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Thermodynamic compatibility of sepiolite-filled poly(vinylidene fluoride)-polystyrene blends

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SUMMARY

Inverse gas chromatography (IGC) and differential scanning calorimetry (DSC) were used to investigate the effect produced by sepiolite on the thermodynamical compatibility of poly(vinylidene fluoride) - polystyrene blends. Polymer-polymer interaction parameters were calculated from the retention data, for various polar and non-polar probes in pure and mixed stationary phases of these polymers, using sepiolite as solid support, as well as from melting point depression analysis of the sepiolite filled blends. Both techniques give us positive values of the interaction parameters, in accordance with the non-compatibility of these blends; However negative values of the interaction parameters were obtained for polystyrene-rich blends ($\Phi_{PS} \geq 85$ wt%) and high sepiolite loadings, indicating that sepiolite acts as a compatibilizing agent for the system PVF_2/PS.

INTRODUCTION

There is currently a great deal of research in compatible polymer blends since such mixtures may represent a valuable and economical alternative to the use of copolymers (1,2). However most of the known polymers form non-compatible systems when mixing. Fillers can act as compatibilizing agents in these kind of systems (3,4); compatibilization is achieved by means of the existence of polymer-filler interactions, different for each polymer blend component, which according to Lipatov et al. (5) should lead to changes in the ratio of the polymer components in the boundary and in the volume of mixing.

In this work inverse gas chromatography (IGC) and differential scanning calorimetry (DSC) were used to evaluate the effect produced by sepiolite on the thermodynamic compatibility of poly(vinylidene fluoride) - polystyrene blends (PVF_2/PS).

EXPERIMENTAL

Materials

Reagent grade solutes C_n, n-alkanes (n = 6,7,8), dichlorometane CH_2Cl_2 and furane C_4H_4O (Merck) were used without further purification. Polystyrene (PS143E) and poly(vinylidene fluoride) (Kynar 720) were obtained from BASF and Penwalt Corp. respectively. The sepiolite samples (PANSIL, SL60) were purchased from Tolsa

SA: PANSIL was used as received in a micronised form (average diameter 3 μm). SL60 particles were treated with H_2O_2 to avoid any trace of organic matter, washed several times in methanol, acetone and distilled water, and vacuum dried at 353K for 12 hours. Particles were then sieved to a diameter of 200-250 μm.
Filled blends for calorimetric measurements were prepared in a Brabender Plasticorder using a thermoplastic mixing chamber type W60 preheated to 473K. Rotor speed was set at 60 rpm; ten minutes of mixing were enough to generate a steady-state response, indicating uniform dispersion of the components.

Columns

The columns were prepared in the usual manner. The polymers and blends were coated (10% loading) from a DMFA solution onto sepiolite SL60. After drying in a vacuum oven for 24 h at 373K, the coated support was resieved and packed into 50 cm length, 1/8" o.d. stainless steel columns. The exact percent loading of polymer in the support was determined by termogravimetry (Mettler TA3000 system) using a suitable blank correction. The relative concentration of polymers in the blends is assumed to be identical to that in the original solution prior to the deposition on the sepiolite. Columns were conditioned under nitrogen for 24 h at 493K.

Instrumentation

The gas chromatographic (IGC) measurements were run on a modified Perkin-Elmer 3920B gas chromatograph equiped with an integrator Spectra-Physics SP4290 fitted with a dual flame ionization detector. Dried nitrogen was used as carrier gas. The flow rate (10-30 ml/min) was measured with a soap bubble flow meter. The inlet and outlet pressures were monitored by a precision digital manometer. Experiments were run at 433K. A 10 μl syringe was used to inject the probes; to avoid saturation the syringe was emptied three times, and only the amount remaining in the needle was injected. Air was used as a non-retained substance for the measurement of the dead time.
The calorimetric measurements (DSC) were carried out with a Perkin-Elmer DSC7 differential scanning calorimeter operating under nitrogen. Samples were melted at 493K for ten minutes an then rapidly cooled (350K/min) to the crystallization temperature T_c. The melting temperature of each sample after isothermal crystallization at T_c were calculated by heating the samples directly from T_c to T_m at a heating rate of 5K/min.

RESULTS AND DISCUSSION

Inverse gas chromatography

Specific retention volumes V_g^0 (cm^3/g) were computed from the expression:

$$V_g^0 = t_n F J / w_L \qquad (1)$$

where t_n is the net retention time for the probe, J is the James-Martin correction factor for gas compressibility (6), w_L is the weight of polymer in the column and F is the carrier gas flow rate at 0°C and 1 atm. which is obtained from:

$$F = 273{,}16 F_0 (P_a - P_w) / 760 (273{,}16 + T_A) \qquad (2)$$

where P_a is the atmosferic pressure (mmHg), F_0 is the flow rate measured from the end of the column (ml/min) and P_w is the water pressure (mmHg) at temperature T_A(°C) of the flowmeter.
From the Flory-Huggins treatment of solutions thermodynamics (7,8) one can obtain the X_{12} parameter, which is a measure of the residual free energy of interaction between solute and polymer. X_{12} is determined from the relationship:

$$X_{12} = \ln(273{,}16Rv_2)/V_g^0p_1^0V_1) - (1-V_1/M_2v_2) - p_1^0(B_{11}-V_1)/RT \qquad (3)$$

where V_1 is the molar volume of pure (liquid) solute, p_1^0 is its vapour pressure at temperature T, R is the gas constant, v_2 is the specific volume of the polymer, M_2 is its molecular weight and B_{11} is the second virial coefficient which is used to correct for vapour phase non-ideality of the probe. Values of B_{11} were obtained from Dymond and Smith compilation (9) and solute vapour pressures were obtained from Riddick and Bunger tabulations (10). Solute densities were obtained from various sources, including the compilations by Orwoll and Flory (11) and Timmermans (12). At infinite dilution of the probe and for high molecular weight polymers the second term of eq 3 approaches 1.

For mixed stationary phases, it has been shown (13) using Scott's ternary solution treatment (14), that the overall interaction parameter between the volatile probe (1) and the stationary phase (2-3) is given by:

$$X_{1(23)} = \ln[273.16\, R(w_2v_2+w_3v_3)/V_g^0 p_1^0 V_1] - (1-V_1/V_2)\Phi_2 - (1-V_1/V_3)\Phi_3 - p_1^0(B_{11}-V_1)/RT \qquad (4)$$

where w_2 and w_3 refer to the weight fraction of PVF_2 and PS in the blend.

$X_{1(23)}$ is related to the polymer-polymer interaction parameter from the expression:

$$X_{1(23)} = X_{12}\Phi_2 + X_{13}\Phi_3 - X_{23}(V_1/V_2)\Phi_1\Phi_2 \qquad (5)$$

thus by determining X_{12} and X_{13} from experiments on the homopolymers and $X_{1(23)}$ from the blend, X_{23} is forthcoming.

The results obtained show a linear relationship between the specific retention volume calculated from Eq 1 and the amount of probe injected. To avoid this situation V_g^0 data where extrapolated to zero sample injected. The same dependence was observed between the retention volume and the carrier gas flow rate. Again data where extrapolated to zero flow rate for calculation of interaction parameters. Table I shows the values of the specific retention volume obtained at 433K of the polar and non-polar probes on PS, PVF_2 and their blends. Looking at the results, an increase in the value of the specific retention volume is observed for the n-alkanes as chain length increases, being the values obtained for the system PS-probe higher than those obtained for PVF_2-probe, indicating a higher degree of solubility. In the case of the blends, a maximum in the solubility of the n-alkanes is observed for the system with a 30% of PS, while the higher solubility was found for furane in the case of the blend containing a 70% of PS. Polymer-solute interaction parameters were calculated using Eq 3. Table II shows the values obtained for X_{12}. The interaction parameter is negative in all cases except for the system PS-furane, thus indicating solubility of the polymers.

Table I.- Specific retention volumes V_g^0 (ml/g) of various probes on PVF_2, PS and their blends at 433K.

Probe	PS weight fraction			
	0	30	70	100
Hexane	13.2	26.8	14.5	29.9
Heptane	25.3	50.6	11.1	101.6
Octane	26.0	80.5	24.0	248.6
Dichlorometane	19.8	11.3	4.1	37.2
Furane	19.2	28.7	32.0	1.1

Table II.- PVF_2-solute and PS-solute interaction parameters (X_{12}) at 433K.

Probe	X_{12}	
	PVF_2	PS
Hexane	-1.40	-1.71
Heptane	-1.46	-2.35
Octane	-0.93	-2.69
Dichlorometane	-1.82	-1.95
Furane	-2.70	0.67

For mixed stationary phases, the overall stationary phase-volatile probe interaction parameters were calculated using Eq. 4. Combining these results with those obtained previously for the pure polymers and applying Eq. 5 polymer-polymer interaction parameter X_{23} were obtained. Table III compiles the values obtained at 433K. Values are positive, thus indicating a non-compatible phase-separated system for the blend having a PS concentration of 30 wt%, while positive and negative values depending of the probe were obtained for the blend with higher PS concentration. In order to have absolute values, independent of the nature of the probe, the values were averaged for the five probes and the resulting numbers plotted in Figure 1. In general X_{23} interaction parameter is positive (non-compatible blend), having a maximum and then decreasing as PS concentration in the blend increases. Extrapolation of the curve leads to the conclussion that in a certain degree of concentration ($\Phi_{PS} \geq 85$ wt%) the system becomes compatible ($X_{23} < 0$).

Table III.- PVF_2- PS interaction parameter X_{23} at different weight fractions of PS.

Probe	PS weight fraction 30	 70
Hexane	5.76	2.19
Heptane	4.73	-0.46
Octane	5.20	-1.99
Dichlorometane	0.85	-4.25
Furane	10.8	12.83

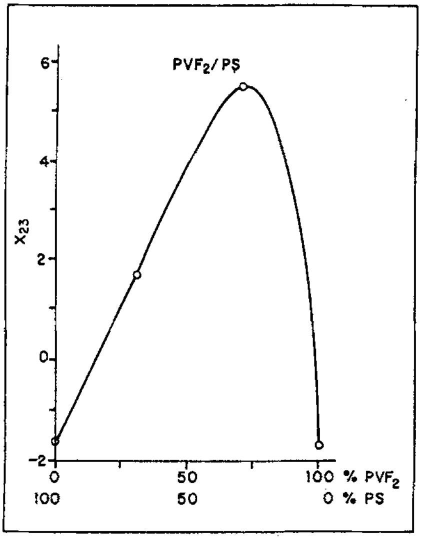

Figure 1.- Average polymer-polymer interaction parameter X_{23} vs blend composition.

Differential Scanning Calorimetry

The determination of interaction parameters by calorimetric measurements is based on the depression experimented in the melting point of the crystallizable polymer component in a compatible system.

According to Scott (14) and Koningsveld (15), polymer-polymer interaction parameter X_{23} can be calculated from the expression:

$$1/T_m - 1/T_m^0 = - \frac{R\, V_{2u}}{H_{2u}\, V_{1u}} X_{23}\, V_1^2 \qquad (4)$$

where subscript 1 and 2 identifies the amorphous and cristalline polymers respectively, V is the volume fraction, V_u the molar volume of the repeating unit. H_{2u} represents the enthalpy of fusion per mole of repeating unit, T_m^0 the equilibrium melting temperature of the pure crystalline polymer and T_m the equilibrium melting point of the crystalline polymer in the blend. The equilibrium melting temperature T_m^0 (or T_m) can be determined following the method of Hoffman and Weeks (16) from a plot of T_m^0 vs T_c, where T_m^0 (or T_m) is the intercept of the extrapolated $T_m{}^*$ with the line defined by $T_m{}^* = T_c$, using the expression:

$$T_m{}^* = (1/\eta)\, T_c + (1-1/\eta)\, T_m \qquad (5)$$

where $T_m{}^*$ is the experimental melting temperature of the sample, and $1/\eta$ is a morphological and stability parameter (17), almost constant and independent of blend composition.

Equilibrium melting temperatures of PVF_2 in the blend vs sepiolite concentration, obtained from Hoffman-Weeks plots, are shown in Table IV. The equilibrium melting temperature remain constant in the unfilled blend,

Table IV.- Equilibrium melting temperatures of the PVF_2/PS blends containing different sepiolite levels.

PVF_2/PS	Sepiolite wt%			
	0	5	10	20
2100/0	448.7	447.6	447.0	446.4
90/10	448.3	447.1	445.5	445.6
70/30	448.5	448.0	447.1	445.7
50/50	448.0	447.1	447.4	444.9
30/70	447.7	448.3	446.7	443.6

independent of blend composition, typical situation of a non-compatible system. On the contrary a decrease in this parameter is observed for the blends containing 10 and 20 wt% of sepiolite as PS concentration in the blend increases, thus indicating a certain degree of compatibility of the system.

By using Eq. 4 polymer-polymer interaction parameters X_{23} were obtained. Values are compiled in Table V. For the unfilled and 5 wt% sepiolite filled blends X_{23} is positive, Characteristic of a non-compatible phase-separated system, in accordance with the constant values found for the equilibrium melting temperature. Nevertheless the system becomes compatible ($X_{23} < 0$) in the case of blends containing levels of sepiolite of 10 and 20 wt%.

Table V.- Polymer-polymer interaction parameter X_{23} obtained from melting point depression analysis of the filled PVF_2/PS blends.

Sepiolite wt%	X_{23}
0	0.013
5	0.017
10	-0.006
20	-0.064

CONCLUSSIONS

Comparison of data obtained by inverse gas chromatography and melting point depression analysis is not possible since the value extracted from IGC has been defined in terms of PS chemical potential, and that obtained from melting point depression analysis is related to PVF_2 chemical potential. Nevertheless both techniques give parallel results, that is the PVF_2/PS blend behaves as a non-compatible, phase separated system, that becomes compatible ($X_{23} < 0$) in a concentration range ($\Phi_{PS} \geq 85$ wt%) at high sepiolite loadings; in agreement with micrographs of fractured samples analysed by scanning electron microscopy (Figure 2).

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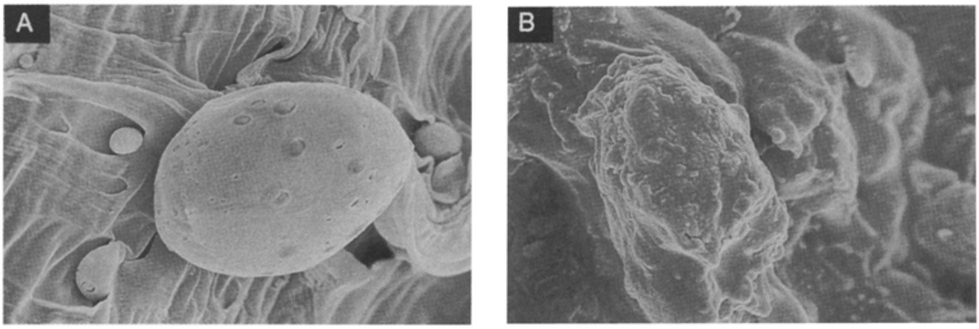

Figure 2.- SEM micrographs of the fractured surface of PVF_2/PS 30/70 blend: (a) unfilled and (b) 20 wt% sepiolite filled.

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