	0.16	0.12	30/70	0.31	0.27
40/60	0.31	0.29	40/60	0.38	0.38
50/50	0.38	0.40	50/50	0.51	0.48
60/40	0.50	0.50	60/40	0.56	0.56
80/20	0.66	0.66	80/20	0.68	0.68
PDIPVPh-POMA			PDIPVPh-PDMA		
20/80	0.26	0.19	20/80	0.27	0.21
40/60	0.42	0.41	40/60	0.50	0.44
50/50	0.51	0.51	50/50	0.53	0.53
60/40	0.58	0.58	60/40	0.59	0.60
80/20	0.67	0.69	80/20	0.68	0.70
			90/10	0.55	0.73
PDIPVPh-PLMA			PDIPVPh-PHDMA		
20/80	0.14	0.23	20/80	0.15	0.26
40/60	0.23	0.45	40/60	0.22	0.49
50/50	0.19	0.54	50/50	0.22	0.57
70/30	0.34	0.66	60/40	0.17	0.63
90/10	0.43	0.74	80/20	0.21	0.71

[a] Calculated using equilibrium constant values of $K_2 = 1.07$, $K_B = 2.71$ and $K_A = 7.20$

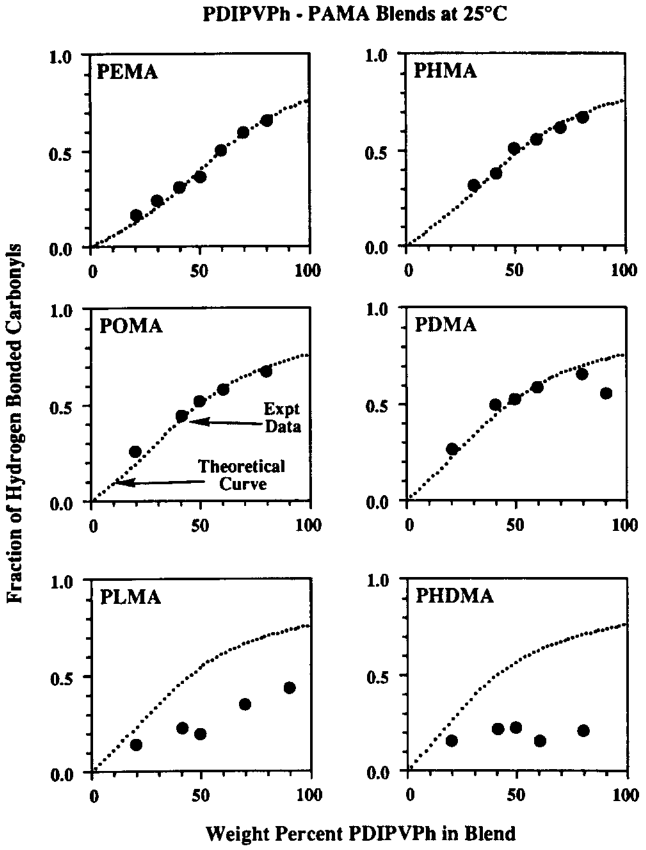


Figure 5 Comparison of experimental data (●) to the theoretical single phase curve of the fraction of hydrogen bonded carbonyl groups as a function of blend composition at 25°C for PDIPVPh blends with PEMA, PHMA, POMA, PDMA, PLMA and PHDMA

those of the 60/40 and 80/20 compositions fall below the theoretical values (outside the error limits) and are consistent with two phase mixtures. The PDIPVPh–EVA[25] and EVA[18] blends are immiscible. Only the

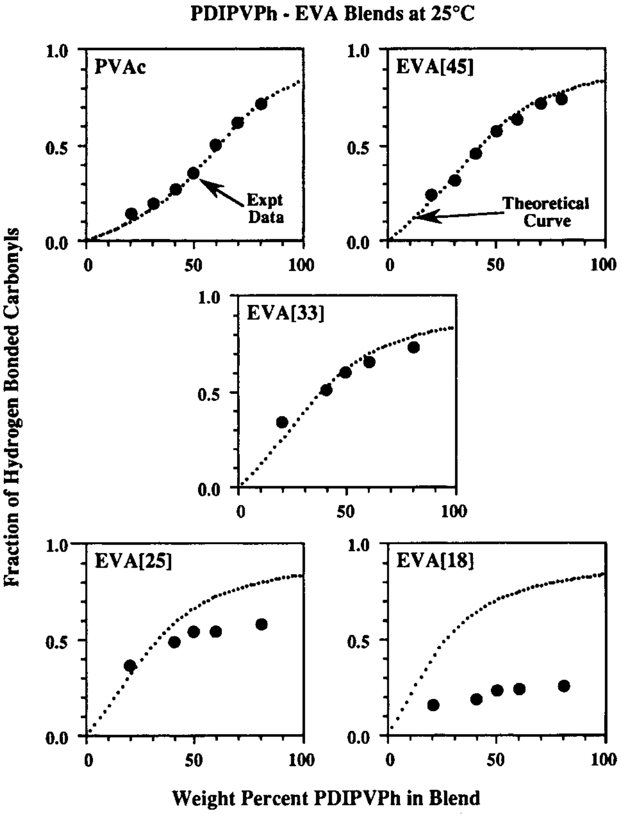


Figure 6 Comparison of experimental data (●) to the theoretical single phase curve of the fraction of hydrogen bonded carbonyl groups as a function of blend composition at 25°C for PDIPVPh blends with PVAc, EVA[45], EVA[33], EVA[25] and EVA[18]

Table 6 Fraction of hydrogen bonded carbonyl groups at 25°C for PDIPVPh–EVA blends

Blend composition (wt%)	Expt	Theory[a]	Blend composition (wt%)	Expt	Theory[a]
PDIPVPh–PVAc			PDIPVPh–EVA[45]		
20/80	0.14	0.10	20/80	0.26	0.20
30/70	0.20	0.17	30/70	0.31	0.34
40/60	0.28	0.25	40/60	0.47	0.47
50/50	0.36	0.36	50/50	0.57	0.58
60/40	0.50	0.48	60/40	0.63	0.67
70/30	0.62	0.62	70/30	0.71	0.73
80/20	0.72	0.72	80/20	0.73	0.78
PDIPVPh–EVA[33]			PDIPVPh–EVA[25]		
20/80	0.33	0.27	20/80	0.38	0.30
40/60	0.51	0.52	40/60	0.49	0.58
50/50	0.60	0.62	50/50	0.54	0.67
60/40	0.65	0.70	60/40	0.54	0.72
80/20	0.72	0.79	80/20	0.58	0.80
PDIPVPh–EVA[18]					
20/80	0.16	0.39			
40/60	0.19	0.64			
50/50	0.22	0.70			
60/40	0.24	0.75			
80/20	0.26	0.80			

[a] Calculated using equilibrium constant values of $K_2 = 1.07$, $K_B = 2.71$ and $K_A = 11.4$

20/80 PDIPVPh/EVA[25] composition has a $f_{HB}^{C=O}$ value consistent with a single phase.

To summarize, PDIPVPh forms miscible blends with EVA copolymers containing greater than approximately 35 wt% vinyl acetate.

Comparison of theoretical miscibility windows to experimental results

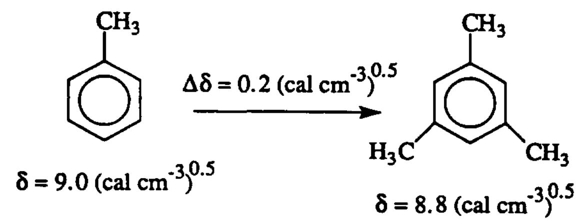
The calculation of the free energy of mixing, phase diagrams, miscibility windows and miscibility maps for hydrogen bonded polymer blends from equation (1) has been described in detail elsewhere[2,3]. Armed with the appropriate segment information and a set of equilibrium constants, theoretical miscibility windows are readily calculated using the computer software that accompanies our monograph[2]. What we are missing for the calculation of PDMVPh and PDIPVPh miscibility windows are the non-hydrogen bonded solubility parameters of these phenolic polymers.

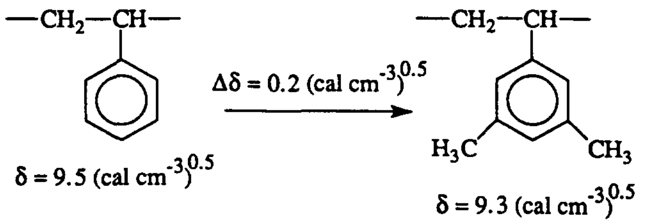
Estimating the solubility parameters of PDMVPh and PDIPVPh. The methodology employed to calculate the free energy of mixing from equation (1) requires values of non-hydrogen bonded solubility parameters that are used to calculate the value of $\chi^{2,3}$. These solubility parameters, like those listed in *Table 2*, are estimated from group molar volume and molar attraction constants that exclude contributions from strong interactions and were developed in our laboratories[2]. In the case of PVPh a rough *initial* estimate of the solubility parameters, $\delta_{PVPh} = 11.0$ $(\mathrm{cal\,cm^{-3}})^{0.5}$, was calculated from a hypothetical segment where an ether oxygen was substituted for the hydroxyl group[2]. After numerous experimental studies, the value of δ_{PVPh} was finally honed to 10.6 $(\mathrm{cal\,cm^{-3}})^{0.5}$ and we have used this value during the past 5 years without adjustment for (co)polymers containing the 4-vinyl phenol segment[3].

Unfortunately, we cannot use the same methodology for estimating the solubility parameters of PDMVPh and PDIPVPh. The problem is that we do not have, nor can we readily determine from available physicochemical data on model compounds, molar volume or molar attraction constants for tetrasubstituted phenyl rings. We can, however, examine the effect of 2,6-dialkyl substitution on the experimental and calculated solubility parameters of appropriate models to obtain a reasonable estimate of the likely difference that 2,6-dialkyl substitution would make on the known solubility parameter of PVPh.

Consider, for example, a comparison of the experimentally determined solubility parameters of toluene and 1,3,5-trimethylbenzene[10].

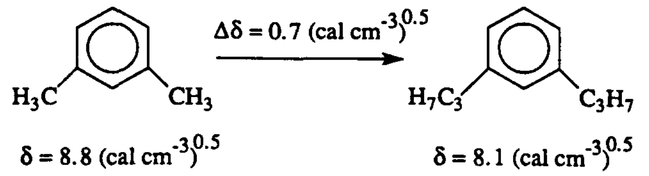
Substitution of two methyl groups onto the phenol ring of toluene only depresses the solubility parameter by $\Delta\delta = 0.2$ $(\mathrm{cal\,cm^{-3}})^{0.5}$. The same result is obtained when we compare the calculated solubility parameters[2] of polystyrene vis-a-vis poly(3,5-dimethylstyrene):



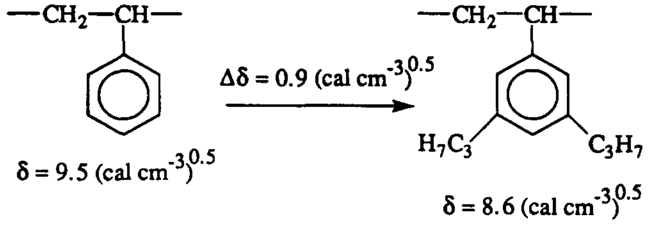


Accordingly, our best initial estimate of the non-hydrogen bonded solubility parameter of PDMVPh is 10.4 $(\mathrm{cal\,cm^{-3}})^{0.5}$ which is 0.2 $(\mathrm{cal\,cm^{-3}})^{0.5}$ less than that of PVPh.

For the case of PDIPVPh it is appropriate to compare the experimental solubility parameters of *m*-xylene with that of 1,3-diisopropylbenzene[10]:



The substitution of the two isopropyl groups for the two methyl groups on the 1,3-positions depresses the solubility parameter by ≈0.7 $(\mathrm{cal\,cm^{-3}})^{0.5}$, which yields a total of 0.9 $(\mathrm{cal\,cm^{-3}})^{0.5}$ with respect to the unsubstituted phenyl ring. Comparing the calculated solubility parameters[2] of polystyrene vis-a-vis poly(3,5-diisopropylstyrene) produces the same result:



Therefore, our best initial estimate of the non-hydrogen bonded solubility parameter of PDIPVPh is 9.7 $(\mathrm{cal\,cm^{-3}})^{0.5}$ which is 0.9 $(\mathrm{cal\,cm^{-3}})^{0.5}$ less than that of PVPh.

Theoretical miscibility windows and comparison to experimental results. *Figure 7* shows the predicted binodal miscibility window for PDMVPh blends with the homologous series of poly(n-alkyl methacrylate) calculated at 25°C, using the equilibrium constant values, molar volumes and solubility parameters given in *Tables 1* and *2*. The degree of polymerization of all the polymers was assumed to be 100. The solubility parameter for PDMVPh was set at 10.4 $(\mathrm{cal\,cm^{-3}})^{0.5}$. It can be seen that the poly(n-alkyl methacrylate)s from methyl to n-hexyl are predicted to be miscible. Two phase blend compositions are predicted to occur in PDMVPh rich blends with poly(n-heptyl methacrylate), and a progressively increasing two phase compositional area is predicted to occur as we proceed to the higher homologues.

The experimental results discussed above (*Table 3* and *Figure 3*) are superimposed onto *Figure 7*. The white (unfilled) ovals represent blend compositions that are unequivocally single phase, while the black (filled) ovals represent blend compositions that are two phase mixtures. The agreement between the theoretical and experimental miscibility window is extraordinary, and even more impressive when one considers that the set of equilibrium constant values employed was determined from a single miscible blend (PDMVPh/PBMA) and we have used no adjustable parameters in the calculation.

The corresponding comparison of predicted to experimental miscibility window for PDMVPh blends with the EVA copolymers is shown in *Figure 8*. To reiterate, the appropriate equilibrium constants etc. are listed in *Tables 1* and *2*; the solubility parameter of PDMVPh was not altered and the symbolism of the white and black ovals is the same as before. Again, the agreement between the predicted and experimental miscibility windows is fine.

Figures 9 and *10* show the predicted binodal miscibility window for PDIPVPh blends with the homologous series of poly(n-alkyl methacrylate)s and EVA copolymers, respectively. The calculations were performed using the equilibrium constant values, molar volumes and solubility parameters listed in *Tables 1* and *2*, and the degree of polymerization of all the polymers was assumed to be 500. The solubility parameter for PDIPVPh was held constant at the value determined above; 9.7 $(\mathrm{cal\,cm^{-3}})^{0.5}$. In this case poly(n-alkyl methacrylate)s from methyl to n-decyl are predicted to be miscible (i.e. single phase over the entire range of blend compositions). Two phase blend compositions are predicted to occur in PDIPVPh rich blends immediately above PDMA, and a progressively increasing two phase compositional area is predicted to occur as we proceed to the higher homologues. The experimental results (*Table 5* and *Figure 5*), superimposed onto *Figure 9*, reveal that the predicted miscibility gap is essentially correct. The breadth of the predicted two phase region for the blends of PDIPVPh with PLMA and the higher homologues is less than the experimental results indicate, however, but the shape of the curve appears correct. The corresponding

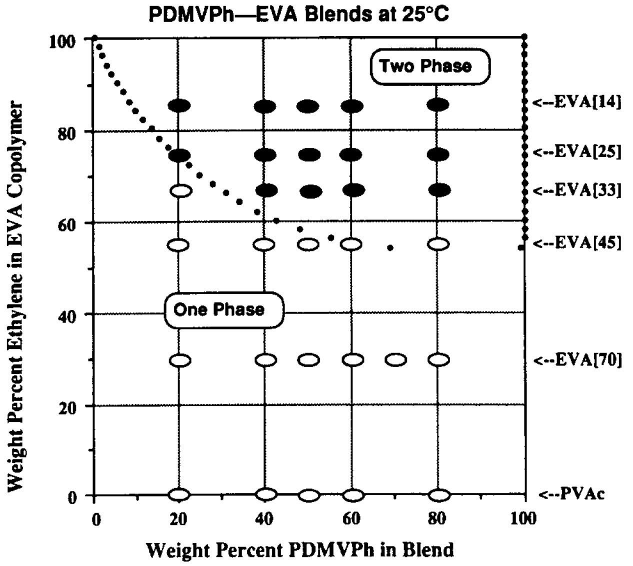


Figure 8 A comparison of the experimental data shown in *Figure 4* to the theoretical binodal miscibility window calculated at 25°C for PDMVPh blends with EVA copolymers. ○ and ● represent experimentally determined single and two phase compositions, respectively

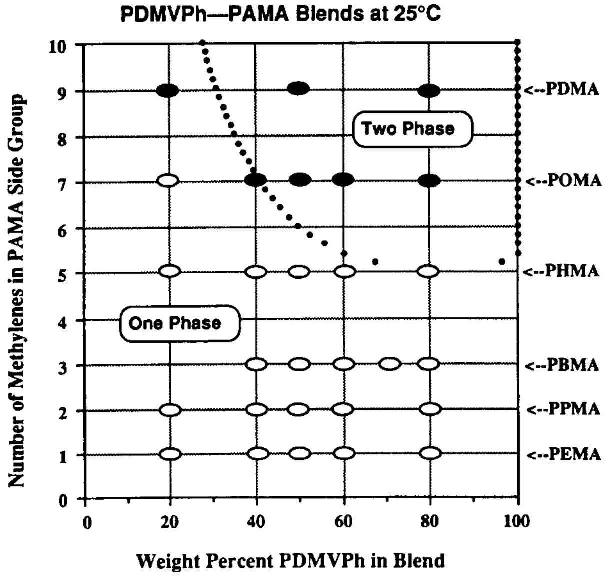


Figure 7 A comparison of the experimental data shown in *Figure 3* to the theoretical binodal miscibility window calculated at 25°C for PDMVPh blends with the homologous series of poly(n-alkyl methacrylate)s. ○ and ● represent experimentally determined single and two phase compositions, respectively

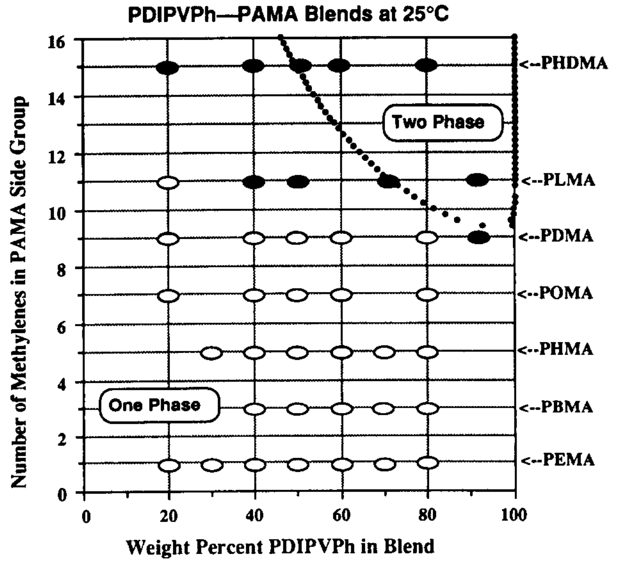


Figure 9 A comparison of the experimental data shown in *Figure 5* to the theoretical binodal miscibility window calculated at 25°C for PDIPVPh blends with the homologous series of poly(n-alkyl methacrylate)s. ○ and ● represent experimentally determined single and two phase compositions, respectively

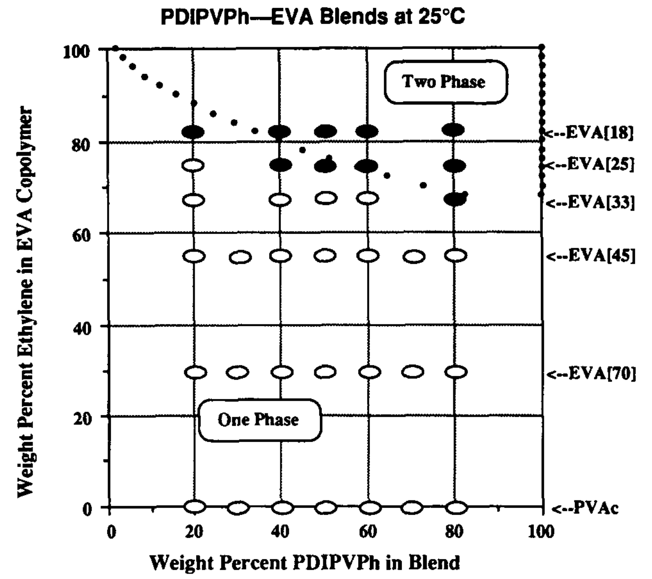


Figure 10 A comparison of the experimental data shown in *Figure 6* to the theoretical binodal miscibility window calculated at 25°C for PDIPVPh blends with EVA copolymers. ○ and ● represent experimentally determined single and two phase compositions, respectively

comparison of predicted to experimental miscibility window for PDIPVPh blends with the EVA copolymers (*Figure 10*) reveals a good agreement between the predicted and experimental miscibility windows. We are perhaps overestimating the miscibility gap to a small degree, but the shape of the miscibility boundary is matched very well. Although minor adjustments to the solubility parameter of PDIPVPh would result in a better fit in both the methacrylate and EVA miscibility windows, the effect is marginal and we prefer not to make adjustments to any of the parameters used in the calculations.

SUMMARY AND CONCLUSIONS

The confines of the miscibility gap for both the homologous series of poly(n-alkyl methacrylate)s and EVA blends are significantly larger for PDIPVPh blends than those of the analogous PVPh blends (where only methyl to n-butyl poly(n-alkyl methacrylate)s and EVA copolymers of >58% vinyl acetate are predicted to be miscible[2]), and the PDMVPh blends (where the range is from methyl to n-hexyl and >45% vinyl acetate, respectively). There are two major factors that are responsible for this increase in the miscibility gaps and they act in concert. First, as the difference between the solubility parameters of the two polymer constituents of the blend decreases, the value of χ decreases[2,3]. Since the solubility parameters of PVPh, PDMVPh and PDIPVPh decrease from 10.6 to 10.4 to 9.7 $(\mathrm{cal\,cm^{-3}})^{0.5}$, the difference in the solubility parameter for any blend with a particular poly(n-alkyl methacrylate) or EVA copolymer, must decrease in relative terms and this is a favourable trend for miscibility. Second, and the principal thrust of this work, accentuation of the 'strength' of interassociation over self-association, which we have demonstrated increases in the order PDIPVPh> PDMVPh>PVPh, enhances the favourable contribution from the $\Delta G_{\mathrm{H}}/RT$ term in equation (1) and is also a favourable trend for miscibility. These issues are addressed in greater detail in our recent review[3].

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