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Hydrogen Bonding in Blends of Phenoxy Resin and Poly(vinylpyrrolidone)

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ABSTRACT: The equilibrium constants and enthalpies describing self-association and interassociation between functional groups in blends of poly(hydroxy ether of Bisphenol A) [phenoxy (PH)] and poly(vinylpyrrolidone) (PVPr) have been employed in an attempt to explain different experimental results of these blends. The methodology of an association model developed by Painter, Coleman, and their coworkers has been used. The simulated glass transition temperatures and enthalpies of mixing agree with experimental results. The same set of association constants and enthalpies reproduces the free carbonyl fraction in a related mixture, epoxy resin/poly(vinylpyrrolidone). Finally, the model gives a reasonable approach to the influence of the hydroxyl groups of phenoxy in its miscibility with PVPr, when these hydroxyl groups are progressively eliminated from the PH molecule by benzoylation.

Introduction

Miscible blends, blends that are homogeneous at the polymer segment level of scale, require two well-known thermodynamic conditions: the first one implies that the free energy of mixing be negative. In addition, the stability against phase separation requires that

$$\frac{\partial^2(\Delta G_M)}{\partial \phi^2} > 0$$

where ϕ is the volume fraction of one of the components.

The enthalpic and the entropic contributions to the free energy of mixing,

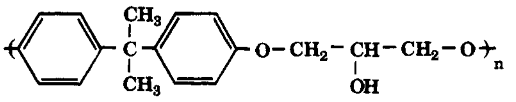
$$\Delta G_M = \Delta H_M - T\Delta S_M$$

are generally functions of composition, temperature, and, in the case of the entropic term, molecular weight. Given that this entropic contribution is quite small for high molecular weights, the requirement of a negative free energy of mixing is usually fulfilled with an exothermic or negative heat of mixing.

In recent years, considerable progress has been made in finding new miscible polymer blends. This progress is, in part, a consequence of the recognition of the importance of specific interactions in the phase behavior of the blends. This type of interaction can be described in terms of association equilibria between the functional groups involved in the interaction, as pointed out by Coleman et al.[1] They modified the Flory–Huggins theory to include a free energy change associated with hydrogen bonding that has both entropic and enthalpic contributions. Constants and enthalpies related to the association equilibria and necessary to quantify this extra free energy can be evaluated via FTIR studies.

Most of the polymer blends adequately described by this association model are blends in which one of the components is a polymer with a marked capacity in forming hydrogen bonds, not only by interassociation equilibria but also by self-association equilibria. According to the model, miscibility in a system with stronger self-association than interassociation is the result of a reduction in the number of configurations available to the chain, owing to the formation of hydrogen bonds. Most of these blends are also polymer mixtures in which the components have functional groups with FTIR signals which can be affected by this interaction. In this sense, carbonyl group signals undergo a marked change in their form and frequencies when specific interactions via hydrogen bonds occur. Therefore, blends of polyesters, polyacrylates, and polymethacrylates with poly(vinylphenol) have been extensively studied.[1]

Blends of poly(hydroxy ether of Bisphenol A) [phenoxy (PH)]



with aliphatic and aromatic polyesters, polymethacrylates, and other carbonyl-containing polymers have been widely studied in the last years.[2] These blends exhibit a variety of phase behavior from completely miscible to completely immiscible, including some systems with low critical solution temperature (LCST) type diagrams. In such types of blends, specific interactions are presumably not as strong as those formed with phenolic or carboxylic acid hydroxyl groups. For this reason they could be excellent systems to test the ability of the above-mentioned association model to predict phase diagrams. However, phenoxy-containing systems present some difficulties in carrying out the necessary calculations of the association parameters introduced by Painter and Coleman. In blends with ester-containing polymers, except those with poly(caprolactone) (PCL) which have been recently studied,[3] a quantitative study of the free and associated carbonyl groups is not feasible in the majority of the cases.

Poly(*N*-vinylpyrrolidone) is a water-soluble polymer

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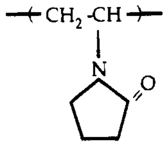
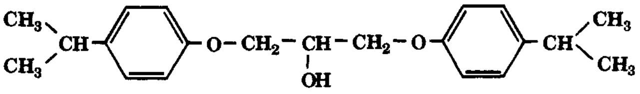


in which a tertiary amide group provides a more marked Lewis-base character to the carbonyl group. This character arises from its strong polar condition, with a dipole moment of around 4 D.[4] The proton acceptor group of PVPr can interact, through the formation of hydrogen bonding, with proton donor polymers. Thus, PVPr was found to be miscible with poly(vinyl difluoride) (PVF$_2$),[5] poly(vinyl alcohol),[6] poly(vinyl chloride) (PVC),[7] poly(epichlorohydrin),[7] and poly(vinylphenol)[8] and with the above-mentioned phenoxy resin (PH).[9] This capacity to generate strong interactions will have important consequences in the FTIR signals of the free and associated carbonyl groups.

In this work, blends of PH and PVPr have been studied by FTIR in an attempt to understand some of their experimental features in light of the association model introduced by Painter, Coleman, and co-workers.

Experimental Section

The copolymer of Bisphenol A with epichlorohydrin (phenoxy, PH) was supplied by Union Carbide (PKHH resin). After purification in a mixture of THF/*n*-hexane, the polymer had a M_w = 50 700 and M_n = 18 000, measured by GPC in THF at 30 °C and using Mark–Houwink constants, previously determined in our laboratory.[10] 1,3-Bis(4-isopropylphenoxy)-2-propanol (IPPHP, a model compound of PH resin) was synthesized in our laboratory and the conditions of its synthesis have been described elsewhere.[11]



Poly(*N*-vinylpyrrolidone) was purchased from Aldrich. Its nominal molecular weight was 40 000. *N*-Methylpyrrolidone was also supplied by Aldrich and was used without further purification.

Infrared spectra were obtained on a Nicolet 5DXC Fourier transform infrared spectrometer. In all cases, a minimum of 64 scans with an accuracy of 2 cm^{-1} was signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained using a Specac accessory mounted inside the sample chamber. All spectra were within an absorbance range where the Beer–Lambert law is obeyed (<0.6 absorbance units).

Polymer blends of various compositions were prepared by codissolving appropriate amounts of the components in chloroform to yield 1% (w/v) solutions. Thin films for FTIR studies were obtained by casting the blend solutions onto potassium bromide windows at room temperature. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The samples were then dried in a vacuum oven for 3 days at 100 °C to completely remove the residual solvent. To minimize water absorption, samples were stored under vacuum desiccation while awaiting study. All blends were optically transparent.

A Setaram C80 D calorimeter was used to determine heats of mixing of the model compounds of the components of the polymer blend. Proper mixing during each single experiment was ensured by using special mixing cells and by the calorimeter's ability to inverse its main body. Typically, the two model compounds were in contact after the first few rotations.

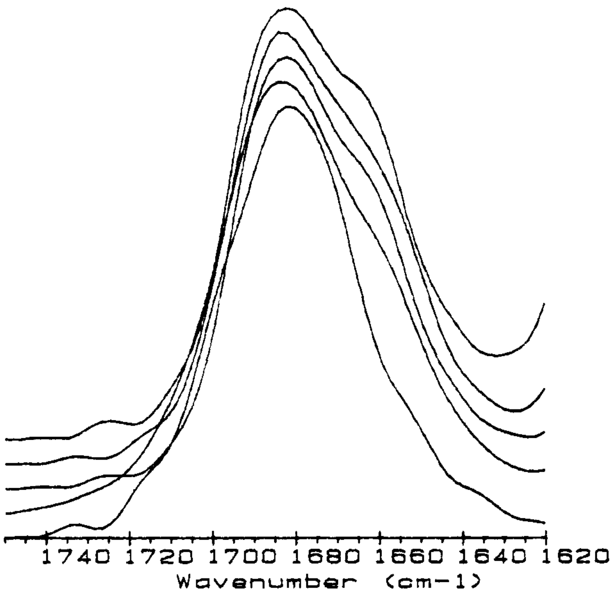


Figure 1. Carbonyl stretching region of PH/PVPr blends recorded at 160 °C. From bottom to top: pure PVPr, 50:50, 70:30, 80:20, and 90:10 wt %.

Table 1. Self-Association Constants and Enthalpies of Phenoxy Resin at 25 °C[12]

dimers	$K_2 = 14.4$	$h_2 = -2.5$ kcal/mol
multimers	$K_B = 25.6$	$h_B = -3.4$ kcal/mol

All calculations have been made using recent versions of the Miscibility Guide & Phase Calculator (MG&PC) software package,[1] kindly provided by the authors.

Results and Discussion

Association Parameters. As in other alcohols and phenols, two equilibrium constants are required to describe phenoxy self-association, one describing the formation of dimers K_2 and the other describing the formation of higher multimers K_B.

Following the evolution of the infrared bands of the hydroxyl group in different solutions of any alcohol (like IPPHP) in cyclohexane allows the characterization of constants and enthalpies of self-association, which, by functional group analogy, can be applied to phenoxy resin. Our group has recently described this study,[12] estimating the constants which quantify the equilibria of the dimers and multimers formation, following the procedure described in 1951 by Coggeshall and Saier.[13]

Enthalpies of phenoxy self-association were estimated[12] from the observed shifts of the associated hydroxyl band in reference to the free hydroxyl band, with the support of a correlation between band shifts and enthalpies.[14] Table 1 summarizes the values of the constants and enthalpies of self-association.

As in PCL,[3] the carbonyl group of PVPr suffers measurable variations when mixed with PH. Thus, the interassociation constant can be obtained without significant errors. The formation of hydrogen bonds between the hydroxyl and the carbonyl groups produces the splitting of the carbonyl band in two bands corresponding to its situation as free and associated. By FTIR the proportion of free and associated fractions at different temperatures and compositions can be evaluated. These data enable the determination of the constant and enthalpy of association.

Figure 1 shows scale-expanded infrared spectra in the carbonyl stretching region (1740–1620 cm^{-1}) of PH/PVPr blends of varying composition cast from chloro-

Table 2. Curve-Fitting Results of the PH/PVPr Blends at 160 °C

	mole fraction	"free" C=O band			"hydrogen-bonded" C=O band		
wt %	of PH	ν (cm^{-1})	width	area	ν (cm^{-1})	width	area
90:10	0.72	1662	31	4879	1686	27	5172
80:20	0.61	1660	31	5273	1686	28	6784
75:25	0.54	1659	29	6238	1685	29	9850
70:30	0.48	1660	28	4946	1684	28	8510
65:35	0.42	1660	27	4216	1685	29	7505
50:50	0.28	1657	27	5079	1685	35	15470
40:60	0.21	1657	26	5874	1685	39	25440

Table 3. FTIR Data of PH/PVPr Blends for the Determination of K_A and h_A

blend composition (wt fraction)	fraction of free carbonyl groups			
	150 °C	160 °C	170 °C	180 °C
0.90	0.495	0.515	0.532	0.544
0.80	0.551	0.563	0.564	0.601
0.75	0.604	0.612	0.621	0.615
0.70	0.598	0.633	0.642	0.662
0.65	0.626	0.640	0.643	0.674
0.50	0.745	0.753	0.760	0.763
0.40	0.821	0.812	0.823	0.832

form and recorded at 160 °C (above the glass transition temperature of the systems). In common with the spectra shown in other publications,[8,16] pure PVPr is characterized by a rather broad band centered at 1685 cm^{-1}. Upon mixing PVPr with PH, a second band is observed at 1659 cm^{-1}. This band increases in relative intensity as a function of PH concentration and is easily assigned to hydrogen-bonded PVPr carbonyl groups. Table 2 summarizes the results of curve fitting[16,17] the carbonyl stretching region of the spectra obtained at 160 °C for all the compositions.

To obtain a quantitative measure of the fraction of hydrogen-bonded carbonyl groups present in the samples of PH/PVPr blends, we require the knowledge of the respective absorptivities a_1 and a_2 for the 1685 and 1659 cm^{-1} bands or, at least, the ratio of the two absorptivities a_2/a_1. Unfortunately, for our system, this ratio is not easily obtained because of the small differences in the relative intensities of the hydrogen-bonded to non-hydrogen-bonded species in the spectra obtained in the temperature range studied. Therefore, although being conscious of the error source, we have considered this ratio equal to 1, following the observation of a constant total area as the two bands vary in intensity with temperature.[17] Table 3 summarizes the fraction of free carbonyl groups of PVPr corresponding to the different temperatures and compositions of PH/PVPr studied.

The methodology followed in order to calculate inter-association constants by means of an adequate fit of the stoichiometric equations which give the fraction of the free carbonyl groups as a function of the PH self-associated volume fraction has been widely detailed elsewhere.[1]

Figure 2 shows the agreement of the experimentally determined fractions of "free" carbonyl groups at 180 °C with those predicted by the theoretical curve.[1] In order to carry out this calculation, it is necessary to know previously the self-association constants of phenoxy resin at the four temperatures investigated, which can be done by means of the constants and enthalpies at 25 °C summarized in Table 1. Table 4 gives the values of the interassociation constants at these temperatures. Knowing the values of these constants and by means of the van't Hoff expression, it is possible to calculate the interassociation enthalpy in the temperature range investigated and extended to room temperature. Figure 3 shows this calculation. From the slope of this representation a value of −4.7 kcal/mol is obtained for the interassociation enthalpy of the PH/PVPr blend. From this representation, the extrapolation at 25 °C gives the value of 43.6 for the interassociation constant at this temperature. The pair of values (43.6, −4.7) will be employed together with those of the self-association constants and enthalpies given in Table 1 in the calculation of the remaining thermodynamic magnitudes available to the previously cited MG&PC software.

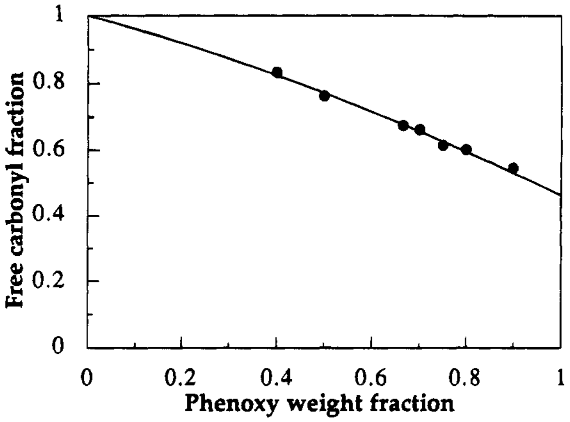


Figure 2. Results of a least-squares fit (solid line) to the experimental fraction of free carbonyl groups versus PH weight fraction at 160 °C.

Table 4. Interassociation Constants of PH/PVPr at Different Temperatures

T (°C)	150	160	170	180
K_A	4.27	3.70	3.37	2.93

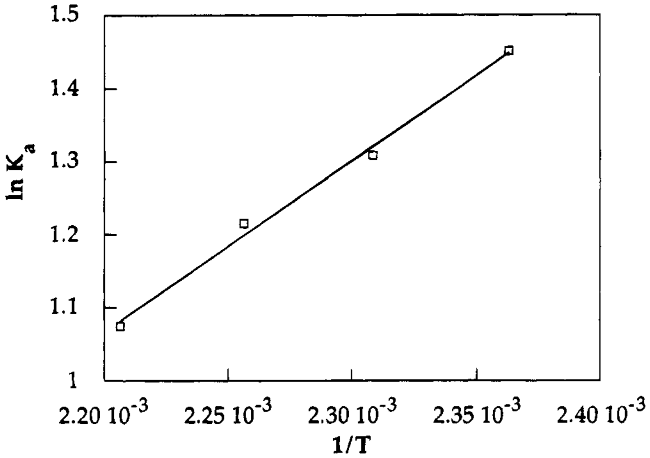


Figure 3. van't Hoff plot for the determination of the interassociation enthalpy in PH/PVPr blends.

To carry out these calculations and besides the interassociation and self-association constants and enthalpies, we need to know a series of magnitudes characteristic of the pure polymers as molar volume, molecular weight of the repeat unit, polymerization degree, and solubility parameters, all of them at 25 °C. The MG&PC software permits access to a bank of group contributions which allows a fast and viable evaluation of all the above-mentioned parameters except the polymerization degree. The value of this parameter was taken in all the cases to be equal to 500. Table 5 summarizes the totality of the data employed in our calculations.

Table 5. Parameters Employed in This Work

segment	mol vol (cm^3/mol)	solubility param (cal/cm^3)$^{1/2}$	mol mass (g/mol)	polymzn degree
PH	216.6	10.2	283.36	500
PHB	306.6	10.3	388.47	
PVPr	73.6	11.0	111.15	500

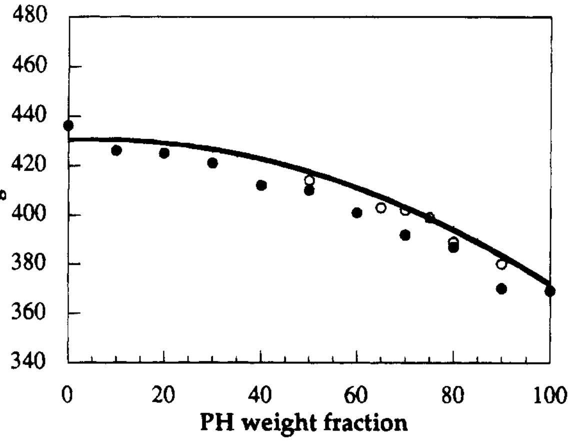


Figure 4. Comparison of theoretical (solid line) and experimental glass transition temperatures in PH/PVPr blends: (●) Reference 9. (○) This work.

Simulation of Various Properties of the Blends. One of the most extended ways of investigating the miscibility between polymers is, as has been already mentioned, the macroscopic criterium of a unique glass transition temperature, intermediate between those of the pure components.

The glass transition temperatures of blends of PH and PVPr were previously determined by our group,[9] and, in this work, the T_g's of all the blends used in the spectroscopic study have also been measured. Both sets of results are shown in Figure 4 together with the simulated variations of temperature as a function of composition using the adequate application of the MG&PC software for the glass transition temperatures, whose bases have been described in the literature.[18] In order to carry out this simulation, we need, besides the constants and enthalpies of self-association and inter-association and the magnitudes summarized in Table 5, the glass transition temperatures of the components and their respective jumps in the specific heat in their solid–liquid transitions. Those values have already been calculated in our laboratory and published in the literature.[9,19]

With all these data, the model permits the simulation, with a reasonable precision, of the variation of T_g with composition. The small differences observed between the two series of data measured in our laboratory can be due to the different experimental strategies followed in order to avoid water absorption of the samples, more strict in the more recent determinations. The most relevant finding of this prediction is the qualitative reproduction of a curve beyond the additivity (Gordon–Taylor parameter higher than 1), a peculiarity not very common in miscible polymer blends except in those cases where the interactions are highly important.

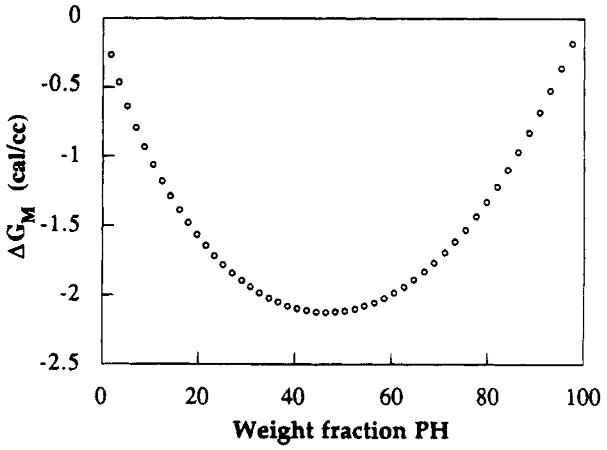


Figure 5. Calculated free energy of mixing against PH/PVPr blend composition.

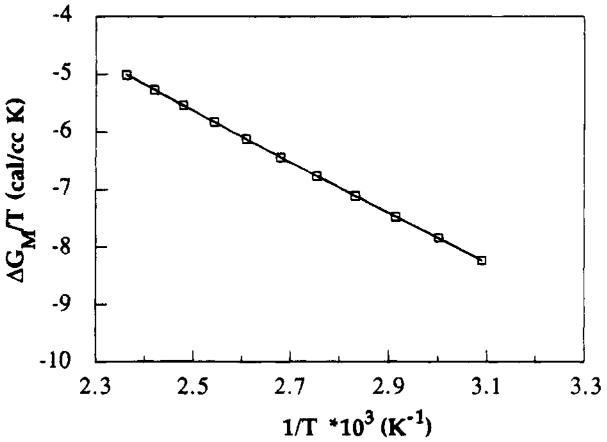


Figure 6. Determination of the enthalpy of mixing from calculated values of free energies at different temperatures in a 50:50 PH/PVPr blend.

This important level of interaction can be visualized when we simulate the evolution of the free energy with composition of the blend at a temperature of 150 °C where the mixture is in the liquid phase. The result is represented in Figure 5. If we repeat the calculation at different temperatures for a single mixture (50:50) and use the classic Gibbs–Helmholtz expression:

$$\Delta H_M = \partial(\Delta G_M/T)/\partial(1/T)$$

it is possible to calculate the enthalpy of mixing of both polymers over a wide range of temperatures. Using free energies between 50 and 150 °C the enthalpy of mixing at 94 °C has been calculated. Although below the T_g of the blend, this allows us to compare it with the enthalpies of mixing experimentally measured at this temperature using model compounds of both phenoxy resin and poly(vinylpyrrolidone). Using IPPHP and *N*-methylpyrrolidone as model compounds, Calvet calorimetry has provided a value of the enthalpy of mixing of −4.5 cal/g for a 50:50 mixture of both compounds. Determinations at higher temperatures had technical problems due to the vaporization of the compounds. Figure 6 illustrates the behavior of the free energy as a function of temperature following the expression of Gibbs–Helmholtz.

In the temperature range investigated, the representation is linear, and from the slope, it is possible to determine an enthalpy of mixing of −4.4 cal/cm^3. A reasonable estimation of the specific volume for a 50:50 mixture of IPPHP and *N*-methylpyrrolidone gives a value of 1.1 cm^3/g at 95 °C which provides an enthalpy of mixing of −4.9 cal/g, very close to the one experimentally obtained by Calvet calorimetry with the model compounds.

In a recent work, Janarthanan and Thyagarajan[15] have studied a mixture of PVPr and an epoxy resin

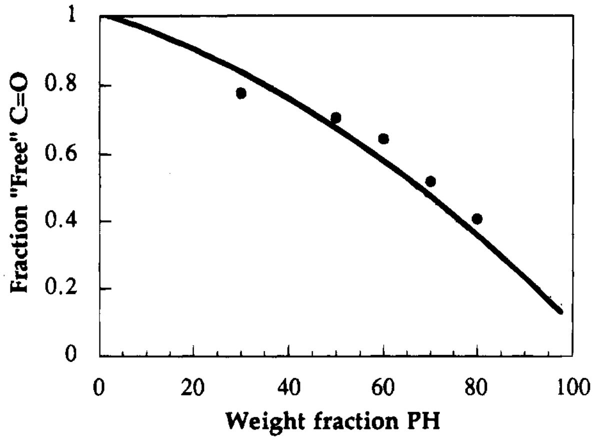


Figure 7. Comparison of theoretical (solid line) and experimental (ref 15) fractions of free carbonyl groups versus concentration in an epoxy resin/PVPr blend at room temperature.

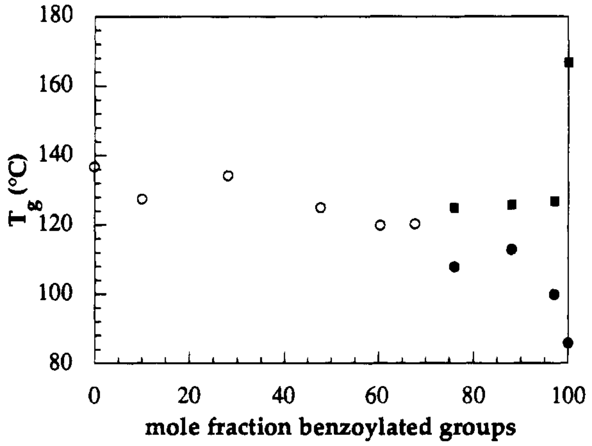


Figure 8. Experimental glass transition temperatures of 50:50 blends of PVPr with phenoxy partially benzoylated.

(structurally very similar to ours) by means of DSC and FTIR. Although FTIR studies were made at room temperature (below the T_g of the blend) and therefore it is difficult to apply the criteria of any liquid–liquid system, the authors calculated free carbonyl fractions at different compositions of epoxy resin. With our constants at 25 °C, we have tried to check the possibilities of the model in reproducing the behavior described by the authors at 25 °C (Figure 7). Surprisingly, the result is quite good in spite of the differences in the treatment of the samples and the difficulties in assuring at 25 °C a real equilibrium between the components.

Role of the Hydroxyl Groups in the Miscibility of the Mixture PH/PVPr. Finally, this mixture of PH/PVPr has been employed in order to study the role of the OH groups of PH resin in its miscibility with PVPr. For this purpose, we have used several modified PH resins with different degrees of benzoylated groups. The synthesis and characterization of these samples have been described elsewhere.[20]

The miscibility of these modified phenoxy resins with PVPr was studied by means of the determination of the glass transition temperatures for 50:50 blends. The experimental data indicate that partially benzoylated PH resin is still miscible with PVPr up to about 70% of benzoylation, as can be seen in Figure 8.

The association model permits one to simulate reasonably this behavior using again the previously tabulated association constants and enthalpies (Figure 9).

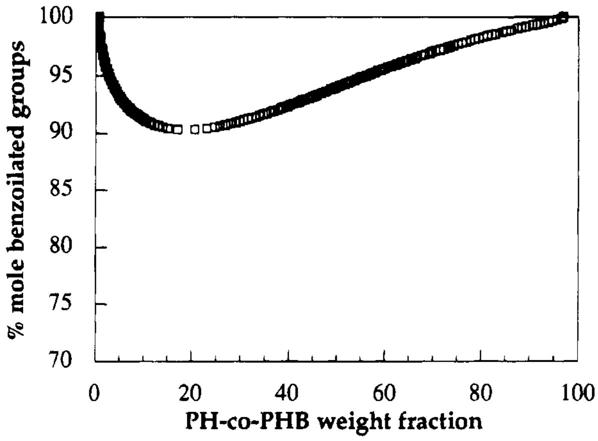


Figure 9. Phase diagram of blends of PVPr with partially benzoylated PH at 180 °C.

The calculation implies the assumption of considering each unit of benzoylated phenoxy as an inert "diluent" of the interaction between hydroxyl groups of phenoxy and carbonyl groups of PVPr. This approximation is not very strict because the benzoylated phenoxy repeat unit has ester groups capable of competing for interaction with those hydroxyl groups not substituted. This would imply a certain degree of supplementary phenoxy self-association, making it difficult to obtain a miscible blend with PVPr.

Conclusions

In comparison with other polymer blends with specific interactions, those occurring in the mixture of phenoxy resin and poly(vinylpyrrolidone) can be classified as high-level specific interactions. This conclusion can be extracted from the values of the association constant and enthalpy determined according to the association model of Painter, Coleman, and co-workers. The model seems to reproduce reasonably well most of the thermodynamic magnitudes experimentally measured in this work. The role of these specific interactions in the stabilization of the mixture has been evidenced by partially substituting the hydroxyl groups of the phenoxy resin by chemical modification. The association model is also capable of reproducing the effect of this partial substitution in the corresponding phase diagram.

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