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On the Application of an Association Model to Blends Containing Poly(hydroxy ether of Bisphenol A)

E. Espi,[†] **M. Alberdi, and J. J. Iruin**[*]

Departamento de Ciencia y Tecnologia de Polimeros, Facultad de Quimica, Universidad del Pais Vasco, P.O. Box 1072, 20080 San Sebastian, Spain

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ABSTRACT: The possibilities and shortcomings of the Painter–Coleman association model (PCAM) to predict some thermodynamic properties of polymer blends are explored. More specifically, enthalpies of mixing, excess heat capacities, melting point depressions in crystalline/amorphous blends, and the evolution of the glass transition temperature with blend composition are simulated for blends of phenoxy (a copolymer of Bisphenol A and epichlorohydrin) (PH) with families of polymers, including poly(alkylene oxides), poly(vinyl alkyl ethers), aliphatic polyesters, and polymethacrylates. Results are compared with some previously reported experimental data.

Introduction

In recent papers[1,2] and a book[3] Painter, Coleman, and co-workers have proposed an association model to determine free energy changes and the phase behavior of binary polymer blends where specific interactions are present. The main equation of this model has the form of the classic Flory–Huggins relation, but with an added term to account for the strong interactions,

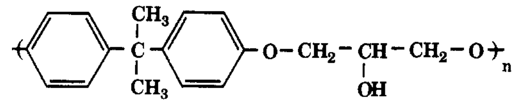
$$\frac{\Delta G_m}{RT} = \frac{\Phi_A}{N_A}\ln \Phi_A + \frac{\Phi_B}{N_B}\ln \Phi_B + \Phi_A\Phi_B\chi + \frac{\Delta G_H}{RT} \qquad (1)$$

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 accounts for the "physical" forces. The first and second terms correspond to 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 a group contribution method proposed by Coleman et al.[4] The $\Delta G_H/RT$ term can be calculated if one knows the molar volumes of the chemical repeat units V_A and V_B and the equilibrium constants describing the association equilibria occurring in the mixture. Finally, 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, and others can be easily derived.

One of the properties more frequently used to describe polymer blends is the enthalpy of mixing. Although in systems with strong specific interactions there is an important change of noncombinatorial entropy which cannot be disdained, a negative value of this magnitude has been taken as a criterion of miscibility.[5-8] The polymer–polymer enthalpy of mixing cannot be directly measured by calorimetric methods because of the high viscosity of the mixture, but some attempts to estimate it in an indirect way, by using Hess' law cycle[9-11] or heats of mixing from model compounds or oligomers,[12-16] have been made. Recently, Lai et al.[17,18] proposed a group contribution method to estimate it from heats of mixing of simple liquids.[19]

Other properties, such as glass transition temperatures or melting point depressions, can be easily measured by DSC. Several equations have been proposed to explain the glass transition temperatures of a blend as a function of composition.[20-26] But, either because they use some adjustable parameters or because they do not run correctly for blends with strong interactions, there was not an actual predictible model for this property. As far as the melting point depression is concerned, it is usually employed to calculate the overall Flory–Huggins polymer–polymer interaction parameter on the basis of the Nishi–Wang equation.[27] However, because of the difficulties in obtaining an accurate value of the overall interaction parameter, the Nishi–Wang equation is not usually employed in the inverse direction as a tool for predicting the melting point depression of a crystallizable polymer in the presence of an amorphous one.

Blends of poly(hydroxy ether of Bisphenol A) (Phenoxy; PH)



with aliphatic[28] and aromatic[29] polyesters, polymethacrylates,[30] polyoxides,[31,32] and poly(vinyl ethers)[33] have been widely studied in the last years. These blends exhibit different phase behaviors, from completely miscible to completely immiscible.

Phenoxy-containing systems show some special difficulties in carrying out the calculation of the Painter–Coleman association model (PCAM) parameters. Since a quantitative study of the carbonyl band is not feasible and the ether asymmetric stretching band is not useful for these kinds of studies, the only possible way is to use the hydroxyl stretching band. The second problem is the strong PH self-association, which prevents a quantitative study of the "free" hydroxyl band in the solid state. For this reason, it is necessary to dilute these self-associations using, for example, a nonpolar solvent. However, phenoxy is only miscible in solvents that form strong interactions with its hydroxyl groups (tetrahydrofuran, dioxane, chloroform, etc.). Low molecular weight analogues, soluble in nonpolar solvents, have been used[34,35] to substitute phenoxy and to perform the study mentioned above. Variations of the free hydroxyl band absorbance with model compound concentration and frequency shifts were used

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[*] To whom correspondence should be addressed.

[†] Present address: Repsol Petroleo S.A., Research Center, P.O. Box 17044, 28080 Madrid, Spain.

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Table I. Summary of PCAM Association Parameters for Phenoxy Blends with Polyesters and Polyethers[35]

interaction	K (25 °C)	Δh (cal/mol)
self-association		
dimer formation	14.4	-2500
multimer formation	25.6	-3400
Interassociation		
with polyethers	3.4	-3000
with polyesters	4.1	-2700

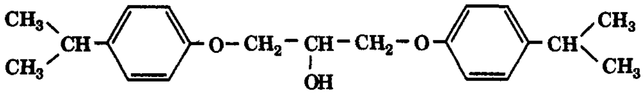
to calculate association constants and enthalpies, respectively.

Methods and Procedures

In a previous study,[35] we have obtained the required parameters for the correct use of the Painter–Coleman Association Model software.[3] In order to estimate the free energy of mixing for a polymer blend using the Painter–Coleman equation, two groups of parameters are required. The first one defines the association equilibria between polymers (equilibrium constants K_B (K_2) and K_A and their respective enthalpies h_B (h_2) and h_A). In the second set characteristic parameters of the polymers such as molecular weights M_w and molar volumes V_m of the repeating unit, solubility parameters δ, and degrees of polymerization DP are necessary. This last set can be easily calculated from group contribution methods, but association parameters have to be estimated from a FTIR study of the appropriate polymer blend or an analogue mixture.

We have followed the procedure applied by Coggeshall and Saier,[36] who studied the self-associations of alcohols and phenols in dilute solutions with nonpolar solvents and their interassociations with some hydrogen-bonding acceptors. They found that two equilibrium constants are required to describe most alcohol self-associations, one describing the formation of dimers K_2 and the other one describing the formation of higher multimers K_B. In the phenoxy case, Coleman et al.[34] also included a third self-association constant describing the association between its hydroxyl and ether groups.

Dilute solutions of an analogue Phenoxy compound, 1,3-bis[4-(2-propyl)phenoxy]-2-propanol (IPPHP) in cyclohexane, were used to determine the self-association constants.[35]



Interassociation constants (K_A) were obtained by fitting the free OH band absorbance at one fixed IPPHP concentration and varying that of the other analogue compound. We used diethylene glycol diethyl ether (DEGDEE) as a model compound of polyethers, and diethyl adipate (DEA) for linear aliphatic polyesters and acrylic polyesters. Equilibrium constants are shown in Table I.

Association enthalpies can be calculated if one knows values of the corresponding constants at different temperatures. However, in our case, the low cyclohexane boiling point made these measurements in an extended temperature range difficult. For this reason, we used[35] an indirect estimation based on the frequency shifts in the IPPHP infrared spectrum.[37] Results also appear in Table I.

The simulations of the model have been compared with experimental data taken from different sources cited in the next paragraphs.

Results and Discussion

Heats of Mixing and Excess Heat Capacities. From the free energy of mixing (ΔG_m) of a system at different temperatures, it is possible to calculate the enthalpy of mixing (ΔH_m) using the Gibbs–Helmholtz relationship:

$$\partial(\Delta G_m/T)/\partial(1/T) = \Delta H_m \qquad (2)$$

The free energy of mixing was calculated using the same procedure described by Coleman et al.[38] and the parameters previously obtained[35] from the FTIR study of low molecular weight analogues.

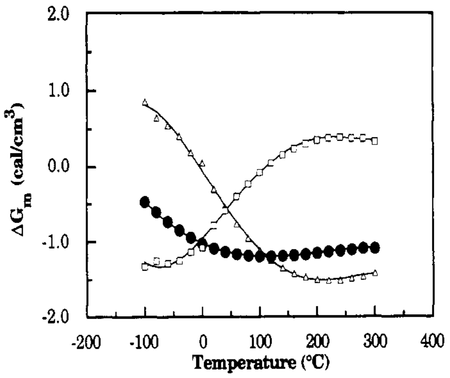


Figure 1. Effect of temperature on the predicted ΔG_m (●) and its components (△, enthalpic term (ΔH_m); □, entropic term ($-T\Delta S_m$)) for a PH/PEO blend 50:50 by weight.

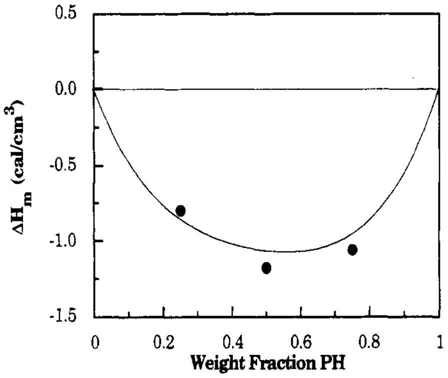


Figure 2. Heats of mixing of PH with PEO at 95 °C: (—) PCAM predictions; (●) experimental results from model compounds[19] (Table I).

First of all, we have centered our attention in the PH/poly(ethylene oxide) (PEO) blend, a system exhaustively studied by our group.[39,40] As is shown in Figure 1, ΔG_m is predicted to be negative in all the studied temperature range, showing a minimum near 100 °C. The shape of the curve suggests that ΔG_m could be positive for very low and very high temperatures. This would imply a phase behavior with both UCST and LCST, but they would appear at temperatures far below the T_g and above the degradation temperature, respectively.

Using eq 2, we can calculate ΔH_m and, by difference, $-T\Delta S_m$ for this blend. Whereas ΔH_m is predicted to be positive at temperatures below -20 °C and negative above it, $-T\Delta S_m$ is negative below 120 °C and positive above it. These tendencies are similar to others predicted by free-volume models, in spite of the fact that PCAM does not take into account this effect. Another point that should be remarked on is that ΔG_m is negative between −100 and +300 °C, but due to different effects. The enthalpic term at low temperature and the entropic one at high temperature are in the origin of the blend miscibility.

In order to check these predictions, simulated enthalpies of mixing have been compared with some experimental data. Experimental results obtained from mixtures of two model compounds (1,3-bis[4-(2-propyl)phenoxy]-2-propanol for PH and diethylene glycol diethyl ether for PEO) have previously been reported by our group.[19] Given that these measurements were carried out at 95 °C, we have calculated ΔH_m for the PH/PEO blend at this temperature. As we can see in Figure 2, the agreement between experimental and calculated results was excellent.

However, some doubts about the identification of heats of mixing from model compounds and those corresponding to high molecular weight polymers could remain. The

Table II. Comparison of Predicted Heats of Mixing for PH/Polyether and Polyester Blends (50:50 by weight and 95 °C) and the corresponding Experimental Results from Model Compounds[19,34]

polymer	CH_2/ether or ester relation	ΔH_m (cal/cm^3) predictn (polymers)	ΔH_m (cal/cm^3) exptl (models)	miscible with PH?
polyoxides				
PMO	1	−1.52	+1.18	no
PEO	2	−1.09	−1.23	yes
PTrO	3	−0.70	−0.63	?
PTHF	4	−0.43	−0.56	?
polyesters				
PGL	1	−0.28		?
PES	2	−0.77	+0.49	no
PEA	3	−0.81	−0.18	yes
PBA	4	−0.62	−0.72	yes
PCL	5	−0.47		yes
P6L	6	−0.39	−0.68	?
PHS	7	−0.34		no

study of PH/poly(vinyl methyl ether) (PVME) can be particularly useful to verify the possibilities of the PCAM analysis. This system separates into two phases upon heating at approximately 160 °C (LCST).[31,41] In a previous work, Uriarte et al.[41] studied the heat absorbed during the separation process using DSC. The obtained result varied with the heating rate but showed a plateau value of 0.48 cal/g. Assuming that the phases consist mainly of the pure components (and the phase diagram supports this assumption), the heat of demixing gives an approximation of the heat of mixing (changing the sign), as was proposed by Ebert et al.[42] PCAM predicts a heat of mixing of −0.56 cal/g for this blend at 160 °C so, in this case, predictions and experiments with polymer mixtures and not with analogues are in good accord, too.

Similar simulations have been done for blends of Phenoxy with poly(alkylene oxides) having methylene/ether ratios between 1 and 4. Blends of Phenoxy with poly(methylene oxide) (PMO, ratio = 1), poly(ethylene oxide) (PEO, 2), poly(trimethylene oxide) (PTrO, 3), and poly(tetrahydrofuran) (PTHF, 4) at 50:50 weight composition and 95 °C have been studied. The most negative value corresponds to the PH/poly(methylene oxide) (PMO) blend, and the trend is to change to less negative values upon increasing the CH_2/O relation. Comparing these predictions with heats of mixing of model compounds[35] (IPPHP with 1,3,5-trioxane (ratio = 1), diethylene glycol dimethyl ether (DEGDME, 2), diethylene glycol diethyl ether (DEGDEE, 2.7), ethylene glycol diethyl ether (EGDEE, 3), and diethylene glycol dibutyl ether (DEGDBE, 4)) (Table II), we can see that agreement is excellent for all blends except the PH/PMO. In this case, the heat of mixing of IPPHP with 1,3,5-trioxane is clearly positive, while the prediction is negative.

The same behavior was observed in blends of PH with a series of linear aliphatic polyesters (see also Table II). A similar study for blends of PH with polyesters having methylene/ester ratios between 1 and 7 has been carried out. These polyesters were poly(glycolate) (PGL, ratio = 1), poly(ethylene succinate) (PES, 2), poly(ethylene adipate) (PEA, 3), poly(butylene adipate) (PBA, 4), poly(ϵ-caprolactone) (PCL, 5), poly(ζ-heptanoic lactone) (P6L, 6), and poly(hexamethylene sebacate) (PHS, 7). The simulated enthalpies have been compared with experimental enthalpies of mixing of mixtures constituted by IPPHP and analogue compounds such as dimethyl succinate (DMS, ratio = 2), diethyl succinate (DES, 3), dimethyl adipate (DMA, 3), diethyl adipate (DEA, 4), and dibutyl adipate (DBA, 6).[19] In this case, the deviation of the predictions toward negative values begins for CH_2/COO relations of 3. Taking into account that PCAM association parameters were calculated using DEGDEE (2.7) and DEA (4) for each family, it is evident that deviations occur for lower relations. In light of this findings we can conclude that PCAM runs adequately for all the studied blends, except those having a frequency of hydrogen-bonding acceptor groups higher than that of the molecule used to calculate the association parameters. In this last case, PCAM exaggerates the trend to miscibility.

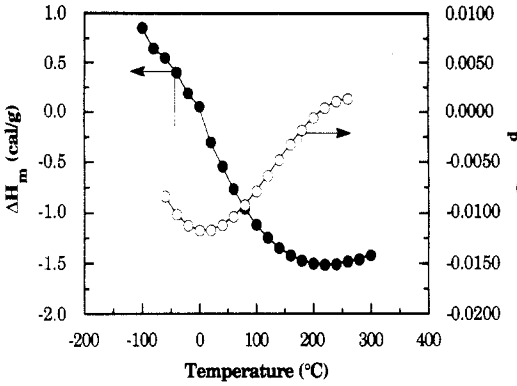


Figure 3. Effect of temperature on the predicted enthalpy of mixing (●) and excess heat capacity (○) for a PH/PEO blend 50:50 by weight.

Having checked the ability of PCAM to predict heats of mixing, it would be interesting to do the same for the variation of the latter with temperature which gives the excess heat capacity:

$$\frac{\partial(\Delta H_m)}{\partial(T)} = \rho\Delta C_p = \rho(C_p - \omega_A C_{pA} - \omega_B C_{pB}) \qquad (3)$$

in this equation ρ is density, ω_i the weight fractions, and C_{pi} the heat capacities of the pure components. Barnum et al.[43] have measured this property for blends of poly(methyl methacrylate) with a copolymer of α-methylstyrene and acrylonitrile and another one of polycarbonate with a copolyester (Kodar). Our group carried out a similar study for PH/PEO[40] and PH/PVME[41] blends. In all these systems, positive values of ΔC_p (on the order of 10^{-2} cal/g·K) were found. This means that ΔH_m would tend to less negative values upon heating the blend, a consistent result with the existence of a LCST diagram. In the framework of the model proposed by ten Brinke and Karasz,[44] this is indicative of systems with "directional specific" interactions. Disappointingly, PCAM predictions seem to have some difficulties in reproducing the experimental ΔC_p. Although it is necessary to consider the important experimental error inherent to these measurements, the PH/PEO blend shows a minimum for ΔH_m in the vicinity of 200 °C (Figure 3). This implies that ΔC_p should be negative between −100 and +200 °C and positive for temperatures above 200 °C. In both ranges the absolute value was very small.

Melting Point Depression. In a recent work,[45] Painter et al. proposed a new equation to predict the melting point depression of polymer blends where one of the components crystallizes. This equation has a form similar to that proposed by Nishi and Wang[27] some years ago but presents an added term to account for the chemical potential derived from the Painter–Coleman equation for the free energy of mixing.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{rR}{\Delta H_f^\circ}[\chi\Phi_B^{\,2} + (\Delta\bar{G}_H)_A] \qquad (4)$$

where T_m and T_m° are the melting temperatures of the blend and of the pure crystallizable polymer (A), respectively, r is the ratio of molar volumes of chemical repeat

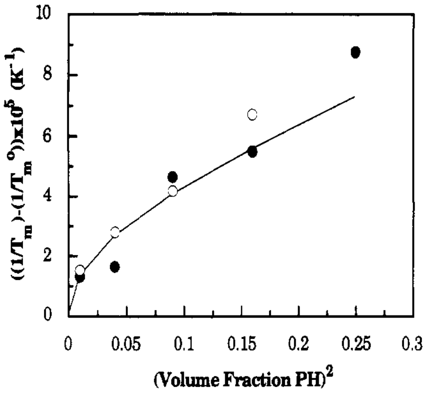


Figure 4. Plot of $1/T_m - 1/T_m°$ vs Φ_B^2 for the PH/PEO blend: (—) PCAM predictions; (●) experimental results from DSC measurements;[39] (○) experimental results from optical microscopy measurements.[39]

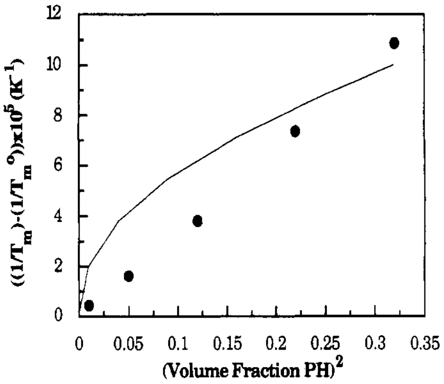


Figure 5. Plot of $1/T_m - 1/T_m°$ vs Φ_B^2 for the PH/PBA blend: (—) PCAM predictions; (●) experimental results from DSC measurements.[52]

units (V_A/V_B), $\Delta H_f°$ is the heat of fusion of polymer A, χ is the "physical" interaction parameter of the Painter–Coleman equation, Φ_B is the volume fraction of the amorphous polymer, and $(\Delta G_H)_A$ is the contribution of the specific term of the Painter–Coleman equation to the partial molar free energy. In some cases, the application of this equation has demonstrated that mixtures with strong specific interactions can show a variation of the overall interaction parameter with the composition.[45] That composition dependence would imply that the classical representation $1/T_m - 1/T_m°$ vs Φ_B^2 could show a non-straight shape. A clear example of this last case is the PH/PEO blend, studied in our laboratory by Iriarte et al.,[39] that shows a plain curvature in the Nishi–Wang representation (see Figure 4), and there are many other blends with the same behavior.[46–51]

Following the procedure described by Painter et al.[45] the parameters for the PH/PEO blend were $r = 0.176$ (from the group contribution method proposed by Coleman et al.,[4] $\Delta H_f° = 2020$ cal/mol,[39] and $\chi = 0.2$ (from the same group contribution method mentioned above). In this case, PCAM predictions agree exactly with the experimental trend (Figure 4). The observed curvature should be a consequence of a composition-dependent interaction parameter for compositions. For the other Phenoxy-containing blend studied, PH/poly(butylene adipate) (PBA), we used the following parameters: $r = 0.395$, $\Delta H_f° = 2950$ cal/mol,[52] $\chi = 0.12$. Predictions (Figure 5) have a form similar to that of PH/PEO. Contrarily, the experimental data of Harris et al.[52] do not show the same tendency and suggest a nearly constant interaction parameter. We attribute this result to the fact that the authors did not use the Hoffman–Weeks[53] procedure to evaluate T_m in equilibrium conditions.

Table III. Properties of Pure Polymers Used in the Simulation of the T_g–Composition Relationship

polymer	M_w	V_m (cm³/mol)	ΔC_p (cal/g·K)	T_g (°C)
PH	284.4	216.6	0.111	89/95
PMMA	100.1	84.9	0.101	106
PVME	58.1	55.3	0.179	−45

Glass Transition Temperatures. Although the glass transition temperature is not strictly an equilibrium property, Painter et al.[54] have proposed an equation to estimate it from their thermodynamic model. This equation can be considered as a modification of that proposed by Couchman[20] but with an additional term which accounts for the enthalpy of mixing due to the specific interactions. The glass transition temperature of the blend is a function of the PCAM association parameters and of some properties of the pure components, such as their T_g's or their heat capacity changes at the T_g.

Painter and Coleman have applied this equation to different blends containing poly(vinylphenol), an amorphous polyurethane, and a copolymer of ethylene and methacrylic acid[54] with amorphous polymers. Disappointingly, there are not many T_g data for blends containing PH and other amorphous polymer with ether or ester groups. (It should be emphasized that a crystalline component, such as an aliphatic linear poly(alkylene oxide) or polyester, would complicate the theoretical layout of the model.) Blends of PH and amorphous polyethers or polyesters where the T_g vs composition relationship had been measured are the PH/PVME and PH/poly(methyl methacrylate) (PMMA) systems. In the first case, the experimental T_g's measured by Uriarte et al.[41] were below those predicted by the additivity rule. On the contrary, the second blend, studied by Chiou et al.,[55] shows a slightly waving form, similar to the S-shaped plots described for other systems,[56,57] but lies in the neighborhood of the additive ones for every composition.

In these cases we have used the PCAM association parameters (Table I) and specific heat changes (ΔC_p) calculated using a group contribution method described in van Krevelen's book (Table III).[58] The use of ΔC_p's calculated in this manner or the experimental ones can have an influence on the predicted T_g's, but not in the general trends, as was shown in a previous work for blends of Phenoxy with poly(2-vinylpyridine) and poly(4-vinylpyridine).[59]

As can be seen in Figures 6 and 7, PCAM predictions agree quite well with the experimental trends. It should be emphasized that in both cases the form of the curve is reproduced by the model. However, the reduced number of studied systems and the appreciable deviation in the PH/PVME system impede us to ensure the good behavior of PCAM to predict glass transition temperatures. Up to this moment, we should limit its use to predict general trends, rather than exact values.

Conclusions

This work has demonstrated the reliability of the Painter–Coleman association model to predict heats of mixing for blends of Phenoxy resin with polyesters and polyethers. The few observed failures seem to indicate that PCAM does not run correctly if the methylene/hydrogen bond acceptor ratio of polymer A is smaller than that of the system where the association parameters were calculated. We have attributed this fail to steric effects of the larger repeating unit of Phenoxy.

Attending to the melting point depression in blends where polymer A crystallizes, PCAM seems to be able to predict it accurately, including the curvature of the Nishi–Wang plot for the PH/PEO blend.

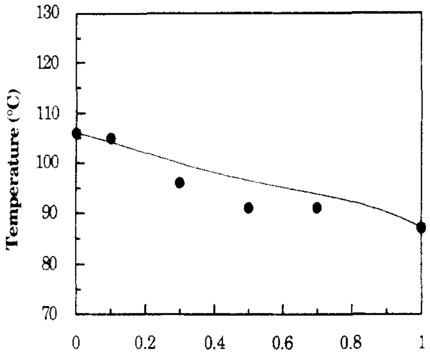


Figure 6. Comparison of predicted (—) and experimental[55] (●) T_g's of the PH/PMMA blend.

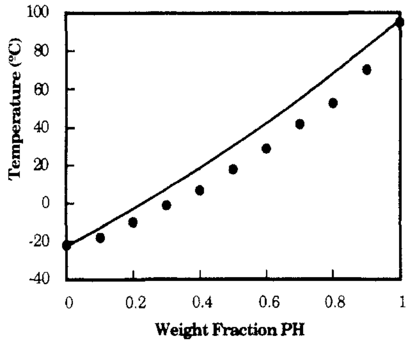


Figure 7. Comparison of predicted (—) and experimental[41] (●) T_g's of the PH/PVME blend.

On the other hand, the small number of systems studied and the deviations resultant in T_g's predictions, do not allow us to ensure a good behavior of PCAM in predicting this magnitude. However, it seems to be able to indicate if the general tendency of the T_g vs composition curve is above, around, or below the additivity rule.

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