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Binary poly(cyclohexyl methacrylate)/poly(styrene-*co*-vinyl phenol) blends: Comparisons of phase behaviour predictions using a single and a double interassociation model

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Abstract

The miscibility in blends of poly(cyclohexyl methacrylate) (PCHMA) with poly(4-vinyl phenol) (PVPh) and with copolymers containing vinyl phenol and styrene units (PSVPh) has been examined by Fourier transform infrared spectroscopy. The phase behaviour of the PCHMA/PSVPh system was predicted by means of association model of Painter and Coleman (PCAM) with a single interassociaton equilibrium constant (K_A) as well as by means of a new double interassociation model (D.I.M). The second interassociation equilibrium includes the weaker interaction between carbonyl and phenyl groups of CHMA and styrene (S) repeat units, respectively. In order to quantify the effect of free volume on miscibility, different contributions to free energy of mixing have been calculated. The predicted miscibility map did not change appreciably when compressibility effects were considered. On the other hand, by taking into account the second weaker interaction, better agreement between experimental and predicted miscibility maps is found for binary PCHMA/PSVPh blends. Finally, the D.I.M. has been extended to the case of ternary PCHMA/PS/PVPh blends.

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Keywords: Association model; Hydrogen bonding; Polymer blends

1. Introduction

Contrary to mixtures of small molecules, where the combinatorial entropy of mixing contributes an important part to stabilize the mixture, blends of high molecular weight components are characterized by an almost negligible value of combinatorial entropy [1–3]. Thus, in polymer systems, the phase behaviour is defined mainly by the compressible nature of the system, and the molecular interactions. In systems with directional specific interactions, such as hydrogen bonding, the thermodynamics of the mixtures have been described in the literature mainly by two theoretical approaches [4,5] based on the assumption that dispersion and relatively weak forces, compared to hydrogen bonds, can be considered separately from strong specific interactions.

The first approach [4], based on association models [6], assumes an equilibrium mixture of different species such as ‘monomers’ (or non-bonded species), hydrogen bonded ‘dimers’, ‘trimers’ and so on. The concentration of such species is quantified by means of equilibrium constants corresponding to their equilibrium formation process. Polymer blends with hydrogen bonding interactions have been widely described in terms of the association model of Coleman et al. In a first version [7–9], the model employs the Flory–Huggins expression of the free energy of mixing, but includes a term that takes into account the contribution corresponding to the changing distribution of hydrogen bonds as a consequence of polymer mixing. The unfavourable ‘physical’ interactions are embodied in a Flory- type χ parameter [10]. In an extended version [11], compressibility or equation of state effects have also been considered by incorporating a number of lattice sites to remain vacant and act as free volume.

The second one considers contacts rather than species, and is based on the combinatorial method introduced by Veytsman [12]. This approach is employed by Panayatou and Sanchez [5,13] to extend the lattice fluid model to hydrogen bonded polymer mixtures. The contribution of chemical interactions to free energy of mixing is calculated by counting the number of hydrogen bonds between hydrogen bonding donor and acceptor groups in the mixture.

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In polymer blends, in which only relatively weak forces, compared to hydrogen bonds are present, the free volume effect has necessarily to be considered in order to explain the experimental phase behaviour. This is the case of the lower critical solution temperature (LCST) behaviour exhibited by the well-known poly(vinyl methyl ether)/poly(styrene) system [14,15]. Apparently, the phase behaviour of PCHMA/PS system that does not show strong specific intermolecular interactions and it is miscible at room temperature can be explained in the same way, since the PCHMA/PS blends showed a single T_g which was composition dependent [16] and presented a LCST behaviour [17,18]. When PS was *para* substituted with a hydroxyl group (–OH), the resultant polymer (PVPh) was immiscible with PCHMA at all compositions [19]. Interestingly, miscibility between PCHMA and PVPh is achieved when PVPh is modified by incorporating [16] more than 50 wt% styrene.

In this paper, the miscibility of the blends formed by PCHMA and copolymers containing vinyl phenol and styrene units (PSVPh) will be examined by FTIR spectroscopy. The first version [7–9] of the PCAM, i.e. which does not take into account free volume effects, was able to predict correctly the experimental limits of miscibility for blends [20] of poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(*n*-butyl methacrylate) (PBMA) with PSVPh. As PS was immiscible with PMMA, PEMA and PBMA, the styrene in PSVPh copolymers was considered as an inert diluent in these blends. However, as was pointed out earlier, PS is miscible with PCHMA. The aim of this work is to determine quantitatively the extent of hydrogen bonding in the PCHMA/PSVPh systems, and check the capability of the PCAM to explain the miscibility behaviour, by studying the role of styrene in these systems, i.e. in what extent styrene can be considered as an inert diluent. The effect of the free volume on phase stability will also be evaluated in terms of the version of an association model extended to take into account the compressible nature of the polymers in hydrogen bonding polymer blends.

Moreover, in order to improve miscibility predictions for systems like PCHMA/PSVPh, where both strong specific interactions (like hydrogen bonding between CHMA and VPh repeat units) and weaker interactions (like between CHMA and S repeat units) can be present, we have extended PCAM by incorporating a second equilibrium constant to develop a double interassociation model (D.I.M). This refinement in the model has also been extended to the case of ternary PCHMA/PS/PVPh blends.

2. Background

The free energy of mixing ΔG_M in the PCAM is expressed through the Flory–Huggins equation, to which a term $\Delta G_H/RT$ has been added, that takes into account the contribution due to the changing distribution of hydrogen bonds in the blend, compared to the pure components. The basic model was revised by choosing a correct state of reference [12,21], and taking into account the screening effects [22], a consequence of the chain bending back upon itself. The general expression for ΔG_M results

$$\frac{\Delta G_M}{RT} = \left[\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B\right] + \phi_A\phi_B(1-\gamma)\chi + \frac{\Delta G_H}{RT} \tag{1}$$

where ϕ_A and ϕ_B, and N_A and N_B are the volume fractions and degrees of polymerizations of polymers A and B, respectively. χ accounts for only the unfavourable contributions arising from dispersion and weak forces. The parameter γ is defined as the fraction of same chain contacts. ΔG_H is the free energy change contributed by the hydrogen bonding between two components, which can be estimated by FTIR [23]. In the blends studied in this work, one of the components, B (PSVPh), self-associates to form hydrogen-bonded chains consisting of hydrogen bond segments linked by $h-1$ hydrogen bonds whereas, component A (PCHMA), does not self-associate and forms hydrogen bonds with B. The distribution of hydrogen-bonded species in the polymer blend is described by equilibrium constants ($\tilde{K}_2$, $\tilde{K}_B$ and $\tilde{K}_A$), which, as required, reflect the screening effects [22,24,25].

The original model was also extended to take into account compressibility effects by applying the Sanchez–Lacombe model [26,27], which considers that a number of the lattice sites remain vacant and act as free volume. A detailed description of the old model with the inclusion of free volume effects, as well as the relevant equations can be found in Refs. [11,22], respectively. The interested reader is referred to Iriarte et al. [28] for details of the obtention of ΔG_M and the definition of the terms employed in this work.

2.1. The double interassociation model (D.I.M.)

In this case, the assumed equilibrium scheme has to be modified when a specific interaction between S repeat units of copolymer PSVPh and carbonyl groups of PCHMA is considered, as it is shown below.

$$B_1 + B_1 \overset{\tilde{K}_2}{\leftrightarrow} B_2 \quad \text{dimer self}-\text{association}$$

$$B_n + B_1 \overset{\tilde{K}_B}{\leftrightarrow} B_{n+1} (n \geq 2) \quad \text{multimer self}-\text{association}$$

$$\left.\begin{array}{l} B_n + A_1 \overset{\tilde{K}_{AB}}{\leftrightarrow} B_nA \\ A_1 + D_1 \overset{\tilde{K}_{AD}}{\leftrightarrow} AD \end{array}\right\} \text{double interassociation}$$

Now, the binary blend studied (PCHMA/PSVPh) is described by a polymer A, composed of A repeat units (i.e. CHMA), and copolymer C, composed of B (i.e. VPh) and D (i.e. S) repeat units able to form A–B and A–D specific interactions, respectively. The repeat unit of copolymer C (PSVPh) is defined such that it contains x repeat units of B (i.e. x VPh repeat units) and y $(=1-x)$ repeat units of D (i.e. S repeat units). In the following, we will refer all our calculations to the molar volume of repeat unit B, V_B. Taking into account the volume fraction of repeat units in the copolymer C, and the volume fraction of components of the polymer A/copolymer C in the blend, we have the following relationships:

$$\phi_C = \phi_B + \phi_D$$

$$\phi_A + \phi_C = 1 \qquad (2)$$

$$\phi_B = x\phi_C$$

$$\phi_D = y\phi_C \qquad (3)$$

By assuming dimer and multimer self-association between B units in copolymer C [4], the different specific interactions in the polymer A/copolymer C blend can be described by equilibria shown in the above scheme being the corresponding equilibrium constants, $\tilde{K}_2$, $\tilde{K}_B$, $\tilde{K}_{AB}$ and $\tilde{K}_{AD}$.

The stoichiometric equations relating the volume fraction of non-bonded repeat units (ϕ_{B_1}, ϕ_{A_1} and ϕ_{D_1}) with the global volume fractions (ϕ_B, ϕ_A and ϕ_D) and the equilibrium constants are given by:

$$\phi_B = \phi_{B_1}\tilde{\Gamma}_2\left(1 + \tilde{K}_{AB}\frac{\phi_{A_1}}{r}\right) \qquad (4)$$

$$\phi_A = \phi_{A_1}\left(1 + \tilde{K}_{AB}\phi_{B_1}\tilde{\Gamma}_1 + \frac{\tilde{K}_{AD}}{s}\phi_{D_1}\right) \qquad (5)$$

$$\phi_D = \phi_{D_1}\left(1 + \tilde{K}_{AD}\frac{\phi_{A_1}}{r}\right) \qquad (6)$$

where $\tilde{\Gamma}_1$ and $\tilde{\Gamma}_2$ are parameters described in Ref. [22], $r = V_A/V_B$ and $s = V_D/V_B$. Following the methodology previously described [4,29] (and choosing the appropriate thermodynamic reference state [12]), the free energy change upon mixing polymer A and copolymer C can be obtained. Finally, miscibility predictions can be performed based on the following well known conditions for a binary blend to be thermodynamically miscible: $(\Delta G_M/RT) < 0$ and $[\partial^2(\Delta G_M/RT)/\partial\phi_B^2] > 0$

3. Experimental section

3.1. Materials

PVPh used in this study was obtained from Polysciences Inc. The other homopolymers used, polystyrene (PS) and poly(cyclohexyl methacrylate) (PCHMA) were synthesized in our laboratory [30] by free-radical polymerization using 2,2-azobisisobutyronitrile (AIBN) as the initiator at 70 °C in benzene. The random copolymers of styrene and vinyl phenol (PSVPh) were synthesized by copolymerization of styrene and acetoxystyrene in dioxane for 8 h at 80 °C using AIBN as initiator. The conversion was kept below 10% to minimize any compositional drift. Deprotection of the acetoxy groups was performed in the following manner: hydrazine hydrate was used to hydrolyse the acetoxy groups to hydroxyl groups allowing the reaction to proceed for approximately 40 h at room temperature. Removal of the protective group was monitored by infrared spectroscopy using the acetoxy carbonyl-stretching mode ($1758\ \text{cm}^{-1}$) as the diagnostic band. Finally, the completely unprotected copolymer was precipitated into a large excess of cold methanol and the excess solvent was removed in a vacuum oven at 130 °C for 24 h.

Ethyl benzene (EB) and cyclohexyl propionate (CHP), were purchased from Aldrich as low molecular weight analogues of PS and PCHMA repeat units, respectively.

3.2. Material characterization

Copolymer composition was determined by ^{1}H NMR spectroscopy with a Bruker 300 MHz instrument. Molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards and tetrahydrofuran (THF) as solvent. The weight distributions ($\bar{M}_w/\bar{M}_n$) of the copolymers appearing in this work are between 1.5 and 1.9. The mean of the average molecular weight of the polymers and copolymer employed in this paper, as well as their weight composition are shown in Table 1. Polymer and copolymers were also thermically characterized by measuring the glass transition temperature T_g in a Perkin–Elmer Pyris 1 differential scanning calorimeter. All the measurements in the DSC were

Table 1
The average molecular weights of the polymers employed in this study and their respective glass transitions

Sample	Abbreviation	$\bar{M}_w$[a]	T_g (°C)
Polystyrene	PS	350,000	100
Poly(cyclohexyl methacrylate)	PCHMA	519,000	117
Poly(vinyl phenol)	PVPh	30,000[b]	155[c]
Poly(styrene$_{75}$-*co*-vinyl phenol$_{25}$)	PSVPh[75-25]	92,000	119
Poly(styrene$_{50}$-*co*-vinyl phenol$_{50}$)	PSVPh[50-50]	90,000	146
Poly(styrene$_{60}$-*co*-vinyl phenol$_{40}$)	PSVPh[60-40]	87,000	140
Poly(styrene$_{70}$-*co*-vinyl phenol$_{30}$)	PSVPh[70-30]	85,000	123
Poly(styrene$_{80}$-*co*-vinyl phenol$_{20}$)	PSVPh[80-20]	82,000	115
Poly(styrene$_{90}$-*co*-vinyl phenol$_{10}$)	PSVPh[90-10]	68,000	108

[a] From GPC calculated using polystyrene standards.
[b] Provided by the supplier.
[c] Literature value [31].

carried out at a heating rate of 20 °C min^{-1} under N_2 atmosphere, calibrated with indium. The T_g was determined at the onset of the transition point of the heat capacity change from the second scan and is shown in Table 1.

3.3. Blend preparation

Blends of various compositions of PCHMA/PSVPh were prepared by solution casting. THF solutions containing 2 wt% of polymer were poured onto glass plates and allowed to evaporate very slowly at room temperature. Residual solvent was then removed in a vacuum oven at 130 °C for up to 48 h.

3.4. Intermolecular interactions

Fourier-transform infrared spectroscopy (FTIR) were mainly employed to determine intermolecular interactions. Thin films for FTIR studies were obtained by casting the blend solutions from 2% (w/v) tetrahydrofuran solutions onto potassium bromide windows. After the majority of the solvent had evaporated, the films were placed under vacuum in an oven at 150 °C for 3 h to completely remove the residual solvent and then they were slowly cooled to room temperature. The films used in this study were sufficiently thin to obey the Beer-Lambert law [32]. Infrared spectroscopic measurements were recorded on a Nicolet 560/Magna-IR spectrometer. A minimum of 64 scans were signal averaged with a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures, 140, 165 and 200 °C, were obtained by using a Spectra-tech heating cell mounted inside the sample chamber, with an accuracy of ± 2 °C. In order to ensure equilibrium conditions at elevated temperatures, the infrared spectra were recorded after an annealing period of approximately 15 min at each temperature.

In some cases intermolecular interactions were also probe by nuclear magnetic resonance (NMR). High-resolution solid-state ^{13}C NMR spectra were carried out on a Bruker Advance DSX300 operating at 75.4 MHz equipped with a cross polarization magic angle spinning (Cp mas) accessory. Cp mas ^{13}C NMR spectra were measured with a 1 ms contact time, a 90° pulse duration of 5.1 µs and 7000–18,000 accumulations. All spectra were acquired with high-power dipolar decoupling (Dd) of ca. 50 KHz and Mas at 7.0 KHz. ^{13}C chemical shifts were calibrated by the methyl resonance of solid glycine (176 and 43 ppm relative to tetramethylsilane).

4. Results and discussion

Blends of atactic polystyrene and poly(cyclohexyl methacrylate) PCHMA form a single phase system over the entire blend composition range [16–18]. In marked contrast, poly(4-vinyl phenol) (PVPh) and PCHMA are immiscible and form two phase materials at any composition and temperature [19]. Introducing styrene segments between phenolic hydroxyl groups via copolymerization, the self-association between hydroxyl (OH) groups should be hindered, which favours the interassociation between hydroxyl groups of vinyl phenol and ester group of methacrylate, and consequently improves the miscibility. T_g measured by DSC confirmed [16] that blends with PCHMA are miscible above 50 wt% styrene in the copolymer. It was also confirmed by FTIR that increasing the concentration of styrene in the copolymer (to around 80% styrene) results in an increase in the hydrogen bonded carbonyl band. This is reflected in the FTIR spectra shown in Fig. 1, where the bands centred at ∼1725 cm^{-1} correspond to stretching vibrations of free carbonyl groups, whereas the bands around ∼1700 cm^{-1} correspond to carbonyl groups bonded to hydroxyl groups. From Fig. 1, it was expected that blends of PCHMA with the copolymer PSVPh[75-25] will show hydrogen bonded carbonyl bands with suitable size to be measured from FTIR spectra.

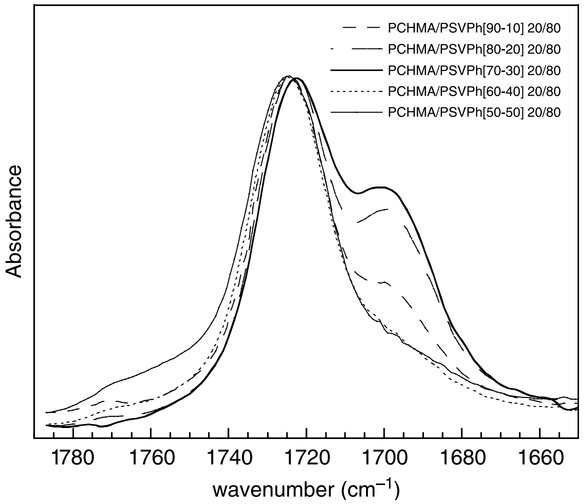

Fig. 1. FTIR spectra of PCHMA/PSVPh 20/80 blends, recorded at 140 °C in the carbonyl stretching region as the copolymer composition is changed.

4.1. Determination of the interassociation equilibrium constant between CHMA and VPh units

It is necessary to know the values of the equilibrium constants describing self-association and inter-association as well as their related enthalpies to predict the free energy of mixing and the miscibility windows of a blend system using the of Painter–Coleman association model. The self-association equilibrium constant for PSVPh copolymers has been calculated from the equilibrium constant for PVPh using the ratio of the molar volumes of PVPh (V_B^{PVPh}) and PSVPh (V_B^{PSVPh}) repeat units by means of Eq. (7) [4].

$$K_B^{PSVPh} = K_B^{PVPh} \frac{V_B^{PVPh}}{V_B^{PSVPh}} \tag{7}$$

The average chemical repeat unit of the copolymer is defined so that it contains one vinyl phenol group. The molar volumes, calculated from group contributions for the average specific repeat of the PSVPh, and other thermodynamic properties such as molar weights and solubility parameters of the polymers used are given in Table 2.

The values of self-association equilibrium constants for PVPh, K_B and K_2 are well established in the literature [4].

Table 2
Summary of polymer parameters

Polymer	Molar volume of repeat unit (cm^3/mol)	Molecular weight of repeat unit	Solubility parameters $(cal/cm^3)^{0.5}$	Degree of polymerization
PCHMA	147.6	168.2[a]	9.19[a]	592
PVPh	100.0	120.1[a]	10.60[a]	250
PS	93.9	104.1[a]	9.48[a]	3333
PSVPh[75-25]	423.9	480.0	9.74	200

[a] Ref. [4].

They have been determined from the equilibrium constants for phenol after appropriate compensation for differences in molar volume. The enthalpies of hydrogen-bond formation were also determined previously and their values, given in Table 3, will be assumed constant across the temperature range considered. The self-association equilibrium constant for PSVPh[75-25] at 25 °C is also given in Table 3. Assuming that the van't Hoff relationship holds, the values of the equilibrium constants can be calculated at any other temperature.

Prior to determining of the interassociation equilibrium constant, $\tilde{K}_A$, a calculation of the fraction of hydrogen bond formed for several compositions of PCHMA/PSVPh[75-25] blends at 140 °C was made, employing arbitrary but most probable $\tilde{K}_A$ values. This determines the range of blend compositions at which the interassociation equilibrium constant $\tilde{K}_A$ can be best determined. The calculation predicts that the most sensitive values of $f_{HB}^{C=O}$ to the magnitude of $\tilde{K}_A$ for PCHMA/PSVPh[75-25] systems are those corresponding to compositions above 50% of PSVPh in the blend. This result was confirmed experimentally by studying the evolution of the carbonyl bands with blend composition by FTIR, Fig. 2, where it can be observed that the band corresponding to associated carbonyl group is hardly detectable for blend compositions low in PSVPh.

Once compositions above 50% of PSVPh[75-25] in blends were chosen to determine the value of $\tilde{K}_A$, the fractions of the hydrogen-bonded carbonyl group were calculated by Eq. (8) from quantitative measure of the areas of the carbonyl bands.

$$f_{HB}^{C=O} = \frac{A_{HB}}{A_{HB} + a_r A_{free}} \tag{8}$$

where A_{HB} and A_{free} are the areas corresponding to hydrogen bonded and free carbonyl bands, respectively. $a_r s$ represents the relationship between the absorption coefficients of the hydrogen bonded and free carbonyl groups. According to previous infrared studies, the ratio of two absortivities is 1.5 [4]. The interassociation equilibrium constant $\tilde{K}_A$ can be determined at a particular temperature by a least squares fit of $f_{HB}^{C=O}$ data to appropriate equations [4] and applying the van't Hoff equation over the temperature range studied the enthalpy of hydrogen bonding can be calculated. The value obtained ($h_A = -3.96$ Kcal/mol) is very close to values obtained ($h_A = -3.8$, $h_A = -4$ Kcal/mol) [33] for blends with similar kind of interactions.

Table 3
Self-association equilibrium constants and enthalpies at 25 °C

Polymer	K_2	K_B	h_2 (kcal/mol)	h_B (kcal/mol)
PVPh	21.0[a]	66.8[a]		
PSVPh[75-25]	4.9	15.7	−5.63	−5.22

[a] Ref. [4].

For comparison purpose, the value of $\tilde{K}_A$ at 25 °C was estimated, scaled to a standard reference molar volume of $V_B = 100\ cm^3/mol$, and it is denoted as $\tilde{K}_A^{std}$. A comparison of the $\tilde{K}_A^{std}$ value obtained here with those found in the literature [34] for blends of polyalkylmethacrylates and copolymers of vinyl phenol with similar spacing between hydroxyl groups are given in Table 4, and the agreement between them is considerable.

In order to ascertain the validity of the equilibrium constant calculated the fraction of the hydrogen-bonded carbonyl group in this blends predicted by means of the PCAM model has been compared to both those obtained by the Panayiatou and Sanchez model [5,13], and the experimentally obtained values. The comparison is shown in Fig. 3. The Panayiatou and Sanchez model is also based on the approximation of 'decoupling' the interactions into physical forces and chemical ones. The chemical forces are calculated taking into account the number of hydrogen bonds distributed between donors and acceptor groups. The agreement between values of $f_{HB}^{C=O}$ predicted with this model as well as PCAM and those obtained experimentally is significant.

It is known that the value of $\tilde{K}_A^{std}$ depends on copolymer composition and gradually increases when the interacting groups are progressively spaced apart, because they became much more accessible to intermolecular interactions. Nevertheless there is a saturation limit above which further separation does not appear to enhance accessibility to a measurable extent. The value of $\tilde{K}_A^{std}$ in the absence of any

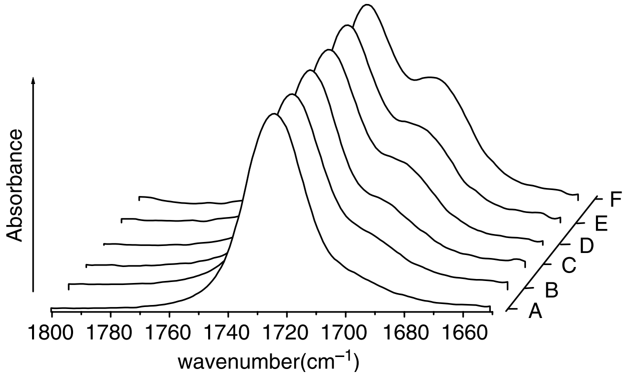

Fig. 2. Infrared spectra recorded at 140 °C in the carbonyl stretching region for PCHMA/PSVPh[75-25] blends at different compositions: (A) 80/20 (B) 70/30 (C) 60/40 (D) 50/50 (E) 40/60 (F) 20/80.

Table 4
Comparison between different values of $\tilde{K}_A^{\mathrm{std}}$ and h_A

Blends A/B	Molar volumes (cm^3/mol) A/B	$\tilde{K}_A^{\mathrm{std}}$	h_A (kcal/mol)
PBMA/DMBVPh[76-24]	134/525[a]	46.1[a]	−4.1[a]
PHMA/DMBVPh[76-24]	167/525[a]	41.1[a]	−4.1[a]
PCHMA/PSVPh[75-25]	147.6/423.9	41.4	−3.96

[a] Ref. [34]; DMBVPh ≡ poly(2,3-dimethylbutadien-stat-vinylphenol); PBMA ≡ poly(*n*-butyl methacrylate); PHMA ≡ poly(hexyl methacrylate).

problems of screening or functional group accessibility is denoted as K_A^{∞}. Pehlert et al. [35] obtained a function that describes the relationship between $\tilde{K}_A^{\mathrm{std}}$ and the average space between functional groups. In this way, the calculated relationship from the experimental infrared data for PCHMA/PSVPh was:

$$\tilde{K}_A^{\mathrm{std}} = 52.9 - \left[\frac{4897}{V_B + R_B}\right] \tag{9}$$

being R_B the molar volumes of the spacer segments between B interacting segments. The value 4897 found in this work is similar to the value of 4100 that Pehlert et al. [35] have found for poly(2,3-dimethylbutadiene-*co*-vinylphenol) blends with poly(ethylene-stat-vinyl acetate) (DMBVPh/EVA). Fig. 4 shows how $\tilde{K}_A^{\mathrm{std}}$ increases with R_B until a plateau is reached, at which further spacing out of the carbonyl groups does not result in a further increase in the magnitude of $\tilde{K}_A^{\mathrm{std}}$.

Assuming that the favourable interactions between the blend components can be represented by a single interassociation equilibrium constant, the miscibility map can now be predicted.

4.2. Miscibility window predictions using single interassociation hydrogen bonding association model with and without free volume effects

Using values of the equilibrium constants $\tilde{K}_2$, $\tilde{K}_B$ and $\tilde{K}_A$, that describe the distribution of hydrogen-bonded species as a function of composition, the total free energy of mixing (ΔG_m) can be calculated as described in [28]. As has been shown in these types of systems [11,28], the main contribution to ΔG_m was found to be that corresponding to the hydrogen bonding term. To determine the theoretical miscibility window for PCHMA/PSVPh system, the second derivative of the free energy of mixing has been calculated at intervals across the entire blend composition range in order to establish, according to spinodal conditions [36], the boundary between miscible and immiscible copolymer compositions, at a given temperature. Fig. 5 shows the miscibility window calculated with PCAM employing the $\tilde{K}_A$ values obtained from Eq. (9) and the experimental window performed by means of T_g analysis on solution-cast blends [16]. The agreement between the theoretical prediction and experimental phase behaviour is good except for the blends with less than 1% of VPh, which were found experimentally to be miscible at ambient temperature whereas they are predicted to form two phase systems by PCAM.

In the above treatment, compressibility of the polymers has been ignored, therefore, in order to know the effect of the free

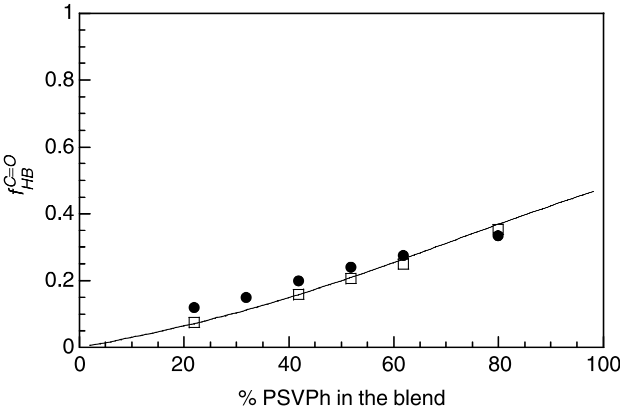

Fig. 3. A comparison of $f_{HB}^{C=O}$ calculated with: (□) Panayiotou and Sanchez model, (line) PCAM and (●) experimentally determined.

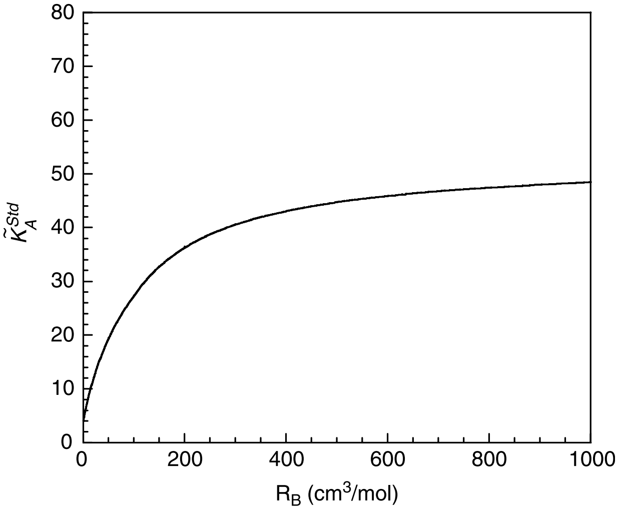

Fig. 4. $\tilde{K}_A^{\mathrm{std}}$ vs. R_B according to Eq. (9).

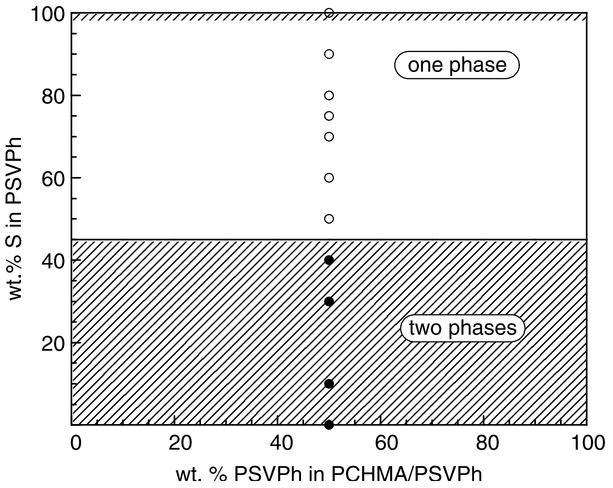

Fig. 5. Miscibility map for PCHMA/PSVPh system. (shadow regions): Predicted two phases; (clear region): predicted one phase; (solid circle): experimentally two phases; (open circle): experimentally one phase.

volume on phase stability of the mixtures a model presented by Graf et al. [11] has been employed. This model uses the Sanchez and Lacombe lattice fluid theory [26,27] of polymer mixtures that includes vacant lattice sites to take into account the different compressibility of the components in the mixture. According to the lattice fluid theory, the mixture is characterized by three scaling constants; a characteristic temperature T^*, a characteristic pressure P^* and a characteristic density ρ^*, which can be obtained from the pure components' characteristic constants (T_i^*, P_i^*, ρ_i^*) with appropriate mixing rules. The characteristic parameters employed for pure components are summarized in Ref. [16] Table 2.

The free energy of mixing (ΔG_m), the contributions from hydrogen bonding, and free volume effects are represented in Fig. 6. A comparison of ΔG_m calculated with incompressible and compressible association models is also shown in Fig. 6. The effect of the free volume in hydrogen bonding polymer blends has not been widely studied in the literature [11,28,37]. Besides, for polymer blends such as poly(*n*-butyl methacrylate)/poly(vinyl phenol) [11,37] and phenoxy resin/poly(methyl methacrylate) [28], it was concluded that the free volume contribution to the free energy of mixing is practically irrelevant, which agrees with the results shown in Fig. 6, in which it can be seen that the hydrogen bonding term is the greatest contribution to the free energy of mixing.

To know the boundary between miscible and immiscible regions predicted with compressible association models, the second derivatives of the free energy with respect to the blend composition were calculated numerically. It was concluded that the miscibility window, shown in Fig. 5, is not modified significantly by the equation of state effects. Referring to PCHMA/PS blends, the miscibility behaviour experimentally found cannot be explained if only 'physical' forces, in the PCAM are considered. When the solubility parameters found in the literature [38,39] are used to estimate the unfavourable 'physical' forces it is found that free energy of mixing has a positive value, $\Delta G_m > 0$. Even though when the values for the solubility parameters of the pure components were considered identical ($\delta_A \equiv \delta_B$), which is the most favourable case [4], miscibility cannot be achieved by PCAM. This fact points out to some kind of favourable interaction between PCHMA and PS.

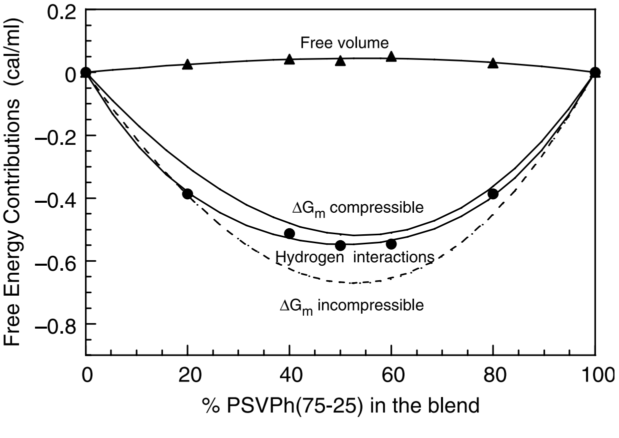

Fig. 6. Comparison of the free energy of mixing calculated with incompressible (broken line) and compressible (continuous line) association model: (▲) free volume and (●) hydrogen bonding contributions in the compressible model.

4.3. Estimation of the interassociation equilibrium constant between CHMA and S repeat units and its temperature dependence

Some authors suggest [18,40–42] the possibility of a dipole–dipole interaction between carbonyl groups of PCHMA and phenyl groups of PS. We have investigated by means of FTIR spectroscopy the absorption bands corresponding to the vibration of the C=O groups of PCHMA ($\sim 1725\ \mathrm{cm}^{-1}$) and the bands corresponding to the vibration of the C–H groups of the benzene ring of PS ($\sim 700\ \mathrm{cm}^{-1}$) for several binary PCHMA/PS blends and ethyl benzene (EB)/cyclohexyl propionate (CHP) mixtures as low molecular weight analogues of the polymers. We observed both a slight broadening towards lower frequencies in the C=O band of PCHMA (or CHP) as the amount of PS (or EB) in the blend is increased, and a significant broadening towards higher frequencies of the C–H band of PS (or EB). In Fig. 7 is shown the broadening corresponding to C–H band. Similar changes have been reported by Prinos et al. [43] for poly(glutaramide)/styrene-*co*-maleic anhydride (SMA) blends and by Feng et al. [44] for poly(methyl methacrylate)/SMA blends. These later authors point to the formation of charge transfer complexes between carboxylic groups and aromatic rings as being responsible of the FTIR spectra changes in the blends. Such an interaction was also supported by C^{13} NMR results.

Since –COO– groups are involved in PS/PCHMA blends (instead of –COOH groups) it is reasonable to assume a weaker interaction (i.e. dipole–dipole type) in this system. Fig. 8 shows an expansion of the Cp mas ^{13}C NMR carbonyl resonance of PCHMA/PS blends as a function of composition, and as can be

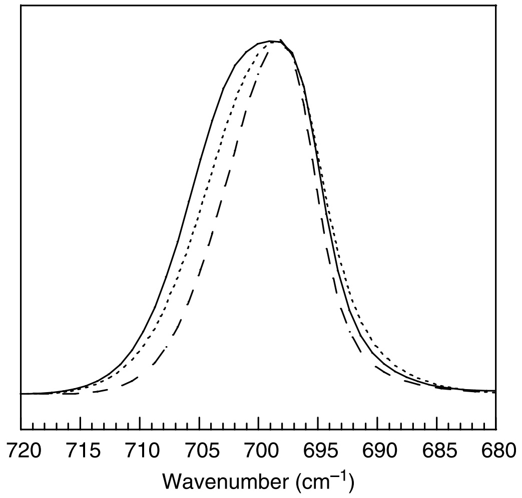

Fig. 7. Infrared spectra of the out-of-plane deformation vibration of the aromatic ring hydrogen atoms for PCHMA/PS blends (intensity in arbitrary units): dashed line, 0/100 PCHMA/PS. Dotted line, 50/50 PCHMA/PS. Solid line, 20/80 PCHMA/PS.

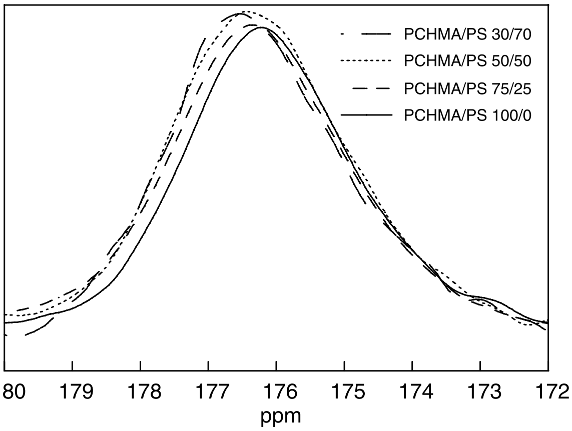

Fig. 8. Cp mas ^{13}C NMR spectra for the carbonyl resonance for different PCHMA/PS blends at room temperature (intensity in arbitrary units).

seen, the carbonyl resonance shifts downfield upon addition of PS. The maximum downfield shift observed (0.32 ppm), although lower than the values measured for some hydrogen-bonded miscible blends [45], can be interpreted as the extent of the intermolecular specific interaction between the components of a blend [45–47]. Therefore, this shift implies the existence of a kind of favourable interaction between carbonyl groups of PCHMA and phenyl groups of PS. In this sense, Nmr results agree well with those obtained from FTIR, supporting the idea of the existence of a weak specific interaction between the carbonyl group of PCHMA and the aromatic ring of PS.

For dipole–dipole interactions (such as those in poly(vinyl chloride)/polyester blends), Coleman et al. [4,48,49] estimate that the enthalpy of such interactions should be lower than −3 Kcal/mol vs. enthalpies of about −4 to −8 Kcal/mol for hydrogen bonding interactions, that lead to shifts of about 20–50 cm^{-1} in the FTIR band of the hydrogen bonded groups. In terms of the present model, we can obtain an estimation of the equilibrium constants ($\tilde{K}_{AD}$) and the corresponding enthalpy of the PCHMA/PS interaction (h_{AD}) by using the experimental LCST data of this system [17], Eqs. (4)–(6) and the thermodynamic conditions for miscibility. Best fitting to the LCST data results in the equilibrium constant and enthalpy values of $\tilde{K}_{AD}=0.026$ and $h_{AD}=-1.70$ Kcal/mol [50]. The relative small values of both the interassociation constant and the enthalpy for the PCHMA/PS system are in good agreement with the previous FTIR and Cp mas ^{13}C NMR data.

4.4. Phase behaviour predictions for PCHMA/PSVPh blends by using the D.I.M.

In order to verify the improvement of the double interassociation model vs. the previous model with single interassociation, the miscibility predictions for binary PCHMA/PSVPh blends with the experimental results described previously will be compared. The miscibility map for the PCHMA/PSVPh system at 140 °C is calculated by means of the D.I.M. with the values of $\tilde{K}_{AD}$ and h_{AD} obtained in Section 4.3 and the equilibrium constants of Tables 3 and 4. The results show that the system is miscible across the entire blend composition range for blends of PCHMA and PSVPh copolymers with styrene contents higher than 30 wt% up to 100 wt%. In this case, good agreement is found between the theoretical predictions and the experimental results [16] for 100% styrene content in copolymer, therefore, the introduction of the second interassociation in the association model leads to improved miscibility predictions for PCHMA/PSVPh blends, especially at very high styrene contents in the PSVPh copolymer.

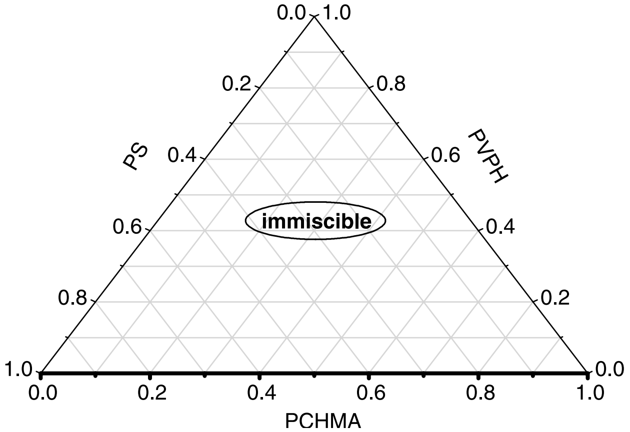

Fig. 9. Ternary PVPh/PCHMA/PS blend miscibility diagram at 140 °C predicted by using double interassociation model (D.I.M.) and parameters from Table 5. The black line represents miscible binary PCHMA/PS blends at such temperature.

Table 5
Equilibrium constant and enthalpy pairs employed in this work for ternary PCHMA/PS/PVPh blends at 25 °C

i/j	$\tilde{K}_{ij}$	h_{ij} (kcal/mol)
PS/PCHMA	0.026	−1.70
PCHMA/PVPh	3.93[a]	−3.96

[a] Estimated from Eq. (9).

4.5. Double interassociation model for ternary polymer blends

The double interassociation model can be easily extended for the prediction of ternary polymer blend miscibility, such as PCHMA/PS/PVPh blends. In Fig. 9 we show the D.I.M. miscibility predictions for the ternary PCHMA/PS/PVPh system at 140 °C using parameters from Table 5. In this case, contrary to the case of the PCHMA/PSVPh system, the ternary diagram shows immiscibility across the entire diagram. This fact confirms the well known scarce ternary polymer blend miscibility arising from $\Delta\chi$ and ΔK effects [51,52].

For ternary polymer blend miscibility predictions, the corresponding thermodynamic conditions are described in Ref. [53].

5. Conclusions

The phase behaviour of the PCHMA/PSVPh system was predicted using an association model with a single and a double interassociation equilibrium constant and compared with experimental results.

The simpler model is able to reproduce the experimental miscibility window of the system except for the case of binary PCHMA/PS, blends which are predicted to be immiscible. No significant differences in the predicted miscibility window of PCHMA/PSVPh blends were found by incorporating free volume effects into this model. Consequently, some kind of favourable interaction (probably a weak specific interaction) between CHMA and S repeat units must to be present to explain the miscibility of PCHMA/PS blends up to high temperatures (where lower critical solution temperature, LCST, behaviour is experimentally found). This weak interaction has been confirmed experimentally.

The introduction of a double interassociation model allows both the prediction of binary and ternary polymer blend miscibility for systems in which two specific interactions are present, such as PCHMA/PSVPh and PCHMA/PS/PVPh blends.

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This paper is dedicated to professor Cecilia Sasasola.

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