

Modelling the Hydrogen-Bonding Interactions in a Copolymer/Biodegradable Homopolymer Blend through Excess Functions

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Abstract: A recent theoretical approach based on the coupling of both the Flory-Huggins (FH) and the Association Equilibria thermodynamic (AET) theories was modified and adapted to study the miscibility properties of a multi-component system formed by two polymers (a proton-donor and a proton-acceptor) and a proton-acceptor solvent, named copolymer(A)/solvent(B)/polymer(C). Compatibility between polymers was mainly attained by hydrogen-bonding between the hydroxyl group on the phenol unit of the poly(styrene-*co*-vinyl phenol) (PSVPh) and the carbonyl group of the biodegradable and environmentally friendly poly(3-hydroxybutyrate) (PHB). However, the self-association of PSVPh and specific interactions between the PSVPh and the H-acceptor group (an ether oxygen atom) of the epichlorohydrin (ECH) solvent were also established in a lower extension, which competed with the polymer-polymer association. All the binary specific interactions and their dependence with the system composition as well as with the copolymer content were evaluated and quantified by means of two excess functions of the Gibbs free energy, Δg_{AB} and Δg_{AC} . Experimental results from fluorescence spectroscopy were consistent with the theoretical simulations derived with the model, which could also be applied and extended to predict the miscibility in solution of any polymer blend with specific interactions.

Keywords: polymer miscibility, thermodynamics, excess functions, hydrogen-bonding, association constants.

Introduction

The development of the polymeric industry has originated ecological and environmental problems especially due to the high volume of solid waste. One way to solve that problem consists on replacing commodity synthetic materials by biodegradable polymers.^{1,2} These materials are receiving increasing interest due to ecological and recycling reasons since after their useful lifetime, a biodegradable and gradual process can environmentally destroy them. Some of the commercialised biodegradable polymers are mainly derivatives of the lactic polyacid, the thermoplastic starch or the poly(hydroxyalkanoates) (PHA), which have been intensively investigated since their synthesis does not consume fossil resources.³⁻⁶

The most well-known PHA is the poly(3-hydroxybutyrate) (PHB), a crystalline, biodegradable and friendly environmental polyester produced by some microorganisms. The PHAs, in

general, are specially used in medicine and in the packaging industry. Particularly, the PHB, possess suitable properties as a barrier for atmospheric fluids (gases and vapors). Nevertheless, and due to its high crystallinity, the pure PHB is particularly fragile and has a very low impact resistance, which has limited its usage in the packaging industry. One of the explored alternative ways to avoid these drawbacks consists on blending the PHAs with other polymeric components able to introduce new and improved targeted properties.^{4,7-12} In this sense, deserves to be mentioned work on mixtures of PHB with poly(vinyl phenol),^{13,14} poly(vinyl acetate),^{15,16} poly(epichlorohydrin)^{17,18} or poly(ethylene oxide).^{19,20} More recently, the PHB miscibility has been improved through intermolecular interactions via hydrogen bonding obtained by blending the PHB with copolymers such as poly(HB-*co*-hydroxyhexanoate)²¹ or poly(styrene-*co*-vinyl-phenol).²²

On the other hand, thermodynamic studies on ternary polymer systems (TPS) use to deal with different types, such as solvent/solvent/polymer,²³⁻²⁵ solvent/polymer/

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polymer^{26,27} and even ternary polymer blends.²⁸⁻³⁰ For TPS with specific interactions, such as hydrogen-bonding, the classical thermodynamic Flory-Huggins (FH) theory cannot explain the blend miscibility. Therefore, more adequate approaches have been explored and developed, mainly based on the existence of association and self-association equilibria.³¹⁻³⁶ Other formalisms are those based on the adaptation of the lattice-gas model by ten Brinke and Karasz,³⁷ the generalization of the lattice-fluid model for specific interactions³⁸ on associated polymer solutions.^{39,40} Recently, these models have been extended to describe the specific interactions occurring in block copolymers.^{41,42} In the case of protein systems, the electrostatic interactions have been modelled with a two-component equation of state describing the liquid/liquid thermodynamic equilibria.⁴³

The aim of the present study is to provide the theoretical basis for the experimental observations of TPSs consisting on two polymers (a proton donor and a proton acceptor) in the presence of a proton acceptor solvent. Concretely, the system is formed by poly(styrene-co-vinyl phenol) (PSVPh)/epichlorohydrin (ECH)/poly(3-hydroxybutyrate) (PHB), being the vinylphenol content in the copolymer varied. In such a system, the donor polymer PSVPh will be the self-associated component and, at the same time, will interact via hydrogen-bonding with the other polymer PHB or with the solvent ECH (both acceptor species). Therefore, the self-association would be an additional driving force for miscibility competing with the interpolymer and polymer-solvent specific interactions. The theoretical approach used is a modification of a recent one based on the coupling of FH and association equilibria (AET) theories.⁴⁴ The contribution of the different specific interactions in the corresponding binary systems has been interpreted on the basis of hydrogen-bond formation through the values of the Gibbs free energy excess function, Δg_{ij} , which have served to predict the compatibility or miscibility of any two components of the TPS as a function of the system composition. Moreover, the interpolymer association has been experimentally monitored using fluorescence spectroscopy by measuring the change in the intensity fluorescence with blend composition. Theoretical predictions and experimental fluorescence measurements have shown a very reasonable agreement and have properly described the balance of hydrogen-bond interactions that controls the miscibility in solution of the present copolymer/homopolymer blend.

Theory

For clarity of presentation, throughout the text we will denote the components of the ternary system as: copolymer(A)/solvent(B)/polymer(C). The component A has proton-donor character whereas components B and C are proton-acceptors, so specific interactions via hydrogen bonding can account between A-B and A-C species. Moreover, the

copolymer A is a self-associating specie, so even in a very low extension, A-A interactions can also occur. All the magnitudes (and their units) appearing in the text are defined, at the end, in the nomenclature list box.

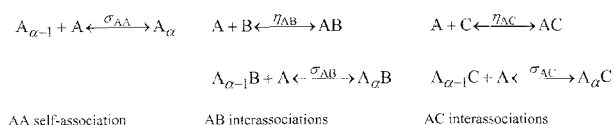
Flory-Huggins (FH) Lattice Theory for a Polymer Blend in Solution. From a thermodynamic viewpoint, specific interactions most often generate a negative heat of mixing and contribute favourably to the free energy of mixing. In this regard, the FH formalism provides a framework to explain the mixing behaviour of a general ternary polymer system.⁴⁵ In particular, for a TPS with specific interactions, as the present case, the Gibbs free energy function of mixing per mol of occupied lattice site, is written as a function of the nominal concentrations, in the form:

$$\left(\frac{\Delta G^N}{RT}\right)_{Ter} = (v_A \ln \phi_A + v_B \ln \phi_B + v_C \ln \phi_C + v_A \phi_B g_{AB} + v_A \phi_C g_{AC} + v_B \phi_C g_{BC}) \quad (1)$$

where R is the universal gas constant, T the temperature and g_{ij} the binary interaction parameter accounting for all type of interactions, specific and non-specific; and the relationship between volume and molar fractions is expressed by $\phi_i = n_i V_i / (n_A V_A + n_B V_B + n_C V_C) = v_i r_i$.

Association Equilibria Theory (AET). On the other hand, the AET theory applied to a donor-copolymer(A)/acceptor-solvent(B)/acceptor-polymer(C) system assumes that thermodynamic equilibria are established between the different components. In the present system, the equilibria depicted in Scheme I are assumed to hold: (i) the self-association of copolymer A molecules; (ii) the interassociation of copolymer A and solvent B molecules to form an AB complex and the association of free molecules of component A to the above complex; and (iii) the interassociation of copolymer A and a segment of polymer chain C to form an AC complex, followed by the association of free molecules of component A to this complex.

As seen in Scheme I, the complex formation processes are driven by the self-association equilibrium constant for copolymer A, σ_{AA} ; the interassociation constants between the dimer or multimeric A chains with solvent B or polymer C, σ_{AB} and σ_{AC} , respectively; and the equilibrium constants describing the formation of hydrogen bonds between the hydroxyl groups of the phenol unit in the copolymer A and the ether oxygen atoms on solvent B or the carbonyl groups on polymer C, η_{AB} and η_{AC} , respectively. Obviously, other type of associations can be imagined but they have not been



Scheme I. Association equilibria taking place in the ternary polymeric system.

considered here since their contribution is practically negligible from a probabilistic point of view.

Secondly, in the light of the AET model, the Gibbs free energy of a ternary system with specific interactions adopts the expression⁴⁴:

$$\frac{\Delta G^N}{RT} = v_A \ln \frac{P_A}{P_A^0} + v_B \ln \frac{P_B}{P_B^0} + v_C \ln \frac{P_C}{P_C^0} - \sum_q v_q + \phi_A \left(\sum_q v_q \right)_A^0 + \phi_B \left(\sum_q v_q \right)_B^0 + \phi_C \left(\sum_q v_q \right)_C^0 + v_A \phi_B g'_{AB} + v_A \phi_C g'_{AC} + v_B r_B \phi_C g'_{BC} \quad (2)$$

where P_i is the molar fraction of the free component i per mole of total lattice sites; $\sum_q v_q$ the summation of molar fractions for all the complexes formed, and the parameters g'_{ij} represent the non-specific interactions between the system components. The superscript "0" refers to the value of a magnitude for a pure component.

Next, taking in mind the detailed and complete procedure recently developed for a solvent(A)/solvent(B)/polymer(C) system,⁴⁴ the extension to the present TPS where is assumed that component B occupies one site in the lattice ($r_B=1$), gives the following relationships in terms of the above-defined association equilibrium constants:

$$v_A = s \phi_A = \frac{P_A}{(1 - \sigma_{AA} P_A)^2} + \frac{\eta_{AB} P_A P_B}{(1 - \sigma_{AB} P_A)^2} + \frac{m \eta_{AC} P_A P_C}{(1 - \sigma_{AC} P_A)^2} \left(1 + \frac{\eta_{AC} P_A}{1 - \sigma_{AC} P_A} \right)^{m-1} \quad (3)$$

$$v_B = \phi_B = \left(1 + \frac{\eta_{AB} P_A}{1 - \sigma_{AB} P_A} \right) P_B \quad (4)$$

and

$$v_C = r \phi_C = \left(1 + \frac{\eta_{AC} P_A}{1 - \sigma_{AC} P_A} \right)^m P_C \quad (5)$$

with s and r standing for the ratios of the segmental B and A or B and C molar volumes, respectively ($s = V_B/V_A$ and $r = V_B/V_C$). The superscript m represents the number of independent sites on polymer C where the specific AC interaction can occur, or in other words, the ratio between the numbers of interacting groups in the donor copolymer A and in the acceptor polymer C. Consequently, the summation for all the complexes should read:

$$\sum_q v_q = \frac{P_A}{1 - \sigma_{AA} P_A} + \left(1 + \frac{\eta_{AB} P_A}{1 - \sigma_{AB} P_A} \right) P_B + \left(1 + \frac{\eta_{AC} P_A}{1 - \sigma_{AC} P_A} \right)^m P_C \quad (6)$$

and the (P_i/P_i^0) ratios:

$$\frac{P_A}{P_A^0} = \frac{Y + X - [X^2 + 2XY]^{1/2}}{\phi_A [2s\sigma_{AA} + 1 - (1 + 4s\sigma_{AA})^{1/2}]} \quad (7)$$

$$\frac{P_B}{P_B^0} = P_B = \phi_B \left(\frac{1 - \sigma_{AB} P_A}{1 - (\sigma_{AB} - \eta_{AB}) P_A} \right) \quad (8)$$

$$\frac{P_C}{P_C^0} = \phi_C \left(\frac{1 - \sigma_{AC} P_A}{1 - (\sigma_{AC} - \eta_{AC}) P_A} \right)^m \quad (9)$$

with $Y = 2s\sigma_{AA}\phi_A$ and $X = 1 + \eta_{AB}\phi_B + mr\eta_{AC}\phi_C$.

Finally, the substitution of eqs. (3) to (9) into eq. (2) allows writing the master equation for the Gibbs free energy of mixing of a TPS with specific interactions through the AET approach, as:

$$\left(\frac{\Delta G^N}{RT} \right)_{Ter} = s \phi_A \ln \left(\frac{P_A}{P_A^0} \right) + \phi_B \ln \left(\frac{P_B}{P_B^0} \right) + r \phi_C \ln \left(\frac{P_C}{P_C^0} \right) - \frac{P_A}{1 - \sigma_{AA} P_A} + \phi_A \left(\frac{P_A^0}{1 - \sigma_{AA} P_A^0} \right) + s \phi_A \phi_B g'_{AB} + s \phi_A \phi_C g'_{AC} + \phi_B \phi_C g'_{BC} \quad (10)$$

FH and AET Coupled Theories. The central idea of the FH theory assumes that the change in free energy of mixing arises from both the changes in the combinatorial entropy and in the interaction energy. Because the intersegmental H-bonding should perturb the randomness of polymeric conformations, AET model is applied to correct the conformational entropy term. The enthalpic term in the extended FH formalism is related to the composition dependent interaction functions, g_{ij} , accounting for all type of interactions, whereas in the AET model is estimated by introducing non-specific interaction parameters, g'_{ij} . Next, we will proceed to analyze the potential donor-acceptor binary interactions accounting in the system in the light of both master eqs. (1) and (10). Their comparisons in the corresponding binary systems will serve to quantitatively evaluate the H-bond contribution to the free energy of mixing.

Copolymer(A)/Solvent(B) Binary System: The lack of component C ($\phi_C=0$), simplifies the eqs. (1) and (10), respectively, to:

$$\left(\frac{\Delta G^N}{RT} \right)_{AB} = s \phi_A \ln \phi_A + \phi_B \ln \phi_B + s \phi_A \phi_B g_{AB} \quad (11)$$

and

$$\left(\frac{\Delta G^N}{RT} \right)_{AB} = s \phi_A \ln \frac{P_A}{P_A^0} + \phi_B \ln \frac{P_B}{P_B^0} - \frac{P_A}{1 - \sigma_{AA} P_A} + \phi_A \frac{P_A^0}{1 - \sigma_{AA} P_A^0} + s \phi_A \phi_B g'_{AB} \quad (12)$$

Therefore, by equating the expressions (11) and (12) and subtracting $g_{AB} - g'_{AB}$, a new excess function, Δg_{AB} , is defined:

$$\Delta g_{AB} = g_{AB} - g'_{AB} = \frac{1}{\phi_B} \ln \frac{P_A}{P_A^0} + \frac{1}{s \phi_A} \ln \frac{P_B}{P_B^0} - \frac{1}{s \phi_A \phi_B} \left(\frac{P_A}{1 - \sigma_{AA} P_A} \right) + \frac{1}{s \phi_B} \left(\frac{P_A^0}{1 - \sigma_{AA} P_A^0} \right) - \frac{\ln \phi_A}{\phi_B} - \frac{\ln \phi_B}{s \phi_A} \quad (13)$$

This parameter, composition dependent, exclusively quantifies the AB specific interactions since is calculated by subtracting from all type of interactions (accounted in g_{ij}) those corresponding to the non-specific ones given by g'_{ij} .

An additional assessment of the adequacy of the FH-AET coupled theory comes from the fact that in a system without specific interactions, both eqs. (11) and (12) should be equal and the new parameter $\Delta g_{AB} = 0$. This requirement is easy to prove from eq. (13) since in these circumstances $\sigma_{AA} = \sigma_{AB} = \eta_{AB} = 0$, and eqs. (7)-(9) reduce to $P_A = s\phi_A$, $P_A^0 = s$, $P_B = \phi_B$, and $P_B^0 = 1$.

Copolymer(A)/Polymer(C) Binary System: Following the same procedure as before, the lack of component B ($\phi_B = 0$), leads to the simplification of eq. (1) to:

$$\left(\frac{\Delta G^N}{RT}\right)_{AC} = s\phi_A \ln \phi_A + r\phi_C \ln \phi_C + s\phi_A \phi_C g_{AC} \quad (14)$$

whereas the eq. (10) transforms into:

$$\begin{aligned} \left(\frac{\Delta G^N}{RT}\right)_{AC} &= s\phi_A \ln \frac{P_A}{P_A^0} + r\phi_C \ln \frac{P_C}{P_C^0} - \frac{P_A}{1 - \sigma_{AA}P_A} \\ &+ \phi_A \left(\frac{P_A^0}{1 - \sigma_{AA}P_A^0}\right) + s\phi_A \phi_C g'_{AC} \end{aligned} \quad (15)$$

For a given composition, eqs. (14) and (15) can be equated and by subtraction of $g_{AC} - g'_{AC}$, another new excess function, Δg_{AC} , defined:

$$\begin{aligned} \Delta g_{AC} = g_{AC} - g'_{AC} &= \frac{1}{\phi_C} \ln \frac{P_A}{P_A^0} + \frac{\gamma}{s\phi_A} \ln \frac{P_C}{P_C^0} - \frac{1}{s\phi_A \phi_C} \left(\frac{P_A}{1 - \sigma_{AA}P_A}\right) \\ &+ \frac{1}{s\phi_C} \left(\frac{P_A^0}{1 - \sigma_{AA}P_A^0}\right) - \frac{\ln \phi_A}{\phi_C} - \frac{r \ln \phi_C}{s\phi_A} \end{aligned} \quad (16)$$

In such a system, this magnitude only accounts for the AC specific interactions. Again, is easy to demonstrate from eq. (16) that in absence of specific interactions, $\Delta g_{AC} = 0$ since now, logically, $\sigma_{AA} = \sigma_{AC} = \eta_{AC} = 0$, and eqs. (7)-(9) give $P_A = s\phi_A$, $P_A^0 = s$, $P_C = r\phi_C$ and $P_C^0 = r$.

Experimental

Chemicals. The proton donor species used in the present

work were poly(styrene-*co*-4-vinyl phenol) random copolymers (PSVPh-x.x) with different vinyl phenol content (denoted by x.x in mole%). The copolymers were synthesized in our lab according to a procedure recently described,⁴⁶ and were characterized by size-exclusion chromatography (SEC) and the phenol content determined by proton NMR spectroscopy (¹H-NMR) at room temperature. The proton acceptor polymer was poly(3-hydroxybutyrate) (PHB) from Aldrich Chemical Co. (Wisconsin, USA). Sample characteristics, such as number-average molar masses, M_n , polydispersity index (M_w/M_n), copolymer content and chemical structures are listed in Table I. Epichlorohydrin (1-chloro-2,3-epoxypropane) (ECH) obtained from Panreac Quimica S.A. (Barcelona, Spain) was used as solvent without further purification.

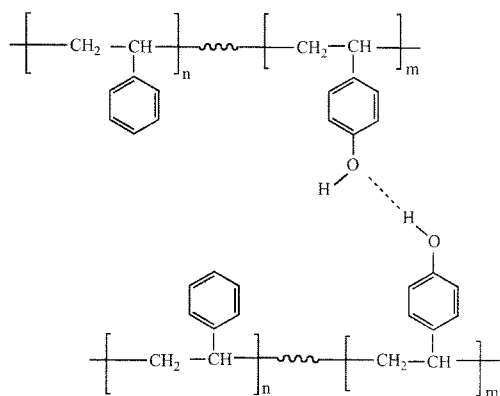
Fluorescence Measurements. Emission fluorescence spectra of the polymer solutions were conducted and recorded at 298 K on an Aminco-Bowman Luminiscence Spectrometer equipped with a thermostated cell holder and a Data Station. Throughout the experiments, samples were excited at a wavelength of 260 nm, being the maximum emission wavelength 302 nm, and the excitation and emission slits were both set at 5 nm. The polymer solutions were prepared with oxygen-free solvent. The concentration of the PSVPh in the solution was kept fixed at 14 μ M (0.05 g.dL⁻¹) and the PHB concentration varied, in order to achieve different molar ratios, $R_i = [\text{PHB}]/[\text{PSVPh}]$, ranging from 0 to 2.6. Samples were annealed at 298 K to assure equilibrium conditions for ten minutes before the measurement was carried out. Then, polymer solutions were placed in a quartz cell, stirred 10 min and purged with nitrogen for at least 1 min prior to each recording. All emission spectra were corrected for background fluorescence as well as for polymer and solvent light scattering by subtraction of the corresponding blanks.

Results and Discussion

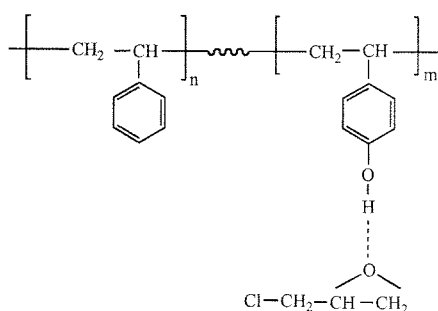
Thermodynamic Modelling of Specific Interactions. Due to the chemical nature of the species constitutive of the ternary system studied, it is expected that specific interactions via hydrogen-bonding should be established between the different components. Concretely, as Scheme II illustrates, the H-donor hydroxyl group (-OH) on the phenolic

Table I. Characteristics of the Polymer Samples

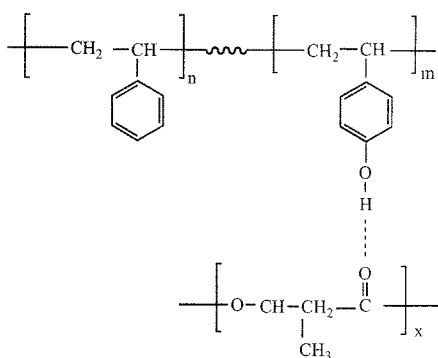
Sample Code	Copolymer Content (mole %)	M_n (kg.mol ⁻¹)	M_w/M_n	V_i (L.mol ⁻¹)	Chemical Structure
PSVPh-2.0	2.0	33.7	1.78	30.9	
PSVPh-3.2	3.2	34.3	1.78	31.4	
PSVPh-4.0	4.0	35.0	1.77	32.0	
PSVPh-5.8	5.8	36.7	1.77	33.5	
PSVPh-7.2	7.2	36.7	1.77	33.5	
PHB		245.0	1.51	208.4	



AA self-association



AB specific interaction



AC specific interaction

Scheme II. Schematic illustration of the three types of hydrogen-bond interactions.

unit of the PSVPh polymer can interact with the H-acceptor groups either in the ECH solvent (ether -O-) or in the PHB polymer (carbonyl -C=O), accounting for AB or AC specific interactions, respectively. Both types of interactions are competitive and will dominate that one which chemical groups possess stronger acceptor character. Moreover, the copolymer A can also self-associate and form AA H-bonds that also compete with the abovementioned.

In such a system, it is possible to theoretically predict the extent, strength and competitiveness of these specific inter-

Table II. Data of Association Equilibrium Constants Needed to Calculate Δg_{AB} and Δg_{AC} Functions According to Equations (13) and (16)

σ_{ij}	η_{AB}	η_{AC}	m
50	3	5	100
150	3	15	500
250	3	25	1,000
350	3	35	1,500
450	3		2,000

actions. To do that, is necessary to calculate the parameters Δg_{AB} and Δg_{AC} according to eqs. (13) and (16), respectively, for the five systems assayed, by using the molar volume data in Table I and the association equilibrium constants compiled in Table II. These values have been varied between logical and different ranges taking into account the following remarks:

(i) since no literature data have been found for the association constants between the polymers here studied, we have selected hypothetical sets of data accounting for simulations ranging from low to high density of intermolecular H-bonds;

(ii) it has been considered that $\sigma_{AA} = \sigma_{AB} = \sigma_{AC}$ as usual,^{31,33} since the self-association ability of component A is independent of the fact that the first link in the chain was AA, AB or AC;

(iii) $\sigma_{ij} > \eta_{AB}$ is also a very common situation for this type of systems;^{32,33}

(iv) finally, the η_{AC} values are higher than the η_{AB} ones since it is well-known that the proton acceptor character of an oxygen atom belonging to an ether group is weaker than that of a carbonyl group. In this regard, Painter *et al.* have recently also assumed in their calculations that the hydroxyl-carbonyl associations involve a much larger free-energy change than other donor-acceptor hydrogen bonds.³⁴

Figure 1 plots the variations of Δg_{AB} and Δg_{AC} functions with the system composition expressed as volume fraction of component A, ϕ_A , for the five systems assayed. The set of the association constant values used in the calculations have specifically been: $\sigma_{ij} = 50$, $\eta_{AB} = 3$, $\eta_{AC} = 15$ and $m = 2,000$. As can be seen in part A of figure, the Δg_{AB} values are always negative which means that, from a thermodynamic viewpoint, the AB specific interactions contribute to stabilize the system. However, the absolute values are relatively low denoting a weak character of the copolymer-solvent H-bonds. Secondly, the Δg_{AB} values decrease continuously as ϕ_A tends to 1, as expected since more copolymer or more hydroxyl interacting groups are present in the system. Moreover, it seems that no apparent variation is produced when changing the copolymer content although a slight change can be appreciated when examining the second or third decimal figure in the punctual values. This fact can be

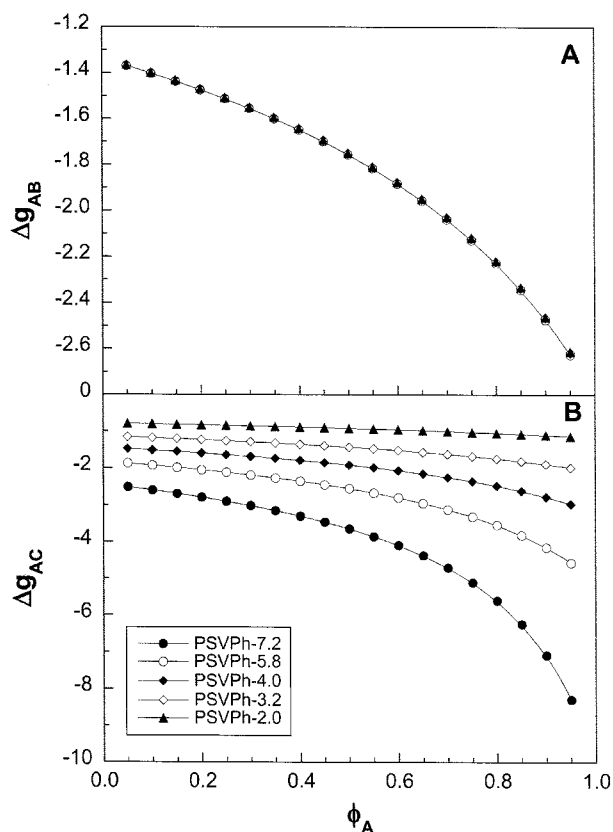


Figure 1. Dependence of the free-energy excess functions on the volume fraction of copolymer A for the systems PSVPh-x.x/ECH/PHB: (A) Δg_{AB} (eq. (13)) and (B) Δg_{AC} (eq. (16)). Lines are drawn to guide the eye.

interpreted as another evidence of the weakness of the AB interactions compared with the AC ones, as we will see next. Figure 1(B) illustrates the behaviour corresponding to the calculated Δg_{AC} parameter. The observed trend is quite analogue to the preceding, that is: (i) negative values for the free-energy change which means favourable thermodynamic interactions in all the composition range; (ii) higher

absolute values than those of Δg_{AB} , in most of systems, denoting stronger AC binary interactions compared with the AB ones; (iii) a sharp decrease as ϕ_A increases, regardless of the copolymer used and specially when the vinylphenol content is raised. This fact implies that the AC hydrogen-bonds are favored as the amount of available interacting groups is increased, although the copolymer content cannot be excessively raised since the polymeric chain can lose degrees of rotational freedom and prevent the approach to the other polymer chain.^{47,48} On the contrary, significant differences in the Δg_{AC} values are found when changing the copolymer content. Another interesting fact to be commented comes from the comparison of Δg_{AB} and Δg_{AC} data for two extreme examples: PSVPh-7.2 and PSVPh-2.0. At a given composition, the comparison is plausible since all the PSVPh possess a similar molar mass and then, similar molar volume (see Table I). For example, at $\phi_A = 0.80$, for PSVPh-7.2, $\Delta g_{AB} = -1.88$ and $\Delta g_{AC} = -4.09$ whereas for PSVPh-2.0, $\Delta g_{AB} = -1.87$ and $\Delta g_{AC} = -0.95$. Therefore, for the highest copolymer content an important difference between both parameters is found with AC interactions stronger than the AB ones, $\Delta g_{AC} \gg \Delta g_{AB}$. The difference between both curves becomes narrower as the copolymer content decreases, for the lowest phenolic content, an inverted behaviour is found, $\Delta g_{AC} < \Delta g_{AB}$, which means that as the amount of hydroxyl groups is lowered, the competence between the solvent and the PHB for the copolymer increases and the AB interactions result favored. In conclusion, the extent and strength of the H-bonds are for copolymer-polymer (AC) stronger than for copolymer-solvent (AB), at least in most of the TPS here studied.

Next, we will analyze the competence established between the copolymer self-association (AA) and the interpolymer interaction (AC) through three-dimensional 3D-plots as a function of different magnitudes. Figure 2 shows the dependences of Δg_{AC} with composition, interaction sites and self-association equilibrium constant at a given $\eta_{AC} = 35$. The general trend observed is that the Δg_{AC} always decrease and

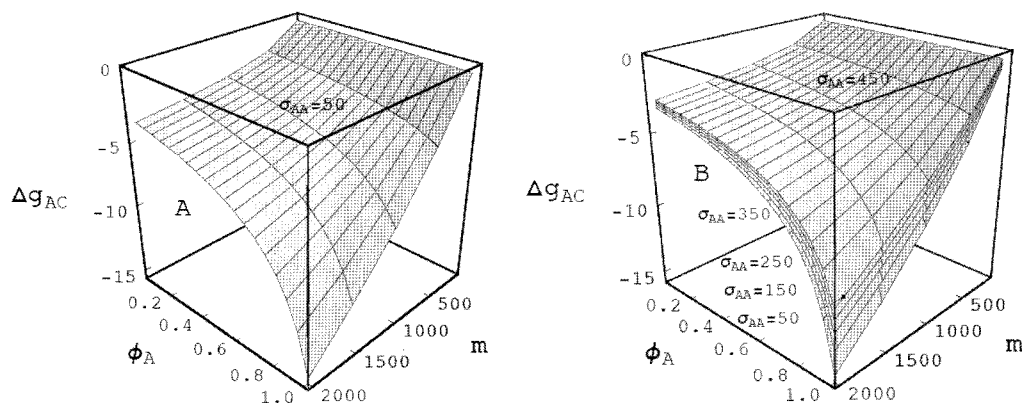


Figure 2. 3D-plots for the dependences of Δg_{AC} with composition and with the number of interacting sites, m , for the system PSVPh-7.2/ECH/PHB at: (A) constant $\sigma_{AA} = 50$ and (B) different σ_{AA} values.

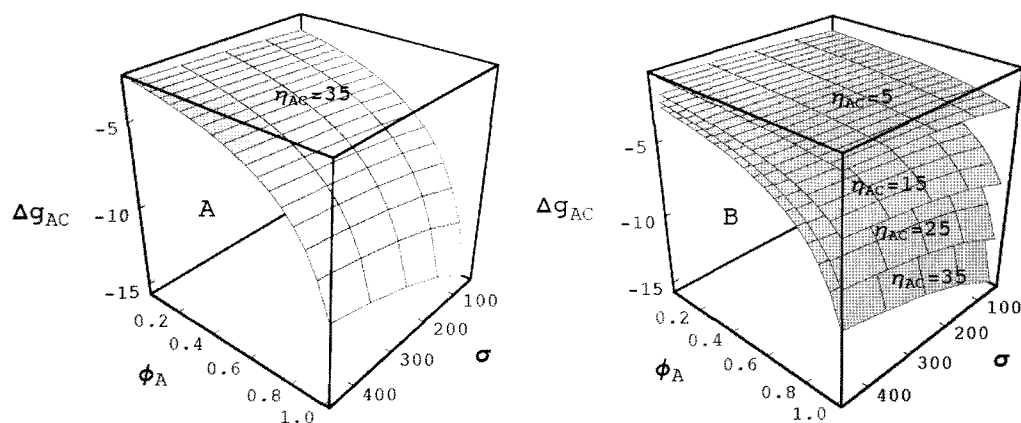


Figure 3. 3D-plots for the dependences of Δg_{AC} with composition and with the self-association equilibrium constant, σ_{AA} , for the system PSVPh-7.2/ECH/PHB at: (A) constant $\eta_{AC} = 35$ and (B) different η_{AC} values.

the system becomes more stable as the amount of copolymer A and the available interaction sites increases. Regarding the variation with σ_{AA} (part B), the contrary behavior is found: Δg_{AC} decreases as σ_{AA} also does, as seen in the different layers or surfaces corresponding to values ranging from 50 to 450 (from bottom to top). This finding can be easily interpreted since σ_{AA} represents the self-association equilibrium constant which competes with the η_{AC} interassociation one. Therefore, as σ_{AA} is raised, the extension of AC interactions will be lowered, the free energy goes to higher values and the system loses stability and miscibility between their components. Figure 3 illustrates the multi-dependence of Δg_{AC} with composition, σ_{AA} and η_{AC} at the most favorable value of $m = 2,000$. Part A evidences again an analogue behavior respect to the system composition and σ_{AA} values, and part B shows the different layers obtained when varying the η_{AC} from 5 to 35 (from top to bottom). As can be seen, the increase in the AC interassociation constant lowers the free energy change accounting for the AC hydrogen-bond, and therefore, favors the compatibility or miscibility of both

polymers in the blend. Finally, Figure 4 plots the 3D variation of Δg_{AC} with composition, η_{AC} and m at the most favorable value of $\sigma_{AA} = 50$ deduced before. In part B, the parameter m has been varied from 100 to 2,000, that is, from low to high density of interaction sites. As expected, the free energy of the AC interaction process is more negative as the amount of sites where the H-bonds can take place increases, denoting that miscibility increases also as more and more sites are available.

Summarizing, the system compatibility or miscibility is thermodynamically enhanced at low values of σ_{AA} and high values of η_{AC} and m . Moreover, from the comparison of Δg_{AC} values in Figures 1-4, it can be stated that the order for the extension and strength of the hydrogen-bond interactions, in the present system, is: interassociation copolymer-polymer (AC) > copolymer self-association (AA) > interassociation copolymer-solvent (AB).

Fluorescence Spectroscopy. In order to validate the abovementioned theoretical predictions on hydrogen-bonding specific interactions, we have experimentally monitored

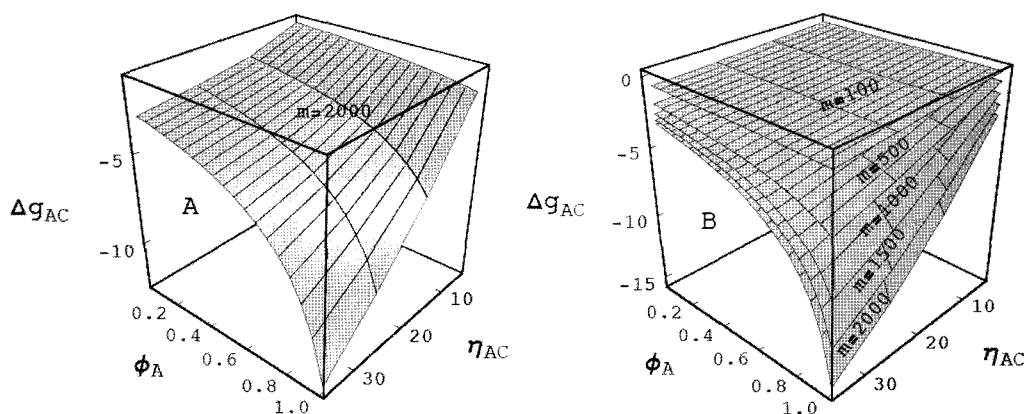


Figure 4. 3D-plots for the dependences of Δg_{AC} with composition and with the inter-association equilibrium constant, η_{AC} , for the system PSVPh-7.2/ECH/PHB at: (A) constant $m = 2,000$ and (B) different m values.

the association of PSVPh-x.x (x.x = 7.2; 5.8; 4.0; 3.2 and 2.0 mole% of vinylphenol) to PHB by fluorescence spectroscopy, a widely used and low time-consuming technique that has been proved to be a powerful tool for monitoring specific interactions.⁴⁹⁻⁵²

In order to interpret the fluorescence experimental results, the simple binding model has been used which relies in two facts: (i) the fluorescence intensity depends linearly on the concentration of the two possible states of the polymer (free and bound); and (ii) the mass of the polymer must be conserved. Therefore, since the copolymer A is the fluorescent specie, the total concentration should be expressed by $[A]_T = [A]_f + [A]_b$, where $[A]_f$ and $[A]_b$ are the free and bound (either AB or AC) concentrations, respectively. The observed intensity due to the emission of the fluorescent specie can be written as:

$$I = \frac{[A]_b}{[A]_T} I_m + \frac{[A]_f}{[A]_T} I_0 \quad (17)$$

or

$$I = \alpha I_m + (1 - \alpha) I_0 \quad (18)$$

where α , the fraction of bound polymer, is the relevant variable for quantifying the degree of association; $(1 - \alpha)$ is the fraction of free polymer in solution, and I_m and I_0 are the fluorescence intensities of copolymer A fully associated (that is when $[A]_T = [A]_b$) and in the absence of polymer C, respectively. From eqs. (17) and (18), is deduced that:

$$\alpha = \frac{I - I_0}{I_m - I_0} \quad (19)$$

Meanwhile the I and I_0 values are experimentally measured, the I_m value has to be obtained by using an indirect procedure, concretely, from the intercept of the well-known dou-

ble reciprocal plots:^{46,53}

$$\frac{I_0}{I - I_0} = \frac{I_0}{I_m - I_0} + \frac{I_0}{(I_m - I_0) K_A [A]_T R_i} \quad (20)$$

where K_A is an apparent association constant between both polymers (A and C) and R_i the molar ratio between polymers C and A, that is $R_i = [\text{PHB}]_T / [\text{PSVPh}]_T$.

Table III compiles the experimental raw data of fluorescence intensities obtained for the five systems assayed at different PHB concentrations and total $[\text{PSVPh}] = 14 \mu\text{M}$. As seen, in all cases, I increases as the R_i ratio decreases, and for a given R_i , increases in general as the comonomer content in the PSVPh diminishes. These data have been used to build up the corresponding association plots, as we will explain later. Previously, the I_m values have been determined from the double reciprocal plots depicted in Figure 5.

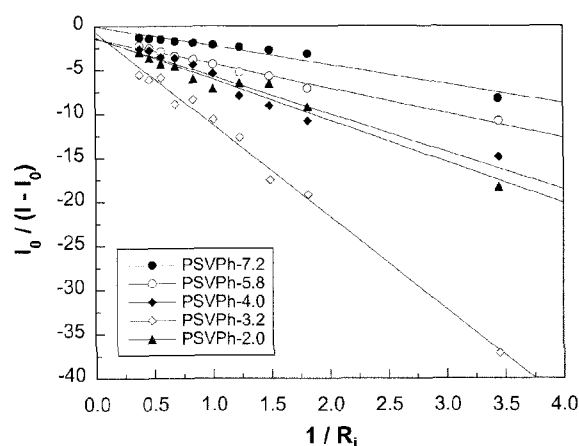


Figure 5. Double-reciprocal plots of the fluorescence measurements of different PSVPh-x.x/ECH/PHB ternary systems. Lines correspond to the linear fits of eq. (20).

Table III. Values of Experimental Fluorescence Intensities and Degree of Association for the Systems PSVPh-x.x/ECH/PHB at Different Molar Ratios, R_i , with $[\text{PSVPh}] = 14 \mu\text{M}$

[PHB] (μM)	R_i	PSVPh-7.2		PSVPh-5.8		PSVPh-4.0		PSVPh-3.2		PSVPh-2.0	
		I (a.u.)	α	I (a.u.)	α	I (a.u.)	α	I (a.u.)	α	I (a.u.)	α
36.7	2.61	23.1	0.63	45.5	0.46	48.2	0.33	48.6	0.22	42.3	0.16
30.2	2.15	32.1	0.56	50.1	0.41	50.3	0.31	49.7	0.20	46.3	0.13
24.8	1.77	36.3	0.53	54.4	0.35	56.5	0.24	49.3	0.20	49.1	0.11
20.4	1.46	44.1	0.47	58.5	0.30	57.2	0.23	52.7	0.13	50.0	0.10
16.7	1.19	50.6	0.42	61.0	0.27	60.7	0.20	52.3	0.14	53.3	0.08
13.8	0.99	57.0	0.37	63.7	0.24	64.1	0.16	53.8	0.11	55.0	0.06
11.4	0.81	62.0	0.34	67.0	0.20	68.8	0.11	54.7	0.09	54.1	0.07
9.3	0.67	67.8	0.29	68.3	0.18	70.0	0.09	56.0	0.07	54.2	0.07
7.7	0.55	73.5	0.25	71.2	0.15	71.4	0.08	56.3	0.06	57.0	0.05
4.0	0.29	94.5	0.20	75.2	0.13	73.4	0.08	57.8	0.05	60.5	0.05
0.0	0.00	107.6		82.9		78.7		59.4		64.0	

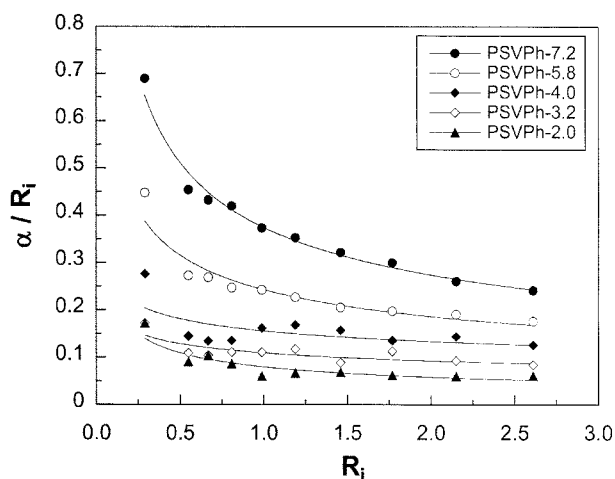


Figure 6. Association isotherms plotting the extent of copolymer A-polymer C binding per mole of accessible sites, α/R_i , as a function of the donor-acceptor molar ratio, R_i , for the different PSVPh-x.x/ECH/PHB ternary systems. Lines are drawn to guide the eye.

As seen, good linear fittings are obtained in all cases, and consequently, the I_m values can be derived from the intercepts. These values together with the I_o and I are the necessary data to evaluate the fraction of PSVPh bound to the PHB, α , at different R_i according to eq. (19). These α values are also listed in Table III denoting a progressive decrease as both R_i and copolymer content decrease. This behaviour is plotted in Figure 6, in a more convenient and usual way of measuring the extent of the polymer incorporation, since α/R_i represents the number of moles of the fluorescent polymer (the H-donor copolymer A) bound per mole of available sites in the other polymeric chain (the H-acceptor polymer C). As can be seen, for a given R_i , the higher the copolymer content in the PSVPh the higher the extent of the association. This behaviour supports the above theoretical predictions: the extent of AC hydrogen-bonding association increases as the number of hydroxyl groups in the copolymer increases. Regardless of the phenolic content, in any system the α/R_i values stand nearly constant for medium and high R_i values but as the molar ratio diminishes up to a certain value, a sharp increase in the interaction is noticed. Such behaviour suggests that may exist an optimum R_i value for which the interaction should be highly effective, the steric hindrance minimized and, the compatibility or miscibility between both polymers maximized.

Moreover, independently of the copolymer tested, the quantitative results show that the interpolymer AC association given by α/R_i increases as R_i decreases, that is as the amount of H-donor component (copolymer A) also increases. Again, these findings are in agreement with the theoretical simulations, since the fact that $R_i \rightarrow 0$ is equivalent to $\phi_A \rightarrow 1$, and correspondingly, the increase in the experimental α/R_i values is equivalent to the observed decrease of Δg_{AC} with ϕ_A .

Conclusions

The theoretical simulations have shown that the coupling of the FH formalism with the AET approach can satisfactorily model the specific interactions via hydrogen-bonding established between all components of a ternary system formed by an H-donor copolymer, an H-acceptor homopolymer and an H-acceptor solvent.

Modelling of copolymer-solvent and copolymer-homopolymer associations have been driven through the excess functions Δg_{AB} and Δg_{AC} , which account exclusively for specific interactions and are obtained by subtracting to the free-energy change due to all type of interactions those corresponding to the non-specific ones. The data reveal that, in general, the PSVPh-PHB specific interactions are: (1) more favourable than the PSVPh-ECH or the PSVPh-PSVPh ones in all the composition range; (2) increase as the volume fraction of the H-donor polymer (PSVPh) in the system increases; (3) are also higher as the phenolic content in the PSVPh copolymer is raised, that is, as the potential number of interacting groups grows up; (4) the miscibility is thermodynamically enhanced at low values of σ_{AA} and high values of η_{AC} and m ; and (5) the extension and strength of the competitive hydrogen-bond interactions, is: interassociation copolymer-polymer (AC) > copolymer self-association (AA) > interassociation copolymer-solvent (AB). Consequently, the values of the Δg_{AB} and Δg_{AC} excess functions can serve to predict which kind of binary interactions will be predominant in a polymer blend in solution, and then, to theoretically assess miscibility or compatibility between the components of a system.

The extent of the copolymer-biodegradable homopolymer miscibility has been substantiated by the fluorescence spectra. The changes in the PSVPh fluorescence intensities, upon addition of different quantities of PHB, have served to experimentally estimate well enough the extent of the interpolymer association. The experimental behaviour is quite consistent with the theoretical predictions, which serves to give confidence to the proposed thermodynamic formalism.

Moreover, the methodology here developed should be applicable to any polymer blend in solution with specific interactions other than hydrogen-bonding. Currently, the same systems are being studied by fluorescence in solid state where only the two polymers are involved (without solvent). For this kind of binary systems, the theoretical model here developed can also be applied, and calculations are in progress.

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Nomenclature

g_{ij} binary specific and non-specific interaction parame-

	ter between i and j species
g'_{ij}	binary non-specific interaction parameter between i and j species
Δg_{ij}	Gibbs free energy excess function accounting for ij H-bond energy
ΔG^N	Gibbs free energy of mixing per mole of occupied lattice site ($\text{J}\cdot\text{mol}^{-1}$)
I	fluorescence intensity of component A in the ternary system (a.u.)
I_0	fluorescence intensity of pure component A (a.u.)
I_m	fluorescence intensity of component A fully associated with C (a.u.)
K_A	apparent AC association constant ($\text{dL}\cdot\text{g}^{-1}$)
m	number of interaction sites to form AC hydrogen bonds
n_i	number of moles of component i
P_i	molar fraction of the free component i per mole of total lattice sites
P_i^0	molar fraction of the pure component i per mole of total lattice sites
r	ratio of the segmental B and C molar volumes
r_i	polymerization degree of polymeric components
R	universal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
R_i	molar ratio between components C and A
s	ratio of the segmental B and A molar volumes
T	temperature (K)
V_i	molar volume of component i ($\text{mL}\cdot\text{mol}^{-1}$)

Greek letters

α	fraction of bound polymer
ϕ_i	volume fraction of component i
σ_{ij}	self-association equilibrium constant
σ_{ij}, η_{ij}	interassociation equilibrium constants
ν_i	nominal concentration of component i in moles per mole of occupied lattice sites

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