Functional Group Accessibility in Hydrogen-Bonded Polymer Blends. 2. Miscibility Map of 2,3-Dimethylbutadiene-*stat*-vinylphenol Blends with Ethylene-*stat*-vinyl acetate

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ABSTRACT: An experimental miscibility map for 2,3-dimethylbutadiene-*stat*-4-vinylphenol (DMBVPh) blends with ethylene-*stat*-vinyl acetate (EVA) is obtained and compared to theoretical calculations. The number of hydrogen-bonded carbonyl groups in these systems is measured by FTIR spectroscopy and some systematic trends are apparent. It is shown that the miscibility of DMBVPh/EVA blends is much more sensitive to the difference in solubility parameters than to the degree of hydrogen bonding. However, the contribution from hydrogen bonding in these mixtures is important and is significantly influenced by screening effects. A simple correlation for the dependence of the screening effect on the average spacing of functional groups in a chain is proposed and tested.

Introduction

Some 5 years have now passed since the publication of our monograph[1] where we resolved ("in the near future") to experimentally test the predicted miscibility map of butadiene-*stat*-4-vinylphenol copolymer blends with ethylene-*stat*-vinyl acetate (EVA) copolymers. We calculated that the single phase region of this system would be much greater than that of the analogous styrene-*stat*-4-vinylphenol (STVPh)/EVA copolymer blends (see Figure 1). But even more intriguing is the prediction that it may be possible to obtain miscible 2,3-dimethylbutadiene-*stat*-4-vinylphenol (DMBVPh)/EVA copolymer blends even though there are only very few carbonyl and phenolic hydroxyl groups on each chain. If true, this conjures up the possibility of an essentially miscible rubberized polyethylene blend.

Although procrastination might be suspected for our delay in testing the accuracy of the predicted DMBVPh/EVA miscibility map, in actuality, priority was assigned to a number of more facile experimental studies and some important new theoretical concepts described in our recent review.[2] We have more recently focused our attention on the synthesis of DMBVPh, but we were again sidetracked by the initial results obtained from EVA and poly(*n*-alkyl methacrylate) (PAMA) blends with a particular DMBVPh copolymer containing 24 wt % 4-vinylphenol (DMBVPh[24]). The enhanced composition range over which we were able to obtain miscible DMBVPh[24] blends with EVA copolymers and PAMA homologues relative to the analogous STVPh blends[1,2] permitted us to test the scaling and transferability of self- and interassociation equilibrium constants and study the accessibility of functional groups.[3] This is an important factor in the mixing of polymers, involving chain connectivity effects, steric shielding, the spacing between identical specific interaction sites, and so on. While this has tended to complicate the simple prediction of miscibility windows and maps for hydrogen-bonded (co)polymer blends, it has opened up a number of new areas of fundamental research. But before we get diverted yet again, we report in this paper the results of the experimental studies of the complete DMBVPh−EVA miscibility map and compare the data to that theoretically predicted.

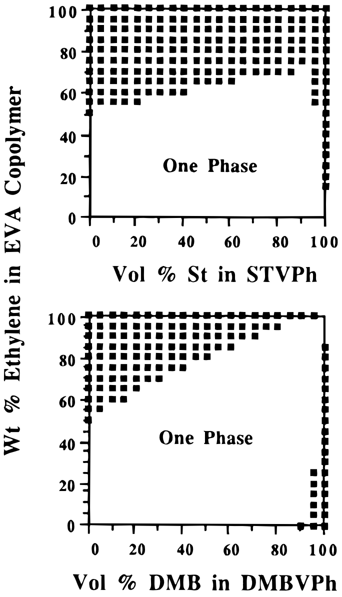

Figure 1. Theoretical miscibility maps calculated at room temperature using a constant K_A^{Std} value of 58.0. (Top) EVA blends with STVPh. (Bottom) EVA blends with DMBVPh.

Experimental Section

Poly(vinyl acetate) (PVAc) and the ethylene-*co*-vinyl acetate (EVA) copolymers containing 70, 45, 33, 25, 18, 14, and 9 wt % VAc, denoted EVA[70], etc., have been described in previous blend studies.[1−3] The synthesis of 2,3-dimethylbutadiene (DMB) copolymers containing 4-vinylphenol (VPh) was described in the previous paper of this series.[3] DMBVPh[84], DMBVPh[52], DMBVPh[24], and DMBVPh[9], DMB copolymers containing 84, 52, 24, and 9 wt % VPh, respectively, were synthesized. These copolymers have number-average molecular weights of 30 000, 15 100, 29 000 and 13 800, respectively, as determined by gel permeation chromatography (GPC) using polystyrene standards. Polydispersities were in the range of 2.1−2.5. Glass transition temperatures of 128, 48, 11, and −7 °C, respectively, were determined from thermal analysis, and the copolymer compositions were determined by ^{1}H NMR.

Polymer blend films for infrared analysis were cast on KBr windows from 1% solutions in a common solvent. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 h to completely remove residual solvent. Several different solvents

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(tetrahydrofuran, methyl ethyl ketone, methyl isobutyl ketone, and toluene) were employed, and the one chosen for a particular blend was predicated upon mutual solubility. The polarity of the EVA (co)polymers changes significantly with copolymer composition and it was necessary to perform solubility studies to find “good” solvents in order to avoid the preferential precipitation of one of the (co)polymers during evaporation of the solvent.[3]

Infrared spectroscopic measurements were recorded on a Digilab model FTS60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. Special attention was paid to ensure that all the samples examined were sufficiently thin to be within the absorption range where the Beer−Lambert law is obeyed. ^1H and ^{13}C NMR spectra were obtained on Bruker WP-200 and 300 MHz FT-NMR spectrometers using tetramethylsilane as an internal standard. Molecular weights and molecular weight distributions were determined by GPC using a Waters 150C GPC/AL equipped with a refractive index detector and four μStyragel columns, 100 000, 10 000, 500, and 100, connected in series. Calibration was performed using polystyrene standards. Thermal analysis was conducted on a Seiko Instruments differential scanning calorimeter (DSC-220CU) coupled to a computerized data station. A heating rate of 20 °C/min was used and the glass transition temperatures recorded as the midpoint of the heat capacity change.

Results and Discussion

Functional Group Accessibility. In a recent paper[3] we defined an interassociation equilibrium constant, K_A^{Std}, that is scaled to a standard reference molar volume of $V_B = 100$ cm^3/mol (the molar volume of the PVPh segment) at 25 °C. K_A^{Std}, in effect, describes the fraction of hydrogen-bonded carbonyl groups formed in a miscible polymer blend of a particular composition that is composed of one (co)polymer containing phenolic hydroxyl groups (e.g. DMBVPh[24]) and another containing ester or acetoxy carbonyl groups (e.g. EVA[45]), with the proviso that the comonomers under consideration (i.e. DMB or ethylene in the above cases) are “inert diluents” (i.e. non-hydrogen bonding). If there were no problems of functional group accessibility, the value of K_A^{Std} experimentally determined from a miscible blend of PVPh (or DMBVPh, STVPh, etc.) with any EVA copolymer should be identical (the differences in the size of the interassociating specific repeat units being accounted for in the stoichiometric equations by the factor r defined as the ratio of the molar volumes of segments A and B, i.e., V_A/V_B, see ref 1, pp 214−220). Recent results obtained from miscible DMBVPh[24] blends with EVA copolymers of varying VAc content demonstrated that this hypothesis is incorrect.[3] It was found that the value of K_A^{Std} increases with increasing space between carbonyl groups along the EVA copolymer chain (expressed in terms of R, the average molar volume between VAc groups in the specific repeat of the EVA copolymer). A saturation limit was observed, however, above which further separation did not appear to enhance accessibility to any measurable extent. This represents a limiting value of K_A^{Std}, i.e. one that reflects the “true” K_A^{Std} value in the absence of any problems of “screening” or functional group accessibility. Furthermore, it was noted that the experimental K_A^{Std} values determined from miscible PVPh blends with EVA[70] were significantly lower than those determined from the analogous DMBVPh[24] blends, inferring a similar “screening” effect associated with the relative spacing of VPh groups in the respective phenolic copolymers. This we will be able to test more rigorously in this work.

Before we commence with the details of this current work, it is perhaps helpful to summarize our experimental methodology. In the first place we have extended our infrared studies to include measurements of the fraction of hydrogen-bonded carbonyl groups, $f_{HB}^{C=O}$, from EVA blends with DMBVPh[84], DMBVPh[52], and DMBVPh[9]. Where appropriate, thermal analysis (DSC) and visual observations of the blends at 100 °C were used to confirm or refute miscibility. These results, together with the data previously published for miscible EVA blends with PVPh[1] and DMBVPh[24],[3] have permitted us to prepare a matrix of results from miscible blends that represent K_A^{Std} values as a function of both the spacing of phenolic hydroxyls and acetoxy carbonyls in the respective copolymers. Next, an equation that expresses K_A^{Std} for any hypothetical single phase blend for DMBVPh/EVA containing specific copolymer compositions has been developed. This permits the calculation of the $f_{HB}^{C=O}$ for any miscible DMBVPh/EVA blend, which can then be compared to experimental infrared data.

Miscible DMBVPh/EVA Blends. Infrared spectroscopy is an excellent molecular level probe of intermolecular hydrogen-bonding interactions. Moreover, it is also possible to positively determine whether or not a particular blend is one- or two-phase from infrared measurements at a given temperature, providing that we have a prior knowledge of the values of the self-association (K_2, K_B) and interassociation (K_A) equilibrium constants that together describe the distribution of hydrogen-bonded species present in a miscible system of the two polymers through the appropriate stoichiometric equations.[1,2] In the absence of precise equilibrium constant values, it is still possible to positively conclude that a particular blend is two-phase from the lack (or only minor presence) of a hydrogen-bonded carbonyl band in systems such as DMBVPh/EVA blends. Where results become equivocal is in the case where a significant $f_{HB}^{C=O}$ is observed and it is not possible to distinguish between a single-phase system and one that is two-phase, where each of the two phases contain significant concentrations of both (co)polymers.

In this study it was crucial to independently verify whether or not particular DMBVPh/EVA blends are miscible in the amorphous state, because it is from these blends that $f_{HB}^{C=O}$ measurements will be made and the values of K_A^{Std} determined. Given the limited amount of the DMBVPh copolymers available we were restricted to thermal analysis and visual examination of blend films at 100 °C (above the T_m of the EVA copolymers).

Starting with the DMBVPh[84] blends, visual examination of the blend films used in the infrared studies at 100 °C revealed that the PVAc and EVA[70] blends were perfectly clear, but the EVA[45] and EVA[33] blends appeared translucent, consistent with one- and two-phase blend systems, respectively. From DSC studies, conventional glass temperatures (T_g) at 128, 22, −14, and −28 °C were determined for DMBVPh[84], PVAc, EVA[70], and EVA[45], respectively. It is also safe to state that the T_gs of EVA copolymers containing <45 wt % VAc occur below −28 °C and decrease with increasing ethylene content. However, any transition observed by DSC is unlikely to be representative of the pure amorphous state because of complications caused by the broad melting, annealing, and recrystallization of ethylene sequences in the EVA copolymers (see Figure 2). Both the DMBVPh[84] blends with PVAc and EVA[70] (50:50 by weight) exhibited single distinct broad T_gs at 60 and 34 °C, indicating that these blends are miscible. In contrast, for the DMBVPh[84] blends with EVA[45] and EVA[33], the thermograms exhibited

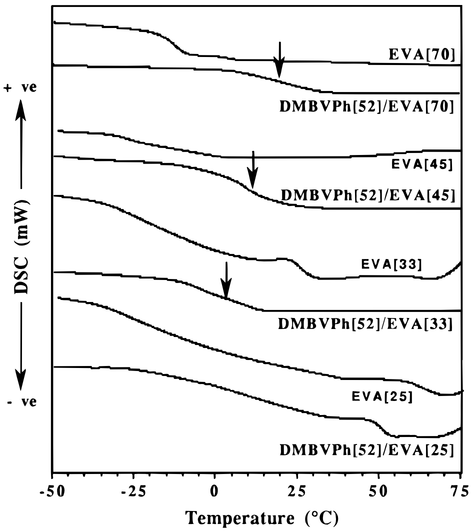


Figure 2. DSC thermograms of pure EVA[70], EVA[45], EVA-[33], and EVA[25] together with the corresponding 50:50 wt % DMBVPh[52] blends.

multiple transitions and it could confidently be concluded that these were indeed immiscible blends.

Pure DMBVPh[52] has a conventional T_g of 48 °C. Typical DSC thermograms of 50:50 blends are shown in Figure 2. All the blends with PVAc, EVA[70], EVA-[45], and EVA[33] are transparent at 100 °C and exhibit clear single T_gs at ≈38, 20, 8, and 0 °C, respectively. This verifies that these are miscible blend systems. It is of interest to note that in the latter two blend systems crystallization of the ethylene sequences appears suppressed (see Figure 2), making it easy to observe the single T_gs. The corresponding EVA[25] blend exhibited multiple transitions and the thermogram is complicated by the presence of crystalline ethylene sequences. More importantly, however, is the appearance of a transition at ≈50 °C (the bottom thermogram in Figure 2), which is close to the T_g of pure DMBVPh[52]. From these observations, and the fact that the film at 100 °C is translucent, it is reasonable to conclude that this blend system is immiscible.

Turning now to the DMBVPh[24] blends, frankly, the interpretation of the DSC thermograms obtained from these blends, especially those containing EVA copolymers rich in ethylene, is ambiguous. Notwithstanding, DMBVPh[24] has a T_g of 11 °C and 50:50 blends of DMBVPh[24] with PVAc, EVA[70], EVA[45], and EVA-[25] exhibited clear single broad T_gs at ≈17 (not truly conclusive, because of the close proximity of the T_gs of the pure materials), 5, 0, and −6 °C, respectively. These results, together with observation that the blend films are transparent at 100 °C, confirms that they are miscible blend systems. The thermograms of the EVA-[18], EVA[14], and EVA[9] blends simply defy unequivocal interpretation. There is reasonable evidence for a single T_g at −12 °C for the EVA[18] blend, but the onset of melting, reorganization, and recrystallization very close to this transition precludes any certainty in assigning this transition to an intermediate T_g. The thermograms of the corresponding EVA[14] and EVA-[9] blends exhibit multiple transitions and are seriously complicated by the presence of the crystalline ethylene sequences, so that no definitive interpretation could be made. Because of this uncertainty, we will not employ the infrared data obtained from the DMBVPh[24] blends with EVA[18], EVA[14] or EVA[9] in the forthcoming calculations of K_A^{Std}.

DMBVPh[9] has a T_g of −7 °C. Judging from the translucent character of DMBVPh[9]/PVAc blend at 100 °C, this blend system is immiscible. The EVA[70] blend appeared transparent at 100 °C, but because the T_g of EVA[70] is so close to that of pure DMBVPh[9] (−12 and −7 °C, respectively), we were unable to unambiguously establish that the blend was indeed miscible by thermal analysis. The EVA[45] and EVA[25] blends, however, could be characterized by thermal analysis. Single intermediate T_gs of −13 and −14 °C, respectively, were observed for the 50:50 blends, although again these are unlikely to be representative of the true amorphous state. These results, together with observation that the blend films are transparent at 100 °C, indicate that these blends are miscible. Thermal analysis of the EVA-[18], EVA[14], and EVA[9] blends were not attempted for the same reason outlined above for the corresponding DMBVPh[24], blends and the infrared data obtained from the DMBVPh[9] blends with EVA[18], EVA[14], or EVA[9] were not used in the forthcoming calculations of K_A^{Std}.

Determination of K_A^{Std} from the Miscible DMBVPh/EVA Blends. Armed with a significant number of miscible DMBVPh/EVA blends of varying VPh and VAc copolymer compositions, we can now proceed to evaluate the affect of functional group accessibility and attempt to develop an equation that relates K_A^{Std} to the spacing between functional groups in both polymer chains. But first we must determine K_A^{Std} from the experimental $f_{HB}^{C=O}$ data.

The reader should note that we have previously determined that poly(4-vinyl phenol) (PVPh) is miscible with PVAc and EVA[70] but immiscible (in the sense that there is not a single phase at all points across the entire composition range at a particular temperature) with EVA copolymers containing less than ≈50 wt % VAc.[1] Copolymerizing DMB with VPh has three major effects pertaining to phase behavior. First, the number of specific interacting sites (phenolic hydroxyl groups) per unit volume is reduced, which, in turn, reduces the magnitude of the potential contribution from the so-called "chemical" forces (the $\Delta G_H/RT$ term in eq 1).

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

This is not a necessarily bad trend for miscibility, as it can be more than offset by the second factor, the value of the average non-hydrogen-bonded solubility parameter (δ_B) of the specific repeating unit (i.e. that containing one phenolic hydroxyl group). Incorporating DMB into the polymer chain decreases the value of δ_B, which brings it closer to that of a typical olefinic (co)polymer, reducing the unfavorable contribution from "physical" forces (the $\Phi_A\Phi_B\chi$ term in eq 1).[1,2] Third, as we have recently reported, the random incorporation of DMB into the polymer chain spaces the phenolic hydroxyl groups further apart and makes them more accessible, which is reflected in an increase in the ratio of the interassociation to self-association equilibrium constants; this favors miscibility.[3]

Figure 3 shows the carbonyl stretching region of the experimentally obtained infrared spectra (LHS) of 60:40 (wt %) DMBVPh[84] blends with PVAc, EVA[70], EVA[45], and EVA[33], recorded at 100 °C (the simulated spectra shown on the right-hand side will be discussed later). (A temperature of 100 °C was chosen because it is a temperature above the T_g of the blends,

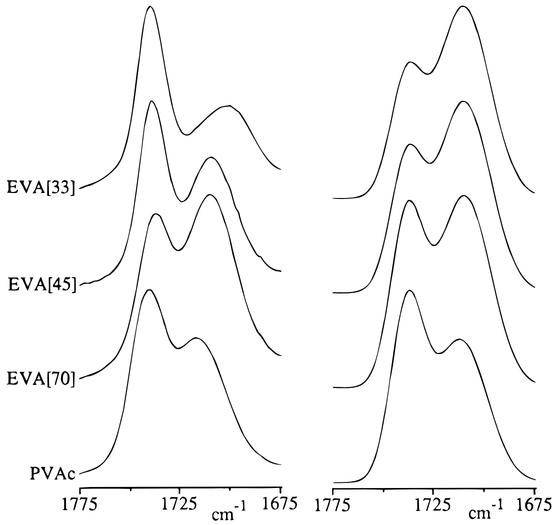


Figure 3. (Left): Infrared spectra of 60:40 wt % DMBVPh[84] blends with PVAc, EVA[70], EVA[45], and EVA[33] recorded at 100 °C in the carbonyl stretching region (1675−1775 cm^{-1}). (Right): Corresponding synthesized spectra for single-phase blends calculated from K_A^{Std} values determined from eq 8.

Table 1. Dimensionless Self-Association Equilibrium Constants at 25 °C

polymer	molar volume (cm^3/mol)	dimer formation, K_2	multimer formation, K_B
PVPh	100	21.0	66.8
DMBVPh[84]	126	16.7	53.2
DMBVPh[52]	224	9.4	29.8
DMBVPh[24]	525	4.0	12.7
DMBVPh[9]	1460	1.4	4.6

which facilitates attainment of equilibrium. It is also above the T_m of any residual EVA crystallinity that could be formed in the blends, but below the point where oxidative degradation becomes a concern). At the risk of boring those who are familiar with our work, the infrared band at ≈1738 cm^{-1} is assigned to "free" (i.e. non-hydrogen-bonded) carbonyl groups, while that at ≈1710 cm^{-1} is attributed to hydrogen-bonded carbonyl groups. Quantitative measurements of $f_{HB}^{C=O}$ from such spectra is now routine, after due consideration is given to the optimum blend composition necessary to minimize errors and a careful self-consistent curve fitting procedure.[1−3] Since this and the methodology used to calculate interassociation equilibrium constants have been discussed in depth in recent publications,[2,3] we simply present in Tables 1 and 2 the values of the molar volumes, V_B, and the dimensionless self-association equilibrium constants K_2 and K_B for the DMBVPh copolymers, the values of $K_A^{100\,°C}$ (the interassociation equilibrium constant determined at 100 °C), $K_A^{25\,°C}$ (the value calculated at 25 °C using the van't Hoff equation with an enthalpy of hydrogen bond formation, $h_A = -4.1$ kcal/mol), and K_A^{Std} (the standard equilibrium constant at 25 °C scaled to a molar volume of 100 cm^3/mol). Those values pertaining to the two miscible DMBVPh[84] blends with PVAc and EVA[70] are included in Table 2.

Proceeding now to the DMBVPh[52]/EVA blends, Figure 4 shows experimental infrared spectra (left-hand side) of 70:30 (wt %) DMBVPh[52] blends with PVAc, EVA[70], EVA[45], EVA[33], and EVA[25], recorded at 100 °C in the carbonyl stretching region. As we have independently determined that the first four DMBVPh[52] blends are miscible, the values of $K_A^{100\,°C}$, $K_A^{25\,°C}$, and K_A^{Std} were determined and included in Table 2.

Table 2. Dimensionless Interassociation Equilibrium Constants Calculated from Miscible DMBVPh/EVA Blends

polymer blend	$K_A^{100°C}$	$K_A^{25°C}$ [a]	K_A^{Std} [b]	R_A	R_B
PVPh/PVAc	6.80[c]	53.0	53.0	0	0
PVPh/EVA[70][1]	7.48[c]	58.3	58.3	43.4	0
DMBVPh[84]/PVAc	11.1	44.9	56.4	0	25.6
DMBVPh[84]/EVA[70]	13.3	53.6	67.3	43.4	25.6
DMBVPh[52]/PVAc	8.27	33.5	75.0	0	124
DMBVPh[52]/EVA[70]	8.70	35.2	79.0	43.4	124
DMBVPh[52]/EVA[45]	9.30	37.6	84.2	124	124
DMBVPh[52]/EVA[33]	9.83	39.8	89.1	205	124
DMBVPh[24]/PVAc[3]	3.80	15.4	80.6	0	425
DMBVPh[24]/EVA[70][3]	4.37	17.7	92.9	43.4	425
DMBVPh[24]/EVA[45][3]	4.53	18.3	96.1	124	425
DMBVPh[24]/EVA[25][3]	4.82	19.5	102	304	425
DMBVPh[9]/EVA[45]	1.68	6.80	99.1	124	1360
DMBVPh[9]/EVA[25]	1.81	7.30	106.4	304	1360

[a] Calculated at 25 °C using $h_A = -4.1$ kcal/mol. [b] Scaled to a reference molar volume of 100 cm^3/mol at 25 °C. [c] Determined at 150 °C.

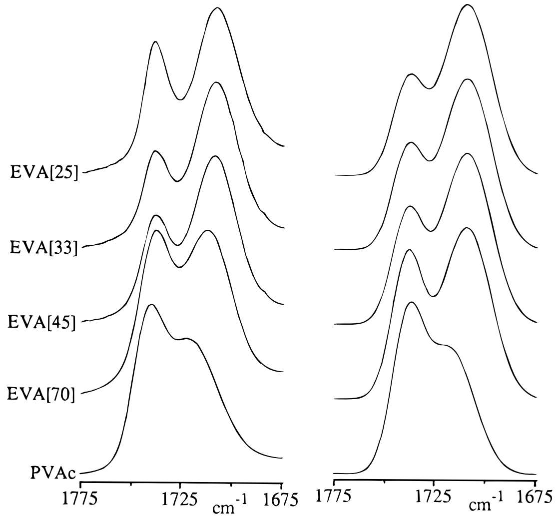


Figure 4. (Left): Infrared spectra of 70:30 wt % DMBVPh[52] blends with PVAc, EVA[70], EVA[45], EVA[33], and EVA[25] recorded at 100 °C in the carbonyl stretching region (1675−1775 cm^{-1}). (Right): Corresponding synthesized spectra for single-phase blends calculated from K_A^{Std} values determined from eq 8.

Similarly, Figures 5 and 6 show the experimental infrared spectra (left-hand side) of 80:20 (wt %) DMBVPh[24] and 90:10 (wt %) DMBVPh[9] blends, respectively, with PVAc, EVA[70], EVA[45], EVA[25], EVA[18], EVA[14], and EVA[9], recorded at 100 °C in the carbonyl stretching region. Again, only those blends where we have independent (i.e. other than infrared) evidence of single phase blends were values of $K_A^{100\,°C}$, $K_A^{25\,°C}$ and K_A^{Std} determined, and these values are also included in Table 2.

An Equation Describing K_A^{Std} as a Function of Screening. The values of K_A^{Std} shown in Table 2 clearly indicate a systematic variation with copolymer composition, in the sense that as we increase the spacing between hydrogen-bonding functional groups K_A^{Std} increases. In this section we will attempt to account for this phenomenon in a simple fashion. Let L_A and L_B be the average spacing between the functional groups for the EVA and DMBVPh copolymers, respectively. These are, of course, linear functions of the molar volumes of the "inert diluents" R_A and R_B, as illustrated schematically in Scheme 1.

Let l_A and l_B be the "screening distance", i.e. the length of the polymer chain that is effectively screened by a carbonyl or phenolic hydroxyl group, respectively.

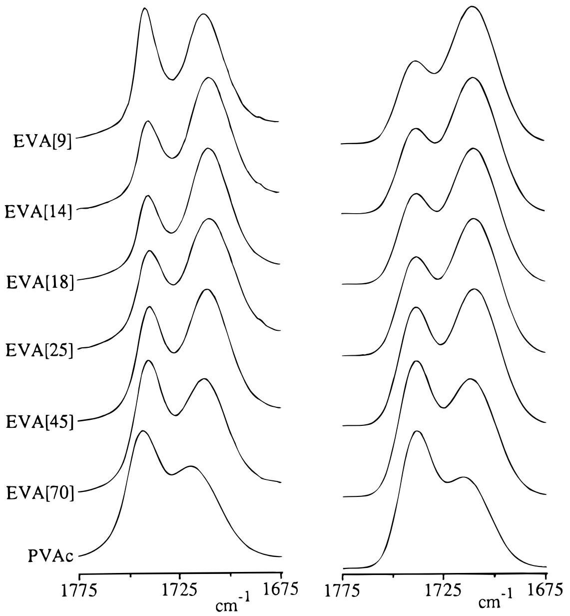


Figure 5. (Left): Infrared spectra of 80:20 wt % DMBVPh-[24] blends with PVAc, EVA[70], EVA[45], EVA[25], EVA[18], EVA[14], and EVA[9] recorded at 100 °C in the carbonyl stretching region (1675−1775 cm^{-1}). (Right): Corresponding synthesized spectra for single-phase blends calculated from K_A^{Std} values determined from eq 8.

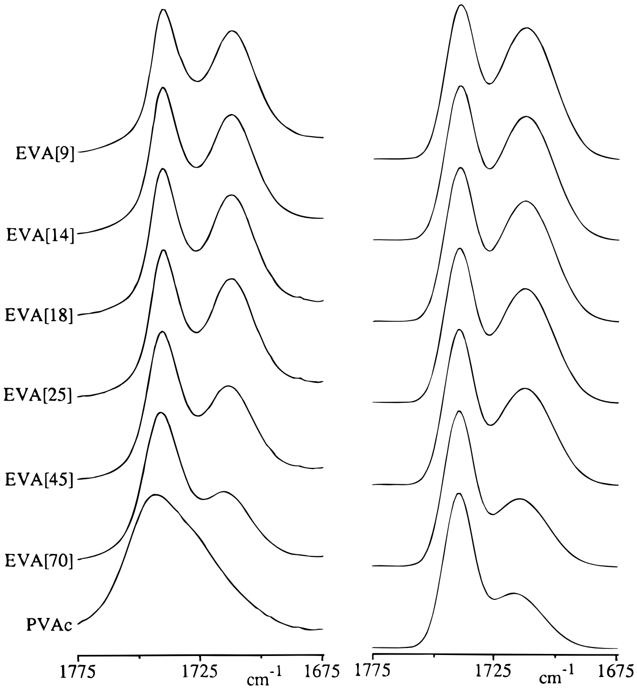


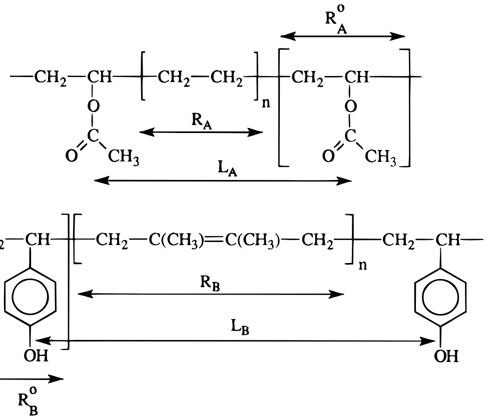
Figure 6. (Left): Infrared spectra of 90:10 wt % DMBVPh-[9] blends with PVAc, EVA[70], EVA[45], EVA[25], EVA[18], EVA[14], and EVA[9] recorded at 100 °C in the carbonyl stretching region (1675−1775 cm^{-1}). (Right): Corresponding synthesized spectra for single phase blends calculated from K_A^{Std} values determined from eq 8.

We will assume that the spacings between functional groups are uncorrelated. Then the effective number of carbonyl and phenolic hydroxyl groups in the mixture per unit volume are

$$n'_A = n_A\left(1 - \frac{l_A}{L_A}\right) \qquad n'_B = n_B\left(1 - \frac{l_B}{L_B}\right) \qquad (2)$$

where n_A and n_B are the "true" numbers of the corresponding groups per unit volume.

Scheme 1



Essentially, by using eq 2 we are assuming that only a certain fraction of the groups are accessible. The molecular origin of this effect is not clear at this point. It might simply be a question of steric accessibility, and/or it might be related to loss of internal degrees of rotational freedom in a chain where functional groups are hydrogen-bonded. For example, a particular phenolic hydroxyl group may be adjacent to a carbonyl group, but because one or more of its nearest same chain neighbors are already hydrogen-bonded to other groups, it may not be able to orient itself to form a hydrogen bond with this adjacent carbonyl group, given the rotational bond angle restrictions found in polymer chains. This latter mechanism lends itself to a theoretical approach through modifications to the entropy of hydrogen bond formation, but until we obtain more experimental evidence, we will at this point limit our analysis to the simpler approach where we assume that for what ever reason only a fraction of the functional groups are available. If we let *m* equal the concentration of hydrogen-bonded groups, we can write a stoichiometric equation for an equilibrium constant in the following form

$$m = (n'_A - m)(n'_B - m)K_A^{\infty} \qquad (3)$$

where K_A^{∞} is the "true" interassociation equilibrium constant describing the hydrogen bonding between carbonyl and phenolic hydroxyl groups in the absence of any problems of accessibility (i.e. at infinite spacing or dilution) and, as mentioned above, *m* is the number of hydrogen-bonds per unit volume.

The apparent stoichiometric equation is

$$m = (n_A - m)(n_B - m)K_A^{eff} \qquad (4)$$

where K_A^{eff} is the *effective* constant for hydrogen bonding determined experimentally from the $f_{HB}^{C=O}$ measured by infrared spectroscopy in single phase polymer blends. This value is less than K_A^{∞} because of the problems of accessibility, which reduces the number of hydrogen-bonded carbonyl groups that can be formed.

Let us now assume that the functional groups in the (co)polymers are spaced far apart from one another. Then

$$\begin{aligned} n'_A &= n_A + \delta n_A \qquad & \delta n_A &\ll n_A \\ n'_B &= n_B + \delta n_B \qquad & \delta n_B &\ll n_B \end{aligned} \qquad (5)$$

As L_i is linearly dependent on R_i, by manipulating eqs 2−4 in the lower order by δn_A and δn_B (i.e.

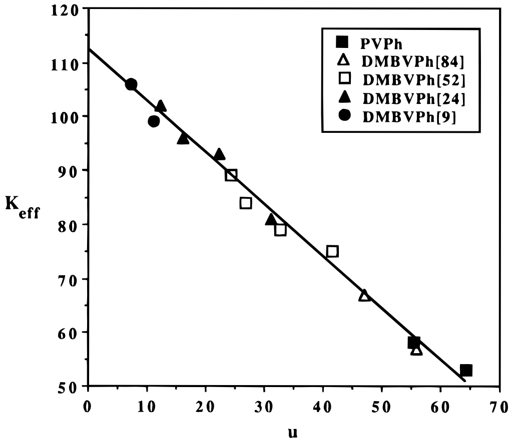


Figure 7. A plot of K_{eff} versus u (eqs 6 and 7) showing a linear least squares fit of the data.

neglecting quadratic terms in $\delta n_{\mathrm{A}}\delta n_{\mathrm{B}}$ etc.), we obtain the following equation

$$K_{\mathrm{A}}^{\mathrm{eff}} = K_{\mathrm{A}}^{\infty} - \left[\frac{C_{\mathrm{A}}}{R_{\mathrm{A}}^{\mathrm{o}} + R_{\mathrm{A}}} + \frac{C_{\mathrm{B}}}{R_{\mathrm{B}}^{\mathrm{o}} + R_{\mathrm{B}}}\right] \tag{6}$$

Here, C_{A} and C_{B} are constants and $R_{\mathrm{A}}^{\mathrm{o}}$ and $R_{\mathrm{B}}^{\mathrm{o}}$ represent the molar volume of the chain "screened" by formation of one hydrogen bond. To further simplify the problem and reduce the number of independent variables, we have made the assumption that $R_{\mathrm{A}}^{\mathrm{o}}$ and $R_{\mathrm{B}}^{\mathrm{o}}$ are equal to the molar volumes of the VAc and VPh segments (Scheme 1), i.e., 70 and 100 cm^3/mol, respectively. Equation 6 therefore predicts that K_{eff} should be linearly dependent on the following dimensionless quantity:

$$u = \left[\frac{C_{\mathrm{A}}}{R_{\mathrm{A}}^{\mathrm{o}} + R_{\mathrm{A}}} + \frac{C_{\mathrm{B}}}{R_{\mathrm{B}}^{\mathrm{o}} + R_{\mathrm{B}}}\right] \tag{7}$$

Accordingly, the experimental interassociation equilibrium constant data obtained from the established miscible DMBVPh/EVA blend systems (Table 2) plotted against the variable u should collapse to a single line, at least for those values obtained from the copolymers where the functional groups are "well spaced". Such a plot is shown in Figure 7, and it is immediately evident that all the data fits, within experimental error, on the same straight line. This is somewhat surprising, in the sense that we have assumed large spacings in order to obtain eq 6. For now we will leave this as an intriging empirical observation, but this is clearly a relationship that requires a deeper theoretical treatment.

A linear least squares fitting of the data was performed, where the values of C_{A} and C_{B} were permitted to vary in order to obtain the best fit. Values of 1630, 4100, and 112.4 were determined for C_{A}, C_{B} and K_{A}^{∞} (from the intercept at $u = 0$), respectively.

Comparison of the Experimental to Theoretical Infrared Spectra. Armed with an equation that expresses $K_{\mathrm{A}}^{\mathrm{Std}}$ as a function of R_{A} and R_{B} for single phase DMBVPh/EVA blends, i.e.,

$$K_{\mathrm{A}}^{\mathrm{Std}} = 112.4 - \left[\frac{1630}{70 + R_{\mathrm{A}}} + \frac{4100}{100 + R_{\mathrm{B}}}\right] \tag{8}$$

we can now calculate the theoretical fraction of hydrogen-bonded carbonyl groups, $f_{\mathrm{HB}}^{\mathrm{C=O}}$, present at equilibrium in a chosen miscible blend at a given temperature, using the computer program that accompanies our monograph.[1] We will not dwell on the details of these calculations, as they have been described in many previous publications.[1,2] They required appropriate values of the molar volume of the specific repeating units, the self- and interassociation equilibrium constants, and the enthalpies of hydrogen bond formation (see Tables 1 and 2). From the value of $f_{\mathrm{HB}}^{\mathrm{C=O}}$ determined for a particular blend at 100 °C, it is a relatively simple task to synthesize theoretical spectra that represent the predicted infrared band envelope in the carbonyl stretching region that would be observed if the blends were truly miscible (single-phase). It is only necessary to have a knowledge of the approximate frequency, shape, and breadth of the two infrared bands and the absorptivity ratio of the hydrogen bonded to "free" carbonyl band.

Let us first return to Figure 3. It can be seen that the experimental and synthesized infrared spectra of the DMBVPh[84] blends with PVAc and EVA[70] are essentially identical, which implies a single phase (but, remember, this is a circular argument as we used the experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ values for these blends in the development of eq 8). On the other hand, the experimental and synthesized infrared spectra of the DMBVPh[84] blends with EVA[45] and EVA[33] are distinctly different. While it is evident that there is some mixing of DMBVPh[84] with EVA[45] (there is a significant contribution from the hydrogen-bonded carbonyl band) and EVA[33] (a much smaller contribution) the blends are obviously immiscible. [Note that for single phase 60:40 wt % DMBVPh[84]/EVA blends the intensity of the hydrogen-bonded band ($\approx$1710 cm^{-1}) should increase relative to that of the "free" band ($\approx$1738 cm^{-1}) with decreasing VAc content of the EVA copolymers (as can be seen by inspection of the synthetic spectra shown on the right-hand side of Figure 3). This is intuitively obvious, because at constant blend composition and temperature, the concentration of phenolic hydroxyl to acetoxy carbonyl groups is increasing as the VAc content of the EVA copolymers decreases, leading to a higher $f_{\mathrm{HB}}^{\mathrm{C=O}}$ at equilibrium. [We caution, however, that this is a bit simplistic as the $f_{\mathrm{HB}}^{\mathrm{C=O}}$ is also affected by the overall concentration of the phenolic hydroxyl and acetoxy carbonyl groups in the blend (i.e. the "dilution" effect), but this is all taken into account in our theoretical calculations[1]].

Proceeding now to the DMBVPh[52]/EVA blends: given the similarity of the experimental and theoretical spectra of the DMBVPh[52] blends with PVAc, EVA-[70], EVA[45], and EVA[33], it is reasonable to conclude that they are miscible (but again this is a circular argument—see above). In contrast, while the DMBVPh-[52] blend with EVA[25] appears intimately mixed and close to single phase (there is a large contribution from the hydrogen-bonded carbonyl stretching band), it is actually two-phases, because the $f_{\mathrm{HB}}^{\mathrm{C=O}}$observed is not sufficient for a single-phase material. In this case this is not a circular argument as the experimental $f_{\mathrm{HB}}^{\mathrm{C=O}}$ for this blend was not used in the development of eq 8.

A similar situation exists for the DMBVPh[24] blends. As expected, the experimental and theoretical spectra of the DMBVPh[24] blends with PVAc, EVA[70], EVA-[45], and EVA[25] are well-matched and consistent with single-phase materials. However, we now also see that the experimental and theoretical spectra of the DMBVPh[24] blends with EVA[18] and EVA[14] are also very similar, which implies that these are also single-phase materials at 100 °C. Recall that it was not possible to

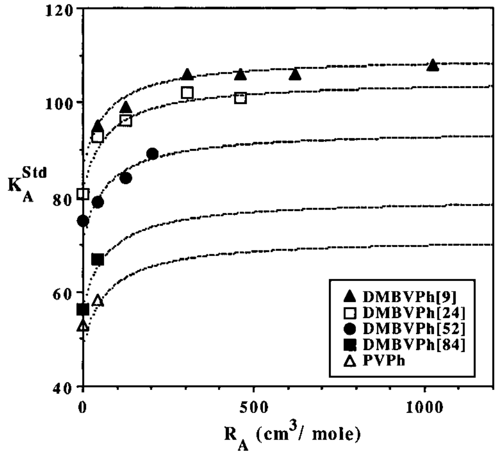


Figure 8. A plot of the K_A^{Std} data experimentally determined from single-phase blends versus the molar volume R_A for DMBVPh/EVA blends. Theoretical curves generated from eq 8 are indicated by the broken lines.

make any definitive conclusion concerning the miscibility of these blends by thermal analysis, because of the complications introduced by EVA crystallinity. In contrast, the DMBVPh[24] blend with EVA[9] is determined to be immiscible because the experimental spectrum is substantially different from that of the simulated single-phase spectrum. In other words, the experimental fraction of $f_{HB}^{C=O}$ is observed to be significantly less than that calculated for a single-phase material.

Finally, we consider the DMBVPh[9] blends. Note that only the EVA[45] and EVA[25] blends were used in the development of eq 8. In addition to these two blends, it is evident from the similarity of the experimental and synthesized spectra that the EVA[70], EVA[18], EVA[14], and EVA[9] are also miscible. Even more interesting is the fact that the DMBVPh[9] blend with PVAc is obviously not miscible.

To summarize the conclusions obtained from the infrared studies, the range of single-phase DMBVPh/EVA blends at 100 °C extends from PVAc to EVA[70] for the PVPh and DMBVPh[84] blends, from PVAc to EVA[33] for the DMBVPh[52] blends, from PVAc to EVA[14] for the DMBVPh[24] blends, and from EVA[70] to EVA[9] for the DMBVPh[9] blends.

Figure 8 shows a comparison of the theoretical curves (dashed lines) calculated from eq 8 for the different DMBVPh blends of K_A^{Std} as a function of the spacing of the VAc segments in the EVA copolymers *assuming a single phase* (miscibility). Also included in Figure 8 are the experimental values of K_A^{Std} that have been obtained from all the blends that were determined to be single-phase at 100 °C. The agreement is very good and suggests that a spacing equivalent to a molar volume of approximately 300 cm^3/mol in the copolymer chain, or about three VPh segments, is required before the affect of functional group accessibility becomes insignificant.

The DMBVPh/EVA Miscibility Map. At the beginning of this paper we stated that one of the primary goals of this work was to experimentally test the predicted miscibility map of the DMBVPh/EVA blend system. Figure 9 shows such a map that was calculated using our original free energy equation[1] and the assumption that the value of $K_A^{Std} = 58$ is invariant and *not* a function of the spacing of the VAc and/or VPh segments in the respective (co)polymers. The calculated two-phase regions are represented by the small black dots. Superimposed onto Figure 9 are the experimental results described above. The larger black circles denote two-phase systems, while the unshaded circles denote miscible (one phase) blends. The agreement between prediction and experiment is quite remarkable, especially given the fact that we now know that K_A^{Std} varies from 53 in the case of the PVPh/PVAc to $\approx$110 (approximately a 2-fold increase) for the DMBVPh[9]/EVA[9] blends. As we have discussed previously,[3] the form and extent of the single-phase region in the DMBVPh/EVA miscibility map is not very sensitive to the K_A^{Std} value, but is dominated by the difference in the solubility parameters of the respective DMBVPh and EVA copolymers. Ironically, with all the new and important insights gained recently concerning intramolecular screening[4] and functional group accessibility,[3] the simple but flawed equation describing the free energy contribution from hydrogen bonding[1] still predicts phase behavior, miscibility windows, and miscibility maps extraordinarily well.

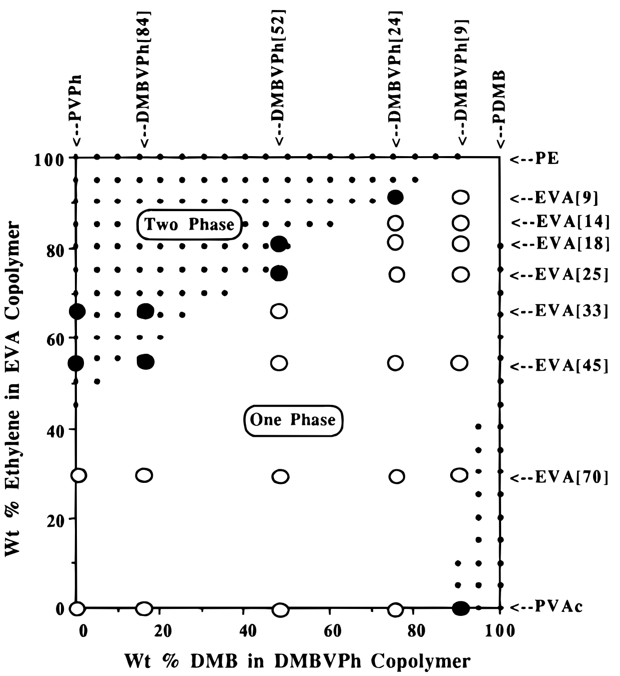


Figure 9. Theoretical miscibility map calculated at 100 °C for DMBVPh/EVA blends using a constant K_A^{Std} value of 58.0. The areas encompassed by the small black dots denote predicted two-phase regions. Experimentally determined single- and two-phase blends are denoted by the unshaded and black-filled large circles, respectively.

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