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Excess Specific Heats in Miscible Binary Blends with Specific Interactions

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ABSTRACT: Excess specific heats of different binary blends involving different levels of relatively strong specific interactions have been determined from specific heats of the pure components and those of the blends. A heat-flux (Calvet) calorimeter and a step-by-step methodology have been used. Blends of poly(hydroxy ether of bisphenol A) (phenoxy resin) with polyesters and polyethers, where specific interactions are supposed to play a role in miscibility, and blends with stronger hydrogen-bond interactions, such as poly(vinyl phenol)/poly(methyl methacrylate) (PVPh/PMMA), have been included in the study. Only the experimental excess specific heat for the PVPh/PMMA blend is negative, whereas those relative to phenoxy blends are all positive. These results have been analyzed on the basis of an association model specifically designed for polymer blends in which miscibility is mainly caused by hydrogen bonding. The model predicts, in all cases, a continuous decrease of the enthalpy of mixing with temperature, i.e., a negative value of ΔC_p. Equation of state effects have been included in the theoretical simulations, giving modified trends of the enthalpy of mixing with temperature in a more reasonable agreement with the experimental results.

Introduction

Although the early idea according to which "miscibility in polymer blends is more an exception than a rule" is basically correct, an important number of miscible polymer mixtures have emerged during the last 15 years.[1] Despite this rapid increase in the number of miscible polymer mixtures, important problems concerning the thermodynamic factors which govern the rules of the polymer−polymer miscibility remain unsolved. Part of the problem arises from the experimental difficulties in determining the adequate excess thermodynamic functions of the mixture. For instance, it is possible to determine the excess partial molar free energy, whether in the form of an interaction parameter (χ) or as an interaction energy density (B), using different experimental methodologies. However, most of them (neutron scattering,[2] inverse gas chromatography,[3] melting point depression,[4] etc.) have important technical or conceptual limitations. The task becomes even more complicated if we try to measure the enthalpy of mixing in a mixture of two highly viscous liquid polymers. Alternatives such as the use of heats of solution in a common solvent and the application of the Hess cycle[5] do not generally solve the problem. Large error bars are usually inherent in this kind of experimental determination.

Perhaps the only excess thermodynamic functions of a mixture directly measurable in polymer blends with reasonable accuracy levels are the excess volumes and the excess specific heats. Excess volumes, although not widely measured,[6] have been used to quantify the variations of free volume due to the mixing. These variations arise from the different geometric forms of the molecules and/or from the interactions occurring between the functional groups of the blend components. As far as the excess specific heats is concerned, Barnum et al.[7] were the first to consider that, given the inherent difficulties in measuring heats of mixing, it could be interesting to evaluate the variation of this enthalpy of mixing with temperature. This variation can be expressed by the equation

$$\left(\frac{\partial \Delta H_{\rm m}}{\partial T}\right)_p = \rho \Delta C_{\rm p} = \rho(C_{\rm p} - \omega_1 C_{\rm p}1 - \omega_2 C_{p2}) \qquad (1)$$

where ω_i is the weight fraction of the i component. The blend density (ρ) is introduced as a form of taking into account that the enthalpy of mixing is usually given in calories per volume unit, whereas the specific heat is expressed by weight unit.

In the above-mentioned paper,[7] the excess specific heats of two different blends were determined by differential scanning calorimetry (DSC). In one of the mixtures, PMMA was mixed with a copolymer of α-methylstyrene and acrylonitrile (αMSAN). The second one was a blend of polycarbonate and Kodar (a copolyester of isophthalic and terephthalic acids and cyclohexane dimethanol). In both cases, the excess specific heat in representative mixtures of about 50/50 by weight was positive and on the order of 10^{-2} cal/g K. This indicates that the enthalpy of mixing increased when the temperature increased, consistent with a tendency to phase separation in a LCST-type diagram. This is a behavior which has been recognized as characteristic of polymer blends by most of the theoretical models proposed for this type of mixture. In the same paper,[7] and using a free volume model (Lattice Fluid model), the authors calculated enthalpies of mixing for the above-mentioned mixtures at different temperatures, from which excess specific heats are immediate. However, calculations gave negative values on the order of 10^{-3} cal/g K. The authors argued that the results could be a consequence of the mean field character of the model, not specifically designed for mixtures in which some level of interactions can occur. These interactions can introduce new order elements in the liquid mixture which cause the system

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to deviate from pure random mixing. They concluded the paper by claiming the need for new models which emphasize the existence of such specific interactions. They also proposed that excess specific heats could be an interesting tool to test the feasibility of these new models.

Most of the miscible mixtures for which strong interactions occur belong to a special class of polymer mixtures with intriguing phase behaviors and not well understood rules. This class is formed by miscible mixtures in which specific interactions, mainly hydrogen bonding, are responsible for the intime miscibility level attained. In the last few years, the literature shows an increasing interest in models for polymer blends with hydrogen bonding. Two different theoretical approaches seem relevant.[8−10] A common feature of both models rests on the assumption that dispersion and weak polar forces can be considered separately from strong specific interactions. Painter, Coleman, and co-workers[9] have been focused on the development of infrared spectroscopy methodologies for determining parameters which describe the stoichiometry of hydrogen bonding. On the basis of these experimental data, they have developed a model which allows calculation of the hydrogen-bond contribution to the free energy of mixing. The main feature of the model is that the equations describing this contribution are expressed in terms of the distribution of present species. When hydrogen bonding is operative, giving chains, these species are “monomers” (or nonbonded), “dimers” (hydrogen-bonded pairs), “trimers”, and so on. The formation of such species can be quantified in terms of the equilibrium constants and enthalpies associated with the equilibria describing the corresponding processes.

The second approach to calculate the hydrogen-bonding contribution to the free energy of mixing[10] is based on a combinatorial method introduced by Veytsman[11] and does not require the existence of species. It counts how hydrogen bonds are distributed between “donor” and “acceptor” groups within the system. Panayiotou and Sanchez[10] have used this aproach as a way to generalize the lattice fluid model[12,13] to mixtures where hydrogen bonding exists. Painter et al.[14] have demonstrated that both alternatives give identical results if a correct reference state is defined in the Painter and Coleman association model[9] instead of the semiempirical one originally used.

As introduced previously, few experimental measurements of excess specific heats in polymer blends have been reported. In the case of hydrogen-bonded mixtures, a marginal reference can be found in one of the first attempts to generalize the lattice fluid model to mixtures with strong interactions.[15] The authors reported positive calculated values for ΔC_p but 2 orders of magnitude (10^{-4}) lower than experimental results such as those reported by Barnum et al.[7] Apart from that, Righetti et al.[16] studied ΔC_p in the vicinity of the glass transition temperature, and in our own group, we have measured excess specific heats of phenoxy and poly(vinyl methyl ether) blends.[17] In a very recent paper,[18] Wu et al. have measured ΔC_p in mixtures of phenoxy with a novolac-type phenolic resin, comparing their signs with the evolution of the enthalpy of mixing with temperature, calculated using the Painter and Coleman approach.[9]

This paper is focused on excess specific heats in polymer blends with specific interactions of different levels. We have carried out experimental measurements in a calorimetric technique alternative to the traditional DSC. The so-called heat-flux (or Calvet type) calorimeter opperates with larger samples than DSC and without the necessity of a calibration with sapphire, directly giving the specific heat of the sample under study. Experimental results will be first compared with the predictions of the recently reformulated Painter and Coleman association model.[19,20] The influence of the equation-of-state terms on the excess specific heats will be also considered, following a treatment similar to that used by Graf et al.[21]

Experimental Section

Poly(hydroxy ether of bisphenol A) (phenoxy resin, PH, M_w = 51 000, M_n = 18 000) was obtained from Quimidroga (Barcelona, Spain) and corresponds to the PKHH product of Union Carbide. Poly(ethylene oxide) (PEO) was used as an unfractioned industrial sample (WSR-35, Union Carbide, M_v = 335,000). A poly(styrene) (PS) standard was obtained from Pressure Chemical Co. with a M_w = 35 000 and a M_n = 33 000. Poly(butylene adipate) (PBA) corresponds to the catalog number 18,150-1 of Aldrich Chemical Co. (M_w = 22 000). Poly(methyl methacrylate) (PMMA, M_w = 108 000) was purchased from ICI (Diacom), and finally, poly(4-vinylphenol) (PVPh, M_w = 30 000) and poly(ϵ-caprolactone) (PCL, M_w = 17 600, M_n = 10 800) were supplied by Polysciences (catalog number 16642 and 07039, respectively).

Blends corresponding to the weight ratio 1:1 were prepared by precipitation with an adequate nonsolvent from different solutions, excluding PVPh/PMMA blend, prepared by dissolving both polymers in methyl ethyl ketone (1%) and a subsequent evaporation of the solvent. The resulting powder or films were dried in a vacuum oven at 40 °C for 48 h until they reached a constant weight and then stored in vacuo to avoid moisture adsorption. One single glass transition temperature was detected in all the investigated samples by DSC. It is interesting to note, however, that PH and PMMA do not give miscible blends by casting due to the $\Delta\chi$ effect, as reported previously.[22] However PH/PMMA miscible blends are obtained when polymers are mixed using solution/precipitation or melting procedures.

A SETARAM C80-D calorimeter was used to determine specific heats in a temperature interval for pure polymers and their blends. The major feature of these Calvet type calorimeters is their extremely good insulation. The temperature of the thermostat can be kept isothermal or can be programmed at rates from 0.1 to 1 K/min. As little as 0.5 mW of heat flow is detectable, and the calorimetric sensitivity is 50 mJ. In the experiments here described, we have used the so-called standard cell (a cylinder with an approximate capacity of 12.3 cm^3) and a sample amount of about 2 g. Despite the standard method of specific heat determination by DSC, which implies a continuous heating mode, the heat-flux calorimeters allow us to measure specific heats either by this method or by a second one based on a step heating mode. At first glance, the last method would appear to be more convenient, given the possibility to reach the thermal equilibrium of the sample after each step of temperature. The fundamental disadvantage of this method is the large amount of time and the tedious procedure involved, but today's computers help us to minimize these problems.[23]

The determination of specific heats in a heat-flux calorimeter only requires two tests under identical experimental conditions: the first one uses two empty cells without sample. In the second one, the sample is placed in one of the cells. No standard sample, as sapphire in the DSC experiments, is required here. In the continuous mode, the difference between the two signals coming from the cells is proportional to the heat capacity of the sample and directly converted in heat power, dH/dT, using the calibration curve of the calorimeter. In the step by step mode, the thermal effect corresponding to

Table 1. Experimental Values of ΔC_p

system	temp interval (°C)	ΔC_p (cal/g K)
PH/PMMA	115−150	0.027(±0.001)
PH/PEO	100−150	0.049(±0.002)
PH/PCL	100−150	0.005(±0.001)
PH/PBA	100−150	0.008(±0.001)
PVPh/PMMA	150−200	−0.011(±0.004)

a sample heating along a defined step of temperature is integrated, yielding the specific heat at each temperature.

In some previous experiments with a polystyrene standard using the continuous method, a starting temperature (80 °C) was selected as well as a time long enough (3600 s) to get the initial baseline. After that, an average scanning rate of 0.1 °C/min was selected in order to have a good thermal balance within the sample. Finally, a temperature of 150 °C and a sufficient time (7200 s) were used to define the final baseline. In the step-by-step mode, a series of heatings with a scanning rate of 0.1 °/min and isothermal levels of 2500 s were selected. In the polystyrene case, C_p determinations were done between 80 and 150 °C in steps of 5 °C. The same procedure was used in the determination of excess specific heats of the blends, although the limits of the scanning were not the same for all the investigated mixtures (see Table 1).

Results and Discussion

Some preliminary tests were done in order to demonstrate the ability of the heat-flux calorimeter to determine specific heats. Using a PS standard and the two experimental protocols previously described (continuous and step-by-step), we compared our data with others reported in the literature using DSC.[24] In comparing data from the two modes we verified that the heat stabilization was better in the second case. Consequently we decided to adopt the step-by-step methodology. In comparing our PS specific heat data using the step-by-step mode and those reported by Gaur et al.,[24] we have found a reasonable agreement between both series of data, given the differences between both experimental techniques. For example, it was not possible to carry out our experiments at the same heating rates, given the low values accessible for the heat-flow calorimeter. Consequently, some differences were found both in the localization of the glass transition temperature and in the C_p values. In this last case, the differences were, in all cases, lower than 2%.

Although the method allows us to measure values of C_p at every temperature, it has been difficult to deduce a precise variation of ΔC_p with temperature. At least in our case, this variation was similar to the experimental error of our measurements and we have preferred to report average values of ΔC_p over a temperature interval. Results for the different investigated blends are summarized in Table 1.

A first consideration of this table reveals the qualitative difference between the value of ΔC_p in the PVPh/PMMA blend and those of the rest of the systems containing phenoxy as a common component. Independent of the second component, all PH blends showed a positive ΔC_p value, whereas PVPh/PMMA gave a negative value. In a previous work,[17] a positive value was also reported for phenoxy (PH)/poly(vinyl methyl ether) (PVME) blends. Although in both types of mixtures specific interactions are supposed to be present, PVPh blends are usually reported as mixtures with stronger interactions.[9] A negative value, as in the PVPh/PMMA blend, indicates that the enthalpy of mixing is becoming less positive or more negative when the temperature increases. This behavior is not usually expected in cases where a polymer mixture undergoes a LCST phase separation as a consequence of the competition between dispersive interactions and free-volume effects. However, it can be found in mixtures where hydrogen-bonding interactions are operative if we consider two important facts. First, the phase diagram is controlled by the free energy and not by the enthalpy. Second, in this type of system there are two types of specific interactions which are competing. Both PH and PVPh can interact (or associate) with themselves through their respective hydroxyl groups. In a mixture, there is a competition between this autointeraction and the interaction with the functional group of the second component (for instance, an ether or an ester group). The enthalpy of mixing results from the difference between specific interactions in the mixture with respect to those occurring in the pure components. The different evolution of these interactions with the temperature can lead to an enthalpy of mixing which becomes more negative when the temperature increases. This tendency may change when more extended temperature intervals are considered.

Our experimental data have been used to check the association model proposed by Painter, Coleman, and co-workers,[9] previously mentioned. In this model a polymer, B (phenoxy, polyvinyl phenol), can autoassociate through its hydroxyl groups or interassociate with a second component, A, through the interaction between its hydroxyl and an ester, ether, or similar acceptor groups. The main equation of this model has the form of the classic Flory−Huggins relation, but with an additional term which accounts for the strong interactions:

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{N_A}\ln \phi_A + \frac{\phi_B}{N_B}\ln \phi_B + \phi_A\phi_B\chi + \frac{\Delta G_H}{RT} \quad (2)$$

where ϕ_A and ϕ_B are the volume fractions, N_A and N_B are the degrees of polymerization of polymers A and B, and χ is the polymer−polymer interaction parameter, which only accounts for the “physical” forces. The first and second terms correspond to the combinatorial entropy and can be neglected for high molecular weight polymers. The third one is unfavorable to mixing and can be calculated from non-hydrogen-bonded solubility parameters, which are readily estimated using the group contribution method proposed by Coleman et al.[25] The ($\Delta G_H/RT$) term can be calculated if one knows the molar volumes of the chemical repeating units, V_A and V_B, and the equilibrium constants describing the association equilibria occurring in the mixture. These constants and their variation with temperature are usually calculated using FTIR spectroscopy. Having all these values, the total free energy of mixing can be calculated at different compositions and temperatures, from which thermodynamic properties, such as phase diagrams, enthalpies of mixing, excess specific heats, can be easily derived.

Although the original formulation of the model has sucessfully reproduced the phase behavior and other thermodynamic properties of different hydrogen-bonded mixtures,[9] it used an incorrect, semiempirically introduced, reference state. When the correct reference state is introduced, predictions and experiments come apart dramatically. In recent papers[19,20] Painter, Coleman, and co-workers have reformulated the original model, trying to solve the above-mentioned problems.

Table 2. Summary of Association Parameters in Different Blends of PH and PVPh

	equilibrium constant, *K* (25 °C)	enthalpy, *h* (kcal/mol)
Self-Association		
dimer formation PVPh[19]	21	−5.60
dimer formation PH[27]	14.4	−2.50
multimer formation PVPh[19]	66.8	−5.20
multimer formation PH[27]	25.6	−3.40
Interassociation		
PH with PMMA and polyesters (from analogues)[31]	7.0	−2.70
PH with ethers (from analogues)[27]	3.4	−3.00
PVPh with PMMA		
(from random copolymers)[28]	70	−3.75
(from polymer blend)[28]	40	−3.75

In this new attempt, the consideration of some of the previous experimental results has been particularly useful. For instance, because of the insoluble character of some polymers in the inert solvents usually employed to determine the equilibrium constants, the only alternative to obtain them is to use low molecular weight analogues of the blend components.[26−28] But it was promptly realized that in other polymer mixtures, where it is experimentally possible to measure association equilibrium constants not only from analogue compound mixtures but also from the actual homopolymer blend or from a random copolymer having the repeating units involved in the polymer mixtures, the association constants so obtained were quite different.[28]

Painter, Coleman, and co-workers[20] have argued that the association constant representing the true random interaction between functional groups (implicitly considered in the models) is that of the analogue compounds. However, in transferring these constants to the polymer/polymer blends, some other factors can affect the association equilibria. Among others, chain connectivity (also called screening effects) is particularly operative. This term refers to the intramolecular interactions between hydroxyl groups pertaining to the same chain. These intramolecular interactions decrease the possibilities of interchain contacts. Consequently, the use of association constants obtained from model compounds overestimates the number of intermolecular interactions existing in the actual blend. A new parameter (γ)[19,20] was introduced to take into account the fraction of intrachain contacts. According to theoretical calculations,[20] γ should be in the 0.3−0.4 range for high molecular weight polymers. Unfortunately, other factors such as the functional group accessibility[29] are difficult to introduce in a general model and can only be estimated for a particular series of a (co)polymer/(co)polymer blend such as PVPh/EVA blends, complicating a universal transfer between model compound mixtures and homopolymer blends.

In comparing our excess specific heat results with the theoretical predictions of the association model, it is illustrative to start our calculations using the original version with the uncorrect reference state selection. We have used an identical procedure to that described by Serman et al.,[30] including the MG&PC software package,[9] pure component parameters which can be calculated by a group contribution method included in the same software, and constants and enthalpies of the association equilibria taken from previous works[19,27,28,31] and described in Table 2. In phenoxy/polyester blends, association constants from analogues and polymer mixtures are not very different. However, it must be considered that given the low values of these constants, the differences between the data from the two sources could be within the experimental error. In the case of phenoxy/polyether mixtures, analogue compound mixtures are the only alternative to get equilibrium constants. In the case of PVPh/PMMA blends we have used the constant (and enthalpy) obtained from the polymer blend. This constant reflects all the screening and shielding effects which were balanced in the uncorrect model with the selection of a semiempirical entropic term.

Table 3. Values of ΔC_p Calculated Using the Original Version of the Association Model at $\omega_A = 0.5$

system	*T* (°C)	ΔC_p (cal/cm^3 K)
PH/PMMA	130	−0.006
PH/PEO	125	−0.006
PH/PCL	125	−0.004
PH/PBA	125	−0.005
PVPh/PMMA	160	−0.023

Using this methodology, the variation of ΔG of a polymer−polymer mixture with the composition at different temperatures can be calculated. From these values, the variation of the enthalpy of mixing with temperature is immediate as well as ΔC_p values. The results of the above-mentioned calculations are summarized in Table 3.

As can be seen, all the values predicted by the original association model are negative. In comparing them with the experimental results, it should be considered that units (cal/cm^3 K) are different. To change them into those used in experimental measurements (cal/g K) we have to use the blend density. Although we do not know these values exactly, we can assume that the density of each blend will be aproximately the average of those of the pure components. Densities and their variation with temperature are included in next paragraphs of this paper, but in any case, this will not alter the ΔC_p sign and its order of magnitude.

It is not very difficult to explain the relatively similar values of all phenoxy mixtures. Specific interactions in blends involving polyesters and polyethers with phenoxy are quite similar. So, the differences should arise from the different characteristics of the pure polymers, but the evolution of the enthalpy of mixing with the temperature (or ΔC_p), mainly dependent on these specific interactions, and its evolution with *T* must be approximately the same. For this reason, we will continue our discussion by comparing only the data of PVPh/PMMA and PH/PMMA, the latter being representative of the different phenoxy blends experimentally tested.

The consideration of the new version of the model with the correct selection of the reference state and the factor quantifying the screening effect (in all our calculations γ was equal to 0.36[20]) did not affect the qualitative conclusions we have summarized in the preceding paragraph. For these new calculations and in the case of the PH/PMMA blend, we have used the previous constants and enthalpies (remember that data from analogue mixtures and polymer blends were quite similar). In the case of PVPh/PMMA blend, we have preferred to use a constant obtained from a random VPh/MMA copolymer.[28] With this new value we take into account some of the shielding factors occurring in a normal blend. In fact, it is not very different from that reported[29] as the limiting value in a series of association constants obtained by studying mixtures of random

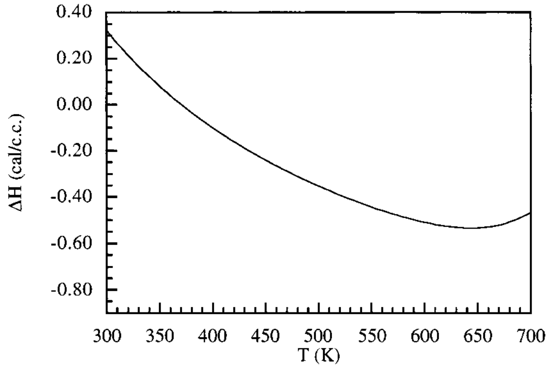

Figure 1. Enthalpy of mixing as a function of the temperature in a PH/PMMA blend, calculated using the association model without free-volume effects (see text).

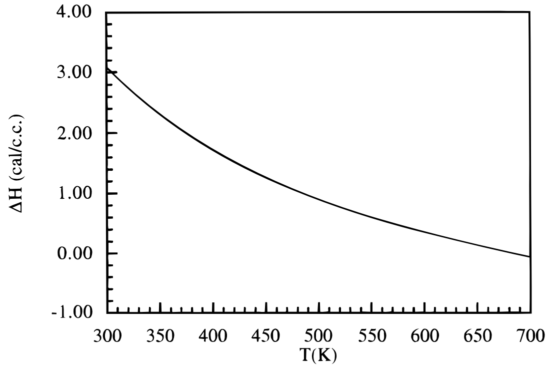

Figure 2. Enthalpy of mixing as a function of the temperature in a PVPh/PMMA blend, calculated using the association model without free-volume effects (see text).

copolymers of vinyl phenol and dimethyl butadiene with random copolymers of ethylene and methyl methacrylate. It is supposed that this limiting value represents the true interaction between the PVPh and PMMA unities in abscence of shielding effects. The γ value takes into account the screening effects.

Figures 1 and 2 illustrate the results of these new calculations. As is shown, there is a continuous decrease of the enthalpy of mixing with the temperature (negative values of the excess specific heat) up to unrealistic temperatures. This behavior seems to be a consequence of the decrease of the association constants with temperature (they are related through a van t'Hoff type expression). Only at very high temperatures and in the PH/PMMA mixture do these constants vanish and the enthalpy reaches a nearly constant value.

Additional calculations have been performed in other blends for which association constants and enthalpies are known, and it becomes apparent that in all cases the enthalpy of mixing tends toward less positive or more negative values up to very high temperatures. The final conclusion seems to be that the association model only gives positive values of the excess specific heats at temperatures at which the association constants tend to zero.

Other factors not included in the model, such as free volume effects, could also affect this balance. In fact, an extension of the original association model including free volume contributions has been reported by Graf et al.,[21] using the lattice fluid formalism. The authors concluded that small free volume differences, as expected in polymer mixtures, between strongly interacting polymers seem to contribute in a relatively minor fashion. But, the mixtures they have studied are based on PVPh, with association constants several times larger than those occurring in phenoxy blends. It could be argued that in these last mixtures the influence of the free volume term could be relevant.

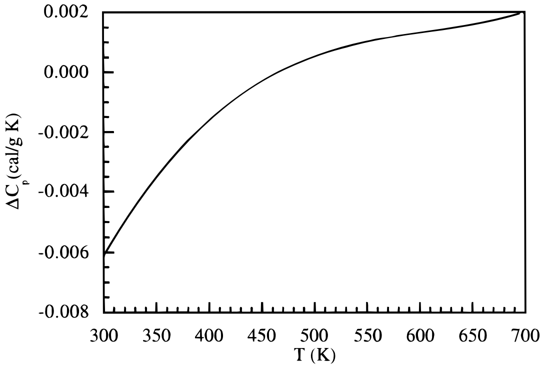

Figure 3. Simulation of the evolution of the excess specific heat with temperature of a 50/50 PH/PMMA blend, using the association model modified with free-volume terms.

To confirm this, we have modified the methodology proposed by Graf et al.[21] including the correct reference state and the possibility of intramolecular screening effects (γ) in order to calculate the free energy change and subsequently the enthalpy change and ΔC_p of the blend. A short introduction to the modifications introduced is summarized in the Appendix.

The equation-of-state required parameters for these new calculations have been taken from the literature. In the case of PH and PMMA, density/temperature relationships were taken from Rodgers.[32] For PH, the author reported a zero-pressure Tait equation for the specific volume (in cm^3/g) of $V(0,T) = 0.76644 \exp(1.92{\cdot}10^{-5}T^{3/2})$ with T in degrees Kelvin, which is the best fit of PVT data from Zoller.[33] The term $V(0,T)$ appearing in this equation is the volume extrapolated at zero pressure, usually identified with the values at atmospheric pressure. In the same Rodgers paper,[32] $V(0,T)$ for PMMA was obtained by adjusting the *PVT* data of Olabisi and Simha[34] to a polynomial expression. In this case, $V(0,T) = (0.8254 + 2.84{\cdot}10^{-4}t + 7.20{\cdot}10^{-7}t^2)$ with t in degrees Celsius.

Using the same series of experimental *PVT* data, Rodgers[32] calculated characteristic parameters for these two polymers in the framework of the lattice fluid model. According to Rodgers (Table 12 in his paper), the characteristic parameters for PH were $P^* = 5844$ bar, $T^* = 740$ K, and $\rho^* = 1.2244$ g/cm^3, whereas in the case of PMMA, $P^* = 4883$ bar, $T^* = 742$ K, and $\rho^* = 1.2298$ g/cm^3

Luengo et al.[35] have published *PVT* data for a sample of PVPh. Data from 130 to 250 °C at 10, 20, 40, 60, 80, and 100 MPa are included in the paper. These data can be used[36] to get a zero-pressure Tait equation: $V(0,T) = 0.75904 \exp(1.73{\cdot}10^{-5}T^{3/2})$ (T in K). Using these same data, the characteristic parameters of PVPh were $P^* = 4607$ bar, $T^* = 768$ K, and $\rho^* = 1.244$ g/cm^3.

Figure 3 shows the theoretical simulation of the evolution of the excess specific heat with temperature for a PH/PMMA 50:50 blend (now ΔC_p is in cal/g K, as the experimental results summarized in Table 1). In this figure, the association model included the correct reference state,[20] screening effects, and free volume effects.[21] In comparing this figure with the slope in Figure 1, it is clear that the free volume effects are important. Although at low temperatures the excess specific heat

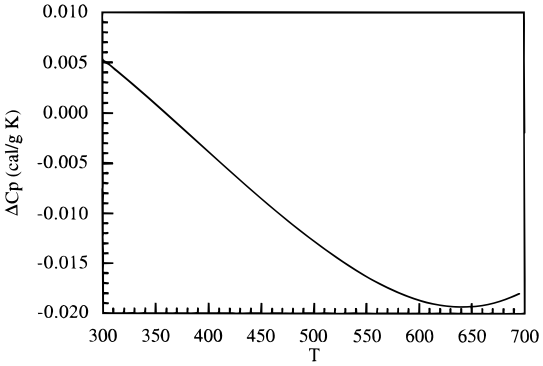

Figure 4. Simulation of the evolution of the excess specific heat with temperature of a 50/50 PVPh/PMMA blend, using the association model modified with free-volume terms.

of mixing is negative, at temperatures not very far from the experimental range this tendency is inverted and ΔC_p becomes positive. However, all around the temperatures included in the graph, ΔC_p is very small (from -0.006 (cal/cm^3 K) at 300 K to 0.002 (cal/cm^3 K) at 700 K). Although shielding effects have not been included in our calculations, it does not seem to be the origin of such discrepancies. Accesibility problems will decrease the actual value of the association constant, but given its low value, it would not solve the problem.

For PVPh/PMMA blends (Figure 4), which involve considerably stronger interactions, the effect of free volume does not change the sign of ΔC_p up to the high considered temperatures. Moreover, between 425 and 475 K (the experimental investigated range) ΔC_p changes from -0.007 to -0.011 cal/g K, in excellent agreement with the experimental result included in Table 1. This confirms the previous statements of Graf et al.[21] in the sense that free volume effects may be neglected for the calculation of phase behavior in systems where hydrogen bonding is very important. Further work involving blends with different levels of interaction strengths is necessary to clarify the role of the intrachain contacts and free volume. In this kind of comparison between theory and experiments, ΔC_p measurements can be a valuable tool to reinforce other experimental determinations such as phase diagrams.

Conclusions

Experimental determinations of excess specific heats in polymer blends have been revealed as a valuable tool to check the influence of different factors affecting miscibility in blends with different levels of specific interactions. It has been confirmed that in blends with strong specific interactions (PVPh/PMMA), free volume effects are not an important factor in the thermodynamic magnitudes of the blends. However, when these specific interactions are weaker (PH/PMMA), the effect of free-volume terms can compensate the role of the hydrogen bonding, specially when the temperature increases.

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Appendix

In the main body of this paper two modifications of the original association model have been mentioned and utilized to compare the results, namely, (1) the new version of the model (correct reference of state) which accounts for intramolecular screening and (2) the association model, which accounts for both the equation-of-state effects and intramolecular screening.

A detailed description of the old model with the inclusion of free volume effects and the first modification, as well as the relevant equations, can be found in refs 21 and 20, respectively. The model which accounts for the free volume and intramolecular screening in hydrogen-bonded mixtures is then a simple extension of these two previous models. Below we give a brief explanation and derive the equations for an association type of model accounting for the equation-of-state effects and intramolecular screening.

The starting point is the equation-of-state model for hydrogen-bonding mixtures. The free energy of the polymer mixture is given[21] as

$$\begin{aligned} G = kT\Big[& N_{\mathrm{A}} \ln\left(\frac{\phi_{\mathrm{A}}}{\omega_{\mathrm{A}}}\right) + N_{\mathrm{B}} \ln\left(\frac{\phi_{\mathrm{B}}}{\omega_{\mathrm{B}}}\right) + n_{\mathrm{e}} \ln(1 - \tilde{\rho}) + \\ & (N_{\mathrm{A}} + N_{\mathrm{B}}) \ln(\tilde{\rho})\Big] + n_0^* v^* \left(-\tilde{\rho} P^* + \frac{P}{\tilde{\rho}}\right) + \\ & kT\left[n_{\mathrm{A}_1} \ln\left(\phi_{\mathrm{A}_1} \frac{\tilde{\rho}}{S_{\mathrm{A}}}\right) + \Sigma n_{\mathrm{B_h}} \ln\left(\phi_{\mathrm{B_h}} \frac{\tilde{\rho}}{h S_{\mathrm{B}}}\right) + \right. \\ & \left.\Sigma n_{\mathrm{B_h A}} \ln\left(\phi_{\mathrm{B_h A}} \frac{\tilde{\rho}}{h S_{\mathrm{B}} + S_{\mathrm{A}}}\right)\right] - kT\left[n_{\mathrm{A}} \ln\left(\phi_{\mathrm{A}} \frac{\tilde{\rho}}{S_{\mathrm{A}}}\right) + \right. \\ & \left. n_{\mathrm{B}} \ln\left(\phi_{\mathrm{B}} \frac{\tilde{\rho}}{S_{\mathrm{B}}}\right)\right] + kT\{(n_{\mathrm{B}} - \Sigma n_{\mathrm{B_h}})[1 - \ln(z - 1)] + \\ & \Sigma n_{\mathrm{B_h}} \ln \sigma\} \end{aligned} \tag{A1}$$

Consequently the pure component free energies can be written as

$$\begin{aligned} G_{\text{pure A}} = {} & \\ & kT\left[N_{\mathrm{A}} \ln\left(\frac{\sigma \mathrm{e}^{\mathrm{M_A} S_{\mathrm{A}}^0 - 1}}{M_{\mathrm{A}} S_{\mathrm{A}}^0 (z-1)^{M_{\mathrm{A}} S_{\mathrm{A}}^0 - 1}}\right) + n_{\mathrm{e,A}} \ln(1 - \tilde{\rho}_{\mathrm{A}}) + \right. \\ & \left. N_{\mathrm{A}} \ln \tilde{\rho}_{\mathrm{A}}\right] + n_{\mathrm{A}} S_{\mathrm{A}}^0 v_{\mathrm{A}}^* \left(-\tilde{\rho}_{\mathrm{A}} P_{\mathrm{A}}^* + \frac{P}{\tilde{\rho}_{\mathrm{A}}}\right) \end{aligned} \tag{A2}$$

$$\begin{aligned} G_{\text{pure B}} = {} & \\ & kT\left[N_{\mathrm{B}} \ln\left(\frac{\sigma \mathrm{e}^{\mathrm{M_B} S_{\mathrm{B}}^0 - 1}}{M_{\mathrm{B}} S_{\mathrm{B}}^0 (z-1)^{M_{\mathrm{B}} S_{\mathrm{B}}^0 - 1}}\right) + n_{\mathrm{e,B}} \ln(1 - \tilde{\rho}_{\mathrm{B}}) + \right. \\ & \left. N_{\mathrm{B}} \ln \tilde{\rho}_{\mathrm{B}}\right] + n_{\mathrm{B}} S_{\mathrm{B}}^0 v_{\mathrm{B}}^* \left(-\tilde{\rho}_{\mathrm{B}} P_{\mathrm{B}}^* + \frac{P}{\tilde{\rho}_{\mathrm{B}}}\right) + \\ & kT\left[-\mathrm{n}_{\mathrm{B}} \ln\left(\frac{\tilde{\rho}_{\mathrm{B}}}{S_{\mathrm{B}}}\right) + \Sigma \mathrm{n}_{\mathrm{B_h}}^0 \ln\left(\phi_{\mathrm{B_h}}^0 \frac{\tilde{\rho}_{\mathrm{B}}}{h S_{\mathrm{B}}^0}\right)\right] + \\ & kT\{(n_{\mathrm{B}} - \Sigma n_{\mathrm{B_h}}^0)[1 - \ln(z-1)] + \Sigma n_{\mathrm{B_h}}^0 \ln \sigma\} \end{aligned} \tag{A3}$$

The free energy of mixing can now be obtained as

$$G_{\mathrm{mix}} = G - G_{\text{pure A}} - (G_{\text{pure B}} - kT\Omega_{\mathrm{swell}}) \tag{A4}$$

where the term

$$\Omega_{\mathrm{swell}} = \left[\phi_{\mathrm{B}}\frac{\tilde{\rho}\ S^{0}_{\mathrm{B}}}{\tilde{\rho}_{\mathrm{B}}S_{\mathrm{B}}}\right]^{n_{\mathrm{B}}-(n_{\mathrm{B}}/\overline{n^{0}_{\mathrm{B_h}})}} \qquad \text{(A5)}$$

was included by Graf et al.[21] to account for the difference in the number of configurations of hydrogen-bonded pure component B at different volumes, namely, at pure component volume (B) and, on the other hand, volume equivalent to the volume of the mixture.

This difference in volume arises because in the original model Painter et al. adopted the mixed covalent chains as the reference state for calculating all the contributions to the free energy of mixing instead of the standard Flory reference state.[14] Formally, this choice of the reference state is incorrect, but it compensates for the effect of long-range correlations and compositional heterogenities arising from intramolecular screening effects. As previously mentioned, the association model was revised[19,20] by using the correct reference state and incorporating the screening effects. This approach can be easily extended to the present case, where equation-of-state terms are also considered.

In doing so, the term Ω_{swell} need no longer be considered and we then have a slightly different equation for the free energy of mixing and the stoichiometry, though the form is essentially the same as that obtained by Graf et al.:[21]

$$G_{\mathrm{mix}} = G - G_{\mathrm{pure\ A}} - G_{\mathrm{pure\ B}} \qquad \text{(A6)}$$

The change in the free energy of mixing can now be obtained by using the chemical potentials of the species A and B:

$$\frac{\Delta G_{\mathrm{mix}}}{kT} = n_{\mathrm{A}}\frac{\mu_{\mathrm{A}} - \mu^{0}_{\mathrm{A}}}{kT} + n_{\mathrm{B}}\frac{\mu_{\mathrm{B}} - \mu^{0}_{\mathrm{B}}}{kT} \qquad \text{(A7)}$$

Leading to

$$\begin{aligned}\frac{\Delta G_{\mathrm{mix}}}{kT} = {} & \frac{\phi_{\mathrm{A}}}{r^{*}M_{\mathrm{A}}}\ln\phi_{\mathrm{A}} + \frac{\phi_{\mathrm{B}}}{M_{\mathrm{B}}}\ln\phi_{\mathrm{B}} + \\ & \frac{S^{0}_{\mathrm{B}}v^{*}_{\mathrm{B}}}{kT}\left\{-[\tilde{\rho}P^{*} - \phi_{\mathrm{A}}\tilde{\rho}_{\mathrm{A}}P^{*}_{\mathrm{A}} - \phi_{\mathrm{B}}\tilde{\rho}_{\mathrm{B}}P^{*}_{\mathrm{B}}] + \right. \\ & \left. P\left(\frac{1}{\tilde{\rho}} - \frac{\phi_{\mathrm{A}}}{\tilde{\rho}_{\mathrm{A}}} - \frac{\phi_{\mathrm{B}}}{\tilde{\rho}_{\mathrm{B}}}\right)\right\} + \frac{\phi_{\mathrm{A}}}{r^{*}}\left\{S^{0}_{\mathrm{A}}\left[\left(\frac{1}{\tilde{\rho}} - 1\right)\ln(1-\tilde{\rho}) - \right.\right. \\ & \left.\left.\left(\frac{1}{\tilde{\rho}_{\mathrm{A}}} - 1\right)\ln(1-\tilde{\rho}_{\mathrm{A}})\right] + \frac{1}{M_{\mathrm{A}}}\ln\left(\frac{\tilde{\rho}\ S^{0}_{\mathrm{A}}}{\tilde{\rho}_{\mathrm{A}}S_{\mathrm{A}}}\right)\right\} + \\ & \phi_{\mathrm{B}}\left\{S^{0}_{\mathrm{B}}\left[\left(\frac{1}{\tilde{\rho}} - 1\right)\ln(1-\tilde{\rho}) - \left(\frac{1}{\tilde{\rho}_{\mathrm{B}}} - 1\right)\ln(1-\tilde{\rho}_{\mathrm{B}})\right] + \right. \\ & \left.\frac{1}{M_{\mathrm{B}}}\ln\left(\frac{\tilde{\rho}\ S^{0}_{\mathrm{B}}}{\tilde{\rho}_{\mathrm{B}}S_{\mathrm{B}}}\right)\right\} + \frac{\phi_{\mathrm{A}}}{r^{*}}\ln\phi_{\mathrm{A_1}} + \phi_{\mathrm{B}}\ln\frac{\phi_{\mathrm{B_1}}}{\phi^{0}_{\mathrm{B_1}}} - \Sigma\frac{\phi_{\mathrm{B_h}}}{h} + \\ & \phi_{\mathrm{B}}\Sigma\frac{\phi^{0}_{\mathrm{B_h}}}{h} - \left[\frac{\phi_{\mathrm{A}}}{r^{*}}\ln\phi_{\mathrm{A}} + \phi_{\mathrm{B}}\ln\phi_{\mathrm{B}}\right] \qquad \text{(A8)}\end{aligned}$$

Further, the equation of state can be obtained by minimizing the free energy change with respect to the number of empty lattice sites or alternatively the reduced density ($\tilde{\rho}$):

$$\tilde{\rho}_i^{2} + \tilde{P}_i + \tilde{T}_i\left[\ln(1-\tilde{\rho}_i) + \left(1 - \frac{1}{S_i}\right)\tilde{\rho}_i\right] = 0 \qquad \text{(A9)}$$

where

$$\frac{1}{S_i} = \frac{1}{S_i}\left[\frac{1}{M_i} + \frac{\Gamma^{0}_{1}}{\Gamma^{0}_{2}} - 1\right] \qquad \text{(A10)}$$

and

$$\frac{1}{S_i} = \frac{v^{*}_{\mathrm{ref}}}{V^{*}_{i}} \qquad \text{(A11)}$$

For the nonself-associating component (i.e. A)

$$\frac{\Gamma^{0}_{1}}{\Gamma^{0}_{2}} = 0$$

Stoichiometry. The equilibrium constants (self-association and interassociation) are both modified by the intramolecular screening effects. A detailed discussion of this point is given in ref 20. The equilibrium constants and the stoichiometry of the equation of the state model are modified to include the screening effects. Thus,

$$K_{\mathrm{B}} = \tilde{K}_{\mathrm{B}}\frac{f_{\mathrm{B}}}{p} \quad \text{and} \quad K_{2} = \tilde{K}_{2}\frac{f_{\mathrm{B}}}{p} \qquad \text{(A12)}$$

$$K_{\mathrm{A}} = \tilde{K}_{\mathrm{A}}\frac{f_{\mathrm{A}}}{(1-p)} \qquad \text{(A13)}$$

where f_{A} and f_{B} are the true volume fractions (obtained by taking into account empty lattice sites or "free volume") and are related to the volume fraction through the reduced density

$$f_{\mathrm{A}} = \tilde{\rho}\phi_{\mathrm{A}} \qquad \text{(A14)}$$

The probability of a B segment being adjacent to another B segment, p_{BB}, is

$$p = p_{\mathrm{BB}} = \gamma + (1-\gamma)f_{\mathrm{B}} \qquad \text{(A15)}$$

where γ is the fraction of intramolecular or same chain contacts. It is assumed that $\gamma_{\mathrm{A}} \approx \gamma_{\mathrm{B}} \approx \gamma \approx 0.36$. This value of γ was obtained by Monte Carlo simulations (ref 20). $\tilde{K}_{\mathrm{B}}$, $\tilde{K}_{2}$, and $\tilde{K}_{\mathrm{A}}$ are the equilibrium constants including the cooperative effects (or screening). As in ref 21, the stoichiometric equations are given by

$$\phi_{\mathrm{B}} = \phi_{\mathrm{B_1}}\tilde{\Gamma}_{2}\left(1 + \tilde{\rho}\frac{\tilde{K}_{\mathrm{A}}\phi_{\mathrm{A_1}}}{r^{*}}\right) \qquad \text{(A16)}$$

$$\phi_{\mathrm{A}} = \phi_{\mathrm{A_1}}(1 + \tilde{\rho}\tilde{K}_{\mathrm{A}}\phi_{\mathrm{B_1}}\tilde{\Gamma}_{1}) \qquad \text{(A17)}$$

where

$$\tilde{\Gamma}_{1} = \left(1 - \frac{\tilde{K}_{2}}{\tilde{K}_{\mathrm{B}}}\right) + \frac{\tilde{K}_{2}}{\tilde{K}_{\mathrm{B}}}\left(\frac{1}{1 - \tilde{\rho}\tilde{K}_{\mathrm{B}}\phi_{\mathrm{B_1}}}\right) \qquad \text{(A18)}$$

and

$$\tilde{\Gamma}_2 = \left(1 - \frac{\tilde{K}_2}{\tilde{K}_B}\right) + \frac{\tilde{K}_2}{\tilde{K}_B}\left(\frac{1}{1 - \tilde{\rho}\tilde{K}_B\phi_{B_1}}\right)^2 \qquad (A19)$$

The hydrogen-bond distribution term in the free energy (equation A8) can now be written as

$$\left(-\Sigma\frac{\phi_{B_h}}{h} + \phi_B\Sigma\frac{\phi^0_{B_h}}{h}\right) = -\phi_B\frac{\Gamma^0_1}{\Gamma^0_2} + \phi_{B_1}\Gamma_1 \qquad (A20)$$

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