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A miscibility window in PVC/EVA system

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ABSTRACT

The existence of a miscibility window in the PVC/EVA system was investigated using a binary approach. The miscibility window was observed for 45 or 50% to 80% acetate content depending on thermodynamic parameters used. Experimental data on PVC/PVA system give no evidence for the existence of miscibility. The cloud point curves indicated a lower critical solution temperature (LCST) for the PVC/EVA system. This behavior was corroborated using equation of state analysis.

INTRODUCTION

Lower critical solution temperature (LCST) or closed loop phase diagrams may appear in two situations: polar blends with hydrogen linkages, where entropy changes related to association are not a critical factor or entropy changes derived from significant volume differences between mixture components. They occur mainly in polymer/solvent blends or in some non polar blends where volume differences are small as compared to a polymer-solvent mixture (1-3).

The specific interactions observed in PVC/EVA system are relatively weak and may be influenced by comonomer intramolecular repulsive effects in such a way that a balance between enthalpic and entropic contributions (free volume) is essential for miscibility. In this work a binary interaction model was applied to investigate the existence of a miscibility window in homopolymer-copolymer blends like PVC-EVA (4-8). Phase separation behavior was studied by cloud point observation and the temperature dependence of the Flory Huggins parameter was investigated using the equation of state formalism.

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EXPERIMENTAL

The poly(vinyl chloride) used in this work was a commercial product of Companhia Petroquímica Camaçari (CPC). Six ethylene vinyl acetate copolymers were obtained from commercial sources. Relevant parameters of the polymers are listed in Table 1 and were described elsewhere (9). The vinyl acetate (VA) contents of copolymers samples were obtained by thermogravimetric analysis carried out in a Perkin Elmer TGA-7 thermobalance calibrated with alumel (T_c =163°C), nickel (T_c =354°C) and perkalloy (T_c =596°C) standards. Expansion coefficient was obtained by thermomechanical analysis (Perkin Elmer TMA-7). PVA samples were synthesized by mass polymerization initiated by azobisisobutyronitrile (AIBN) in a bath at 60°C, to a low conversion to ensure low ramification content. The characteristics of the synthesized PVA are described in Table 1.

TABLE 1 - Characterization of polymers used in this study

Polymer	% VA Nominal	% VA Calc.	Density (g.cm^{-3})	T_g (°C)	M_w	M_n	M_w/M_n
PVC	---	---	1.390	86	152,000	101,000	1.5
EVA 31	31	32	0.949	-39	72,000	23,000	3.1
EVA 41	41	43	0.967	-40	65,000	29,000	2.2
EVA 45	45	45	0.975	-36	95,000	29,000	3.2
EVA45A	45	46	---	-38	72,000	34,000	2.2
EVA 50	50	52	0.990	-37	157,000	38,000	4.2
EVA 70	70	70	1.055	-23	176,000	54,000	3.3
PVA 1	---	---	1.210	25	167,000	70,000	2.6
PVA 2	---	---	1.210	25	6,200	4,200	1.5

Blends were obtained by solvent casting mixtures of PVC and copolymers (with 10 phr of Ba/Cd/Zn oleate) from 2% (w/v) THF solutions onto glass plates. Supported films were covered with a glass slide and cloud points were observed in an optical microscope with polarized light and hot stage. The samples were heated above the glass temperature (T_g) in order to get uniform thickness and no air bubbles. Cloud points were observed using a heating rate of 10°C/min. They were determined by the first cloud observed in the films. Heating rate was controlled by adjusting the voltage to the hot plate (4).

RESULTS AND DISCUSSION

The association between the cloud point temperatures and thermodynamic phenomena is important for the evaluation of the nature of the phase separation process even without quantitative correlation.

Phase separation appears in the observed temperature range on heating the blends from 25°C to 300°C. This means that a LCST occurs and it was reported for PVC/EVA systems (2,6,8). Figure 1 shows the cloud point temperatures of PVC/EVA as a function of composition. Phase separation mechanisms such as nucleation and growth and spinodal decomposition (3) were not observed. PVC thermal instability caused by the dehydrochlorination process during heating obliterated this examination.

In order to reduce decomposition problems a lower heating rate was tried, but imprecise results were obtained. Reversion in separation process was observed only for PVC/EVA 45 and PVC/EVA 45A blends which showed redissolution on cooling. These blends display similar behavior and the films were transparent. The cloud point temperatures are lower than the observed for PVC/EVA 50 and PVC/EVA 70, respectively. However, PVC/EVA 45 blends were found to be immiscible when studied by calorimetry and viscometry (4). The miscibility of these blends is questionable and depends of the sample preparation and evaluation method, as pointed out by Cruz-Ramos and Paul (6).

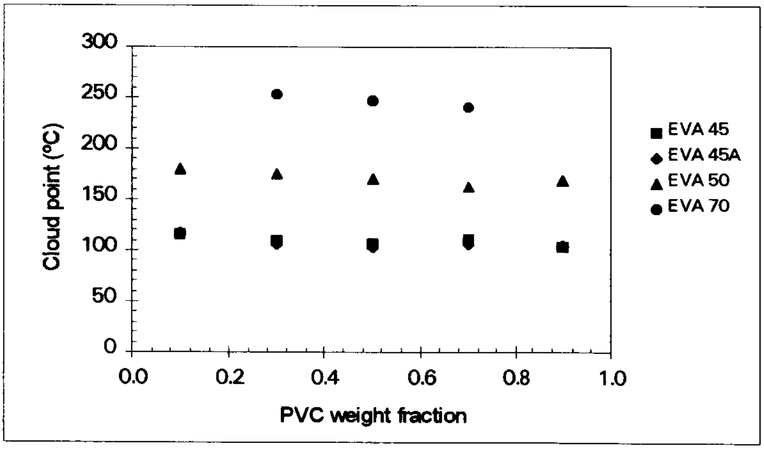

Figure 1 - PVC/EVA cloud point temperatures as a function of composition.

EVA 50 and EVA 70 blends remained clouded on cooling and it is probably due to film degradation that occurs at the temperature needed to observe phase separation. For the last one no points were observed in PVC or EVA rich phase due the high temperature needed to obtain phase separation as mentioned above.

The influence of acetate content in copolymer that can interact with PVC segments is related with the phase separation temperature. Higher acetate content corresponds to higher cloud temperature. High temperatures are related with more negative enthalpies and it means greater thermodynamic stability for the mixture. It must bear in mind that the cloud point is the temperature where the domain size reaches an optical detectable magnitude and has no direct relationship with thermodynamic behavior.

When a binary interaction model for miscibility is applied some additional information about the system may be obtained (5,6). For PVC/EVA the intermolecular exchange enthalpy parameter, X_{12}, can be expressed by the binary interaction energy density, B.

$$X_{12} = B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2$$

where the segmental units in a homopolymer-copolymer blend interact with each other in a pairwise fashion (6); B_{ij} are the interaction energy densities for mixing the *i* and *j* units. Subscript 1 comprises the acetate unit (VA), 2 is the ethylene unit (E) and 3 the vinyl chloride unit (VC); ϕ_1 and ϕ_2 are the volume fractions of units 1 and 2, respectively. The condition to get exothermic values of B is expressed by

$$B_{12} > (B_{13}^{1/2} + B_{23}^{1/2})^2$$

that shows intramolecular copolymer interaction influence in the miscibility.

Table 2 shows the intersegmental parameters obtained from analogue calorimetry measurements (6,10,11) and Table 3 lists the values of X_{12} calculated for PVC/EVA pairs using Table 2 data. Hypothetical PVC/EVA 80 and PVC/EVA 90 blends were employed to evaluate the miscibility window limit.

Table 2 - Intersegmental parameters from literature (6,10,11)

Segment pair	(a) B(cal/cm^3)	(b) B(cal/cm^3)	(c) X(cal/cm^3)	(d) X(cal/cm^3)
VA-E (B_{12})	16.2	11.8	15.0	16.7
VA-VC (B_{13})	4.3	1.2	3.1	2.4
E-VC (B_{23})	2.4	4.8	5.7	4.8

obtained at (a) 150°C (6); (b) 25°C (6); (c) 25°C (10); (d) 25°C (11).

Table 3 - Effective energy contact parameters X_{12}, calculated from intersegmental parameters

Pair	(a) $X_{12}(J/cm^3)$	(b) $X_{12}(J/cm^3)$	(c) $X_{12}(J/cm^3)$	(d) $X_{12}(J/cm^3)$
PVC/EVA 90	9.55	1.46	6.8	3.5
PVC/EVA 80	3.50	-0.42	3.5	-0.48
PVC/EVA 70	-0.40	-0.92	2.0	-2.5
PVC/EVA 50	-3.16	1.34	3.3	-1.57
PVC/EVA 45	-2.96	2.50	4.4	-0.48
PVC/EVA 41	-2.60	3.50	5.5	0.59
PVC/EVA 31	-0.87	6.74	8.8	4.02

The calculations were carried out using values from: (a)- ref. (6); b- ref. (6); c- ref. (10); d- ref. (11).

From Table 3 it can be seen that first column X_{12} values are not coherent because negative values (favorable to mixing) were assigned for the notorious immiscible PVC/EVA31 and PVC/EVA41 pairs. The third column presents only positive values that mean immiscibility for all pairs.

The values listed in columns 2 and 4 are coherent with the miscibility window predicted for PVC/EVA pairs. The second column indicates miscibility for EVA 70 and EVA 80, and the fourth one for EVA 45, 50, 70 and 80. It must bear in mind that PVC/EVA 45 and PVC/EVA 50 are described by some authors as a miscible blend (6,8) and immiscible by others (4,6,8,9).

The intramolecular repulsion model was questioned for blends that contain copolymers (12). The authors reported that PVC/PE or PVC/poly(vinyl acetate) (PVA) blends are immiscible and the inclusion of acetate groups in polyethylene (PE) improves miscibility. It means that repulsion contacts may be responsible for additional miscibility. The miscible PVC/PVA blend described in that work (12), was obtained by casting films from methyl ethyl ketone (MEK) solution, and showed a single glass transition. This solvent was employed to diminish solvent-component preferential affinity, called $\Delta\chi$ effect.

This disagrees with the data given by Table 3 and promoted a revision of PVC/PVA miscibility. One commercial PVC and two different synthesized poly(vinyl acetate)s with similar polydispersion and different molecular weights were used to investigate the chain size effect. The synthesis conditions were adequate to give low ramification content.

These blends were prepared using the experimental conditions described by the mentioned authors, i.e., room temperature, low evaporation rate, and THF or MEK as solvents. All films exhibited two phases and two glass transition temperatures were registered near to that for the pure component values.

It must borne in mind that even if experimental conditions could be reproduced to obtain the single Tg reported in the published results, the glass transition width, ΔTg, was very large (~45K). It means that high inhomogeneity is present and the blend is thermodynamically unstable (metastable state). DSC previous study (4) assigned that PVC/EVA70 blends, which can be considered miscible, showed no more than 35K in ΔTg. Then, even if an ideal film preparation condition exists, a metastable situation occurs for PVC/PVA blends. Therefore, the decrease of favourable interactions promoted by the increase in ethylene content in the copolymer is not the single feature to be considered and the intermolecular repulsion effect cannot be neglected.

In order to evaluate temperature effects on Flory Huggins interaction parameter, χ_{12}, the Patterson-Robard equation (13), that considers the free volume effect on miscibility was applied:

$$\frac{\chi_{12}}{M_1 V_1^*} = \frac{P_1^*}{RT_1^*}\left[\frac{\tilde{V}_1^{1/3}}{(\tilde{V}_1^{1/3}-1)}\left(\frac{X_{12}}{P_1^*}\right) + \frac{\tilde{V}_1}{2(4/3-\tilde{V}_1^{1/3})}\left(1-\frac{T_1^*}{T_2^*}\right)^2\right]$$

where χ_{12} is the Flory-Huggins polymer-polymer interaction parameter, M_1 the molecular weight of the component 1, V_1^* the specific core volume and $\bar{V}_1$ the reduced volume of the component 1, P_1^* is the characteristic pressure, T_1^* and T_2^* the respective characteristic temperatures of each component 1 and 2 and R the gas constant.

Characteristic parameters used are listed in Table 4. A critical value of the polymer-polymer interaction parameter, χ_{crit}, sets the limit for miscibility across the composition range. The critical value of χ for a mixture of r_1 and r_2 mers is (11)

$$\chi_{crit} = 1/2\,(r_1^{-1/2} + r_2^{-1/2})^2$$

The value given by $\chi_{12}/V_1^* \leq \chi_{crit}/V_1^*$ is 2.79×10^{-5} mol/cm^3. From Table 3 two values of X_{12} -0.92 and -2.5 J/cm^3 were employed in order to get χ_{12} as a function of temperature for PVC/EVA70 pair.

When X_{12}= -2,5 J/cm^3 in a temperature range of 100 to 800 K all χ_{12} values were negative and smaller than χ_{crit} so that a LCST would not be expected. However, the cloud point temperature data indicate that PVC/EVA70 shows phase separation at high temperature. This suggests that the value X_{12} = -0,92 J/cm^3 is more adequate. Using this value of X_{12}, the interaction parameter χ_{12} becomes higher than χ_{crit} at temperatures above

500 K. It means that a LCST behavior can be expected in a coherent temperature as indicated by cloud point temperatures.

Table 4 - Characteristic parameters V^*, T^*, P^* and thermal expansion coefficient, α, for PVC and EVA copolymers (14)

Polymer	V^* (cm^3/segment.mol)	T^* (K)	P^* (J/cm^3)	$\alpha 10^4 (K^{-1})$
PVC	72.56	7943	607	5.18
EVA 70	71.01	7093	534	-
EVA 50	77.29	7325	507	-

Table 3 shows X_{12} values of 1.34 J/cm^3 and -1.57 J/cm^3 that could be applied for PVC/EVA50 system. From the former the calculated value of χ_{12} showed immiscibility in the temperature range of 100 to 800K. The second value of X_{12} was not used because it may not be smaller than the value used for PVC/EVA70 pair.

It is known that χ_{12} can be described by one enthalpic contribution, χ_H, and an entropic one, represented by the free volume contribution, χ_{FV} (15,16). Figure 2 shows the behavior of PVC/EVA70 interaction parameter, χ_{12}, its components χ_H and χ_{FV}, and χ_{crit} as a function of temperature. It can be seen that the free volume component is always positive and rises smoothly as the temperature rises. χ_H is always negative. χ_{Total} is negative until temperature reaches 400K. As the temperature increases, the magnitude of the favorable enthalpic term diminishes until positive values appear representing an immiscible region.

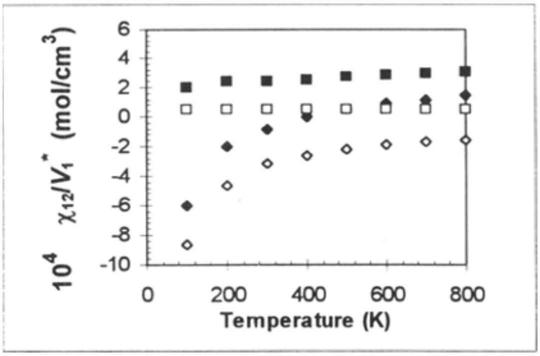

Figure 2-Temperature dependence of PVC/EVA70 interaction parameters: ◇ - χ_H/V^*; ■ - χ_{FV}/V^*; ◆-χ_{Total}/V^* ; □ - χ_{crit}/V^*.

At 500K χ_{12} reaches a critical condition followed by phase separation. The LCST is caused by the enthalpic term becoming less negative, accomplished by the free volume increase at higher temperatures. This corresponds to a breakup of the favorable interactions due to the increased temperature.

The values of the PVC/EVA Flory Huggins parameter agree with lower critical solution temperature behavior indicated in cloud point measurements.

As mentioned above it may be inferred that the enthalpic component, represented by the intermolecular interactions between the oxygen from EVA acetate group and the chlorine atom of PVC, is very important, but the free volume is also a determining factor. This means that for this system a subtle equilibrium between these contributions exists.

CONCLUSIONS

PVC/EVA system presented miscibility windows adequately described by binary interaction model. Experimental results showed total immiscibility of the PVC/PVA system. Cloud point experiments and theoretical Flory Huggins parameter calculation indicated LCST behavior and it was related to acetate content in the copolymer. A subtle equilibrium between enthalpic and entropic contributions was assigned.

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