

Miscibility of poly(ethylene oxide)/poly(ethylene-co-vinyl acetate) blends: simulation of phase diagram

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Blends of poly(ethylene oxide)/poly(ethylene-co-vinyl acetate) (PEO/EVAc-1) have been prepared by casting from a common solvent. The miscibility of the mixture is studied by using differential scanning calorimetry (d.s.c.) and dilatometry. The blends, as obtained, show a single, composition-dependent, glass transition that fits the Fox equation well, indicating the presence of a homogeneous amorphous phase. Some blends phase-separate on heating. The cloud-point curve of the system is drawn by detecting on the d.s.c. thermograms one or two glass transition temperatures depending on whether or not phase separation takes place at a fixed annealing temperature. The cloud-point curve is very skew, with a maximum at around 80 wt% PEO content and $t = 210 \pm 10^\circ\text{C}$. The theoretical approach of group contributions and solubility parameters predicts no miscibility for the system under investigation, whereas a lower critical solution temperature is predicted by Flory's equation-of-state theory. Using values of X_{12} interactional parameter, derived from the experimental thermal expansion coefficients of the blends, a simulated spinodal phase boundary is obtained.

(Keywords: miscibility; blends; poly(ethylene oxide); poly(ethylene-co-vinyl acetate); simulation; phase diagram)

INTRODUCTION

Thermodynamic theories of polymer miscibility are, in principle, capable of predicting or describing phase-separation behaviour. At present several theories, based on simple molecular models, may lead to useful predictions about the miscibility of polymeric systems. The solubility parameter theory¹, the Flory-Huggins theory², the Patterson theory^{3,4}, Flory's equation-of-state theory⁵⁻⁸ and the lattice fluid theory⁹ are examples of theories that give different levels of prediction. The reliability of the prediction depends on the amount of experimental data and the theory used.

The solubility parameter theory (SPT) and the Flory-Huggins lattice theory (FHT) require few experimental parameters but their predictions have to be considered as qualitative. The theory that at present is most extensively applied to the phase diagrams of high-molecular-weight polymer mixtures is the equation-of-state theory of Flory and his coworkers⁵⁻⁸, derived from the Prigogine corresponding-state theory¹⁰.

The main difference between Prigogine and Flory theories lies in the volume dependence assumed for the molar configurational energy. Originally Prigogine used a dependence inspired by the 6-12 Lennard-Jones potential. Flory has used the inverse volume dependence characteristic of a van der Waals liquid. McMaster¹¹ used Flory's theory to calculate the spinodal and the binodal curves of hypothetical polymer mixtures, and showed that the theory is capable of predicting both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behaviour. Both

the UCST and LCST are a result of a combination of three contributions: combinatorial entropy, equation-of-state terms and interactional energy parameter. McMaster also examined the dependence of the phase diagram on factors such as molecular weights, thermal expansion coefficients, thermal pressure coefficients, interaction energy parameter and pressure.

We report here the experimental evidence of compatibility and the miscibility predictions, obtained from the solubility parameter theory and Flory's equation-of-state theory, of poly(ethylene oxide)/poly(ethylene-co-vinyl acetate) (PEO/EVAc-1) blends (the copolymer EVAc-1 containing 69 mol% of VAc). We describe the method of computation of the X_{12} contact energy term from the measured thermal expansion coefficients of the blends and the simulation of the spinodal curve.

Preliminary results¹², concerning the study of the influence of EVAc copolymer composition and crystallization temperature on the morphology and kinetics of isothermal crystallization of PEO/EVAc 80/20 wt% blends (the VAc content in the copolymer varies from 100 to 18 mol%), show that the blends containing a copolymer with VAc content higher than 56 mol% do not present any optical evidence of segregated domains of copolymer, whereas for the other blends with a copolymer containing less than 56 mol% VAc the non-crystallizable material forms spherical domains in intraspherulitic regions. For all the blends, at a given T_c , a decrease in the spherulite radial growth rate G is observed. The size of such a decrease depends on copolymer composition. For blends containing a copolymer with VAc content ≤ 56 mol%, the G decrease is less marked than that observed for blends with copolymers having VAc content ≥ 56 mol%. The mor-

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phological and kinetic results can lead to the hypothesis that miscibility at the molecular level is present for blends with VAc content in the copolymer greater than 56 mol%. The blends with VAc content less than 56 mol% could be phase separated in the melt, so that the composition of PEO-rich phase involved in the crystallization process is higher than the nominal one.

THEORETICAL BACKGROUND

The notation and meaning of symbols not explained in the text are reported in the Appendix. The indices 1, 2 and 12 present in some equations are related to the individual components PEO and EVAc-1 and their blends, respectively.

Solubility parameter theory

The solubility parameter¹ δ was introduced as a useful quantity for the characterization of the strength of interactions in simple liquids. Subsequently, it was extended to polymer-solvent systems and finally to polymer-polymer blends.

The Flory-Huggins interaction parameter χ_{12} is related to the difference between the solubility parameters of the components 1 and 2 through:

$$\chi_{12} = V_u(\delta_1 - \delta_2)^2/RT \quad (1)$$

As is evident, χ_{12} can assume only positive values or zero in the case $\delta_1 = \delta_2$. Miscibility is predicted when χ_{12} becomes lower than its critical value $(\chi_{12})_{cr}$:

$$(\chi_{12})_{cr} = \frac{1}{2}(1/m_1^{1/2} + 1/m_2^{1/2})^2 \quad (2)$$

where m_1 and m_2 are the degrees of polymerization of the components.

According to the group contribution method, δ is given by:

$$\delta = (1/v) \sum F_i/M_u \quad (3)$$

where $\sum F_i$ is the sum of all the molar attraction constants of all the chemical groups in the polymer repeat unit; M_u is the molecular weight of the repeat unit in the polymer; and v is the specific volume at the temperature of interest. In this work the quantity $\sum F_i$ will be computed following Hoy's table¹.

Flory's equation of state

The equation of state, at atmospheric pressure ($\bar{P} = 0$), is given by:

$$\bar{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/3} \quad (4)$$

In this theory the basic quantities characterizing a liquid are reduced temperature (\bar{T}), volume (\bar{v}) and pressure (\bar{P}), defined by:

$$\bar{T} = T/T^* \quad (5)$$

$$\bar{v} = V/V^* = v/v^* \quad (6)$$

$$\bar{P} = P/P^* \quad (7)$$

The asterisked quantities are constant reference parameters; V^* and v^* , called hard-core volumes, are the molar and the specific volumes, respectively, at 0 K ($V^* = Mv^*$).

Flory's equation of state gives the Gibbs free energy

of mixing ΔG_m as follows:

$$\begin{aligned} \Delta G_m = & RT(N_1 \ln \Phi_1 + N_2 \ln \Phi_2) \\ & + \bar{r}Nv^*[\Phi_1 P_1^*(1/\bar{v}_1 - 1/\bar{v}) + \Phi_2 P_2^*(1/\bar{v}_2 - 1/\bar{v}) \\ & + \Phi_1 \Theta_2 X_{12}/\bar{v}] + 3\bar{r}Nv^*\{\Phi_1 P_1^* \bar{T}_1 \\ & \times \ln[(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] + \Phi_2 P_2^* T_2 \\ & \times \ln[(\bar{v}_2^{1/3} - 1)/(\bar{v}^{1/3} - 1)] + \Phi_1 \Theta_2 T Q_{12}/3\} \quad (8) \end{aligned}$$

The interaction energy term X_{12} denotes the energy change for the formation of contacts between species 1 and 2 in exchange for contacts between like species. The interaction entropy parameter Q_{12} was introduced by Flory in order to take into account the local densification in the case of the existence of strong specific interactions between the components since the theory was based on a random mixing assumption.

Walsh and Rostami¹³, applying the spinodal condition:

$$\partial^2 \Delta G_m / \partial \Phi_2^2 = 0 \quad (9)$$

to equation (8), obtained the following equation for the simulation of the spinodal curve:

$$\begin{aligned} -1/\Phi_1 + (1 - r_1/r_2) - (P_1^* V_1^*/RT_1^*) \\ \times [(\partial \bar{v}/\partial \Phi_2)/(\bar{v} - \bar{v}^{2/3})] \\ + (P_1^* V_1^*/RT_1^*) \times (\partial \bar{v}/\partial \Phi_2) \\ + (P_1 V_1^*/RT) \times (\partial \bar{v}/\partial \Phi_2) \\ + V_1^* 2\Theta_2^2(1 - \Theta_2)X_{12}/RT\bar{v}\Phi_1\Phi_2 \\ - (V_1^* \Theta_2^2 X_{12}/RT\bar{v}^2)(\partial \bar{v}/\partial \Phi_2) \\ - V_1^* 2\Theta_2^2 Q_{12}/R\Phi_1\Phi_2 = 0 \quad (10) \end{aligned}$$

where

$$\begin{aligned} \partial \bar{v}/\partial \Phi_2 = \{ \partial \bar{P}/\partial \Phi_2 - [(\bar{P} + 1/\bar{v}^2)/\bar{T}] (\partial \bar{T}/\partial \Phi_2) \} \\ / [2/\bar{v}^3 - \bar{T}(\bar{v}^{1/3} - 2/3)/(\bar{v}^{1/3} - 1)^2 - \bar{v}^{5/3}] \quad (11) \end{aligned}$$

$$\partial \bar{P}/\partial \Phi_2 = P/P^* [P_1^* - P_2^* - X_{12}\Theta_2(1 - \Theta_1/\Phi_2)] \quad (12)$$

$$\begin{aligned} \partial \bar{T}/\partial \Phi_2 = T/P^* (P_2^*/T_2^* - P_1^*/T_1^*) \\ + \bar{T}/P^* [P_1^* - P_2^* - X_{12}\Theta_2(1 - \Theta_1/\Phi_2)] \quad (13) \end{aligned}$$

Knowing the thermal expansion coefficients $\alpha = (\partial \ln V/\partial T)_p$ and the thermal pressure coefficients $\gamma = (\partial P/\partial T)_v$ of the pure components, it is possible to calculate the reduced volume \bar{v} , hard-core temperature T^* and hard-core pressure P^* from:

$$\bar{v} = [1 + \alpha T/3(1 + \alpha T)]^3 \quad (14)$$

$$\bar{T} = (v^{1/3} - 1)/v^{4/3} = T/T^* \quad (15)$$

$$P^* = \gamma T v^2 \quad (16)$$

Then one can calculate the hard-core temperature T^* and pressure P^* of the mixture from:

$$T^* = P^*/(\Phi_1 P_1^*/T_1^* + \Phi_2 P_2^*/T_2^*) \quad (17)$$

$$P^* = \Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \Theta_2 X_{12} \quad (18)$$

The X_{12} contact energy term can be obtained from the experimental heats of mixing or from any other binary quantity, such as the thermal expansion coefficient of the mixture, or by fitting the experimental excess volume ratio of mixing.

In this paper we will use $Q_{12} = 0$ and values of X_{12} obtained from the experimental thermal expansion coefficients.

Table 1 Molecular characteristics of polymers

Polymer	Code	M_w^a	M_n^a	M_v	VAc content	
					(wt%)	(mol%)
Poly(ethylene oxide)	PEO	2.0×10^4	—	2.0×10^{4b}	—	—
Ethylene-vinyl acetate copolymer	EVAc-1	2.0×10^5	6.7×10^4	—	87.1	68.7

^aObtained by g.p.c. measurements in tetrahydrofuran, relative to polystyrene standards

^bIn water at 30°C¹⁸; $(dl\ g^{-1}) = 1.25 \times 10^4 M_v^{0.79}$

EXPERIMENTAL

Materials and blend preparation

The molecular characteristics of the polymers are reported in *Table 1*. PEO and EVAc-1 were supplied by Fluka A.G. (Germany) and Kuraray Co. (Japan), respectively.

The binary blends were prepared by casting a 10% (w/v) solution of a preweighed mixture of PEO and EVAc-1 dissolved in chloroform onto flat Petri dishes at room temperature. To ensure complete removal of the solvent, the resulting films were kept under vacuum at 70°C for 24 h.

D.s.c. measurements

The index of crystallinity and the glass transition temperatures (t_g) of the pure PEO, pure EVAc-1 and the blends are obtained by using differential scanning calorimetry (Mettler DSC-30).

The weight crystallinity indices of the PEO phase, $X_c(\text{PEO})$, and of the overall blends, $X_c(\text{blend})$, are calculated from:

$$X_c(\text{PEO}) = \Delta H^*(\text{PEO})/\Delta H^\circ(\text{PEO}) \quad (19)$$

$$X_c(\text{blend}) = \Delta H^*(\text{blend})/\Delta H^\circ(\text{PEO}) \quad (20)$$

where $\Delta H^\circ(\text{PEO})$ is the heat of melting per gram of 100% crystalline PEO ($= 188\ \text{J}\ \text{g}^{-1}$) and $\Delta H^*(\text{PEO})$ and $\Delta H^*(\text{blend})$ are the apparent enthalpies of melting per gram of PEO in the blend and per gram of blend, respectively.

In order to determine the t_g of the blend as obtained by casting, the sample is scanned from -100 to 120°C at heating rate of $20^\circ\text{C}\ \text{min}^{-1}$ and the heat evolved is recorded as function of temperature. The t_g value is taken as the temperature corresponding to the maximum of the peak obtained by the first-order derivative of the transition trace.

In order to verify if the PEO/EVAc-1 blends separate on heating, the sample is heated at $100^\circ\text{C}\ \text{min}^{-1}$ to a selected annealing temperature and held at this temperature for 15 min. This period has been shown to provide phase equilibrium and yet avoid degradation in the temperature range investigated. The sample is then rapidly quenched to -100°C and scanned at rate of $20^\circ\text{C}\ \text{min}^{-1}$. From the thermograms one or two glass transitions are revealed depending on whether or not phase separation takes place at the annealing temperature. Annealing treatments are effected at temperatures up to 350°C . Thermogravimetric analysis carried out up to 500°C shows that the system under investigation does not undergo thermal degradation during the annealing treatment.

Table 2 Temperature ranges where liquid specific volumes are measured for polymer, copolymer and blends of various composition

	t (°C)
PEO	80–170
EVAc-1	30–170
PEO/EVAc-1 80/20 (wt/wt)	80–170
PEO/EVAc-1 60/40 (wt/wt)	80–170
PEO/EVAc-1 40/60 (wt/wt)	80–170
PEO/EVAc-1 20/80 (wt/wt)	80–170

Dilatometry

The specific volumes v and the thermal expansion coefficients α are measured using a Pyrex dilatometer at intervals of temperature of about 10°C . The blend composition and the temperature range investigated to determine the liquid specific volume are reported in *Table 2* for PEO, EVAc-1 and PEO/EVAc-1 blends. The dilatometer and experimental procedure have been described in detail elsewhere⁴. The experimental specific volumes, subjected to a multiple regression analysis, are best represented by a quadratic function as $v = a + bt + ct^2$ where a , b and c are constants.

RESULTS AND DISCUSSION

Glass transition temperature by d.s.c.

In *Figure 1* are reported the thermograms of PEO, EVAc-1 and their blends. The glass transition temperature of PEO is found to be $-44 \pm 2^\circ\text{C}$ and that of EVAc-1 is $20 \pm 2^\circ\text{C}$. The thermograms relative to the blends, as obtained by casting, present only one glass transition temperature.

The values of the glass transition temperatures of the pure components and of the blends are reported in *Table 3*. In the same table are also shown the overall crystallinity index (referred to the pure PEO and to the blend), the real amorphous phase composition of the blend and the calculated values of t_g of the blends by using the Fox equation¹⁴. For all the blends studied, the t_g values computed by the Fox equation are in good agreement with the experimental ones.

These results show clearly that PEO and EVAc-1 are compatible in the amorphous phase of the blends. In order to explore the higher limits of compatibility of the components, the blends are subjected to an annealing treatment as described in the 'Experimental' part. The phase separation is followed by d.s.c. and it is taken when the single transition begins to split into two transitions. This procedure allows one to draw a pseudo-cloud-point curve, shown in *Figure 2*, which is very skew with a minimum at about 80 wt% PEO content and $t = 210 \pm 10^\circ\text{C}$.

Solubility parameter theory

In order to compute the χ_{12} interaction parameter, it is necessary to have accurate values of specific volumes of PEO and EVAc-1 relative to the liquid state. The required specific volumes v are computed by using the following equations obtained as explained in the 'Experimental' section:

$$v(\text{PEO}) = 0.878 + 5.676 \times 10^{-4}t + 6.82 \times 10^{-7}t^2 \quad (21)$$

$$v(\text{EVAc-1}) = 0.863 + 5.160 \times 10^{-4}t + 7.70 \times 10^{-7}t^2 \quad (22)$$

In Figure 3 are reported the χ_{12} interaction parameter and its critical value versus temperature. The critical value of χ_{12} is obtained by setting $m_1 = 454$ and $m_2 = 2948$ in equation (2). The analysis of Figure 3 shows that the χ_{12} interaction parameter is always higher than its critical value, and hence the PEO and EVAc-1 components are predicted to be immiscible according to this theory, in disagreement with the experimental evidence.

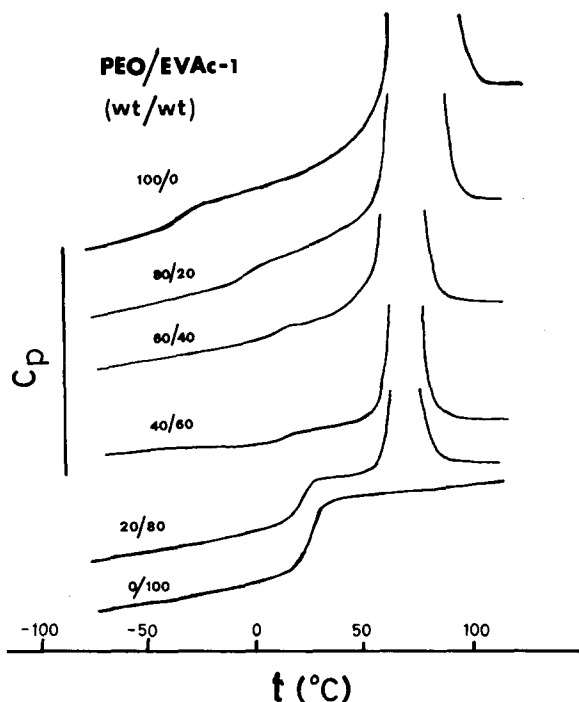


Figure 1 D.s.c. thermograms of PEO and EVAc-1 components and their blends

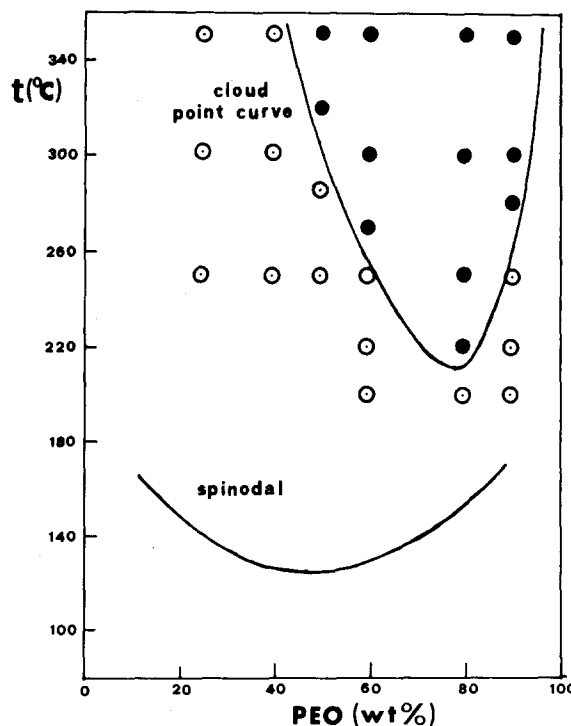


Figure 2 Cloud-point curve (○) one phase; (●) two phases) and calculated spinodal curve of PEO/EVAc-1 system

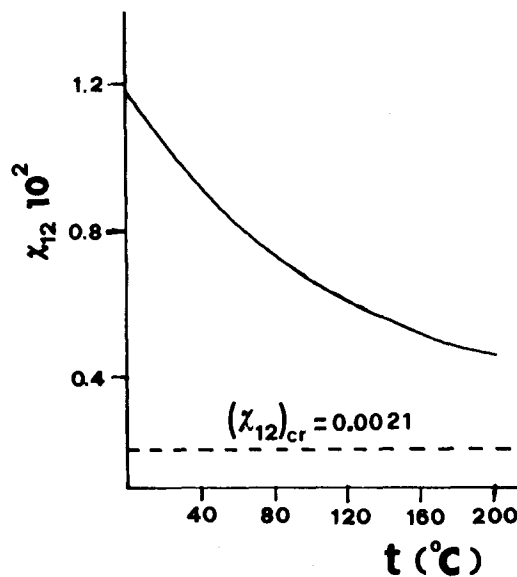


Figure 3 Interaction parameter versus temperature. The broken line represents the critical value

Table 3 Overall crystallinity index, composition of the amorphous phase and relative calculated t_g of PEO/EVAc-1 blends

Nominal blend composition, PEO/EVAc-1 (wt/wt)	Overall crystallinity index (%)		Blend amorphous phase composition (wt/wt)	t_g (°C)	
	$X_c(\text{blend})$	$X_c(\text{PEO})$		Exp.	Calc.
100/0	90	90	100/0	-44 ± 2	-
90/10	81	90	46/54	-11	-12
80/20	67	84	39/61	-7	-8
60/40	52	87	18/82	7	8
40/60	31	77	13/87	10	10
20/80	17	87	3/97	17	17
0/100	0	0	0/100	20	-

Table 4 State parameters of the pure materials

(a) PEO

t (°C)	v (cm ³ g ⁻¹)	$\alpha \times 10^4$ (K ⁻¹)	γ (J cm ⁻³ K ⁻¹)	\bar{v}	v^* (cm ³ g ⁻¹)	V^* (cm ³ mol ⁻¹)	T^* (K)	P^* (J cm ⁻³)
80	0.928	7.29	1.37	1.219	0.761	15221	6736	720
90	0.935	7.38	1.34	1.227	0.762	15238	6764	718
100	0.942	7.47	1.26	1.234	0.763	15257	6795	717
110	0.949	7.56	1.21	1.242	0.764	15279	6828	715
120	0.956	7.65	1.16	1.249	0.765	15302	6864	712
130	0.963	7.73	1.12	1.257	0.766	15328	6903	710
140	0.971	7.81	1.07	1.264	0.768	15357	6944	707
150	0.978	7.89	1.03	1.272	0.769	15388	6987	704
160	0.986	7.97	0.990	1.279	0.771	15422	7032	701
170	0.994	8.04	0.953	1.286	0.773	15458	7079	698

(b) EVAc-1

t (°C)	v (cm ³ g ⁻¹)	$\alpha \times 10^4$ (K ⁻¹)	γ (J cm ⁻³ K ⁻¹)	\bar{v}	v^* (cm ³ g ⁻¹)	V^* (cm ³ mol ⁻¹)	T^* (K)	P^* (J cm ⁻³)
30	0.879	6.39	1.58	1.171	0.751	150126	6914	658
40	0.885	6.53	1.51	1.179	0.750	150052	6897	659
50	0.891	6.66	1.45	1.188	0.750	150001	6886	659
60	0.897	6.78	1.38	1.196	0.750	149975	6880	659
70	0.903	6.91	1.33	1.204	0.750	149973	6880	659
80	0.909	7.03	1.27	1.212	0.750	149998	6885	659
90	0.916	7.15	1.22	1.220	0.750	150048	6894	659
100	0.922	7.26	1.17	1.229	0.751	150125	6907	658
110	0.929	7.38	1.12	1.237	0.751	150230	6925	657
120	0.936	7.49	1.08	1.245	0.752	150361	6946	656
130	0.943	7.59	1.03	1.253	0.753	150520	6970	654
140	0.950	7.70	0.994	1.261	0.753	150707	6998	653
150	0.958	7.80	0.956	1.269	0.755	150923	7029	651
160	0.965	7.90	0.919	1.277	0.756	151166	7063	649
170	0.973	7.99	0.884	1.285	0.757	151437	7099	647

Flory's equation of state: spinodal curve simulation

The required quantities for the computer simulation of the spinodal curve are reported in *Table 4* for PEO and EVAc-1, and in *Table 5* for the blends. The ratio of contact sites per segment (S_2/S_1), which is included in Θ_2 by definition, was evaluated by Bondi's technique¹⁵ and is equal to 1.05.

The thermal pressure coefficients γ of the pure components are estimated from the solubility parameters¹⁶, which themselves are related to the cohesive energy density and hence to the strength of the internal pressure of the structural molecules:

$$\gamma = m\delta^2/T \quad (23)$$

where for polymers m generally assumes a value close to 1. According to the results of our study¹⁷ concerning the comparison between the experimental determination and theoretical computation of the thermal pressure coefficient, we have here calculated γ of PEO and EVAc-1 setting $m = 1.35$ in equation (23). This causes a difference in values of P^* of PEO, reported here in the ninth column of *Table 4*, from those we have published in ref. 4, where m was set equal to 1.

In any case we have also determined the spinodal points by using values of γ setting $m = 1$ and 1.4. The results show no effect on the position of the spinodal

curve, indicating that γ , for this system, has little influence on the simulation.

The X_{12} contact energy term can be calculated from the experimental heats of mixing or any other binary quantity of the mixture. The calorimetry experiment involving direct mixing is not possible because of the high viscosity of the polymers. This problem can be bypassed by using oligomeric analogues of the components and assuming that the oligomeric mixture is equivalent to the corresponding polymeric mixture. This procedure may not always give reliable results owing to the differences between the high polymers and the analogues used, which arise from chain-end effects, steric differences and hence density differences. It is also possible to determine the value of the enthalpy of mixing through Hess's law by using solutions of the single components and of the mixture. However, this procedure also may not always give trustworthy results because of the very low amount of energy involved during the dissolution, and hence the final calculated value of ΔH_m can be affected by a very large error.

In this paper we use a different procedure. From the thermal expansion coefficient of the blends and using, in order, equations (14), (15), (17) and (18), we have computed X_{12} of each blend as a function of temperature. The X_{12} values are reported in the seventh column of

Table 5 State parameters of PEO/EVAc-1 mixtures

Blend composition, PEO/EVAc-1 (wt/wt)	t (°C)	v (cm ³ g ⁻¹)	\tilde{v}	T^* (K)	P^* (J cm ⁻³)	X_{12} (J cm ⁻³)
80/20	80	0.927	1.201	7152	749	-247
	90	0.933	1.213	7066	736	-176
	100	0.940	1.224	6996	724	-113
	110	0.947	1.236	6939	713	-58
	120	0.954	1.248	6895	703	-10
	130	0.961	1.259	6862	694	32
	140	0.969	1.271	6839	685	70
	150	0.977	1.282	6824	677	102
	160	0.985	1.293	6817	670	131
	170	0.993	1.304	6818	662	156
60/40	80	0.928	1.201	7144	732	-147
	90	0.935	1.213	7066	721	-105
	100	0.941	1.224	7002	710	-68
	110	0.948	1.235	6951	701	-36
	120	0.955	1.247	6912	691	-7
	130	0.962	1.258	6882	684	18
	140	0.970	1.269	6862	676	41
	150	0.978	1.280	6850	669	60
	160	0.986	1.291	6846	662	77
	170	0.995	1.302	6849	655	92
40/60	80	0.927	1.208	6976	699	-63
	90	0.933	1.218	6940	693	-41
	100	0.940	1.228	6913	687	-22
	110	0.947	1.238	6894	681	-4
	120	0.954	1.278	6882	676	11
	130	0.962	1.258	6877	671	25
	140	0.969	1.268	6879	666	38
	150	0.977	1.278	6886	661	49
	160	0.985	1.288	6898	656	59
	170	0.993	1.297	6915	651	67
20/80	80	0.919	1.209	6966	683	-68
	90	0.925	1.218	6954	680	-53
	100	0.932	1.227	6949	676	-40
	110	0.939	1.236	6949	673	-27
	120	0.946	1.244	6955	670	-16
	130	0.953	1.253	6965	667	-5
	140	0.960	1.262	6980	663	4
	150	0.968	1.271	6999	660	12
	160	0.975	1.280	7022	657	19
	170	0.983	1.288	7048	653	26

Table 5 and the behaviour of X_{12} as a function of temperature and blend composition is shown in Figure 4. Considering X_{12} at a fixed temperature, we find that up to about 120°C it is negative (or very close to 0) and decreases on increasing the PEO content in the blend; whereas at higher temperatures it is positive and increases with the composition. For a given composition the contact energy term increases with temperature, changing its sign from negative to positive. The higher the PEO content in the blend, the higher is the rate of change of X_{12} with temperature. These results seem to indicate the existence of some specific interactions between the two components that are functions of composition and

temperature. The temperature dependence of X_{12} could probably arise from the dissociation of the specific interactions present at lower temperatures and the formation of dispersive forces at higher temperatures, and the size of this phenomenon seems to be dependent on the composition.

The spinodal simulation obtained is presented in Figure 2. The spinodal curve is not as skewed at high PEO content as the cloud-point curve, but it is almost symmetric with composition. Moreover, it lies much below the cloud-point curve. We think that the spinodal curve in our case should not be compared with the cloud-point curve, which is determined here only to verify

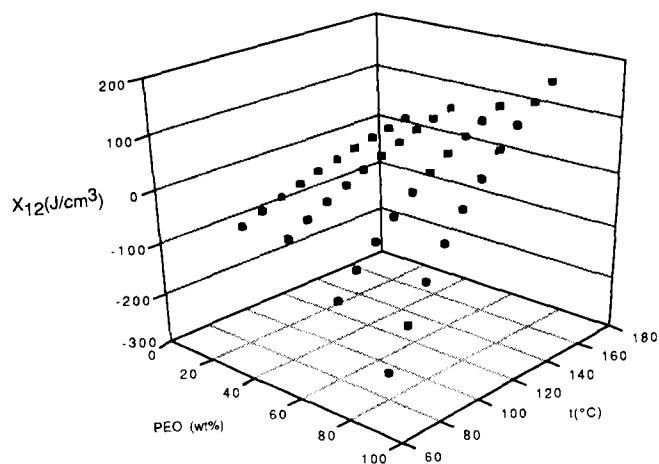


Figure 4 Contact energy term of the PEO/EVAc-1 system as a function of temperature and composition

that the system under investigation undergoes phase separation on heating. So we do not try to change the value of X_{12} or to introduce the term Q_{12} in the simulation in order to obtain matching of the spinodal and cloud-point curves.

CONCLUSIONS

Mixtures of PEO and EVAc-1, as obtained by casting, are shown to be compatible and undergo phase separation on heating. The compatibility between the two components in the amorphous phase is demonstrated by the presence of only one glass transition temperature, which fits the Fox equation well. In order to understand the thermodynamics and to simulate the phase boundary of this system, two theories have been applied: solubility parameter theory and Flory's equation-of-state theory. The response of the solubility parameter theory is that the χ_{12} interaction parameter is positive and always higher than its critical value. This prediction is not reliable because the theory is not suitable to describe some phase behaviours of polymer-polymer systems, such as the *LCST*. Flory's equation-of-state theory, which is at present the most suitable theory capable of describing the possible phase behaviours of polymer-polymer mixtures, predicts for this system a *LCST*. This kind of behaviour derives directly from the sign and the values of the X_{12} contact energy terms obtained from the thermal expansion coefficients of the blends.

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APPENDIX: NOTATION

- ΔG_m = free energy of mixing (J cm^{-3})
 ΔH_m = enthalpy of mixing (J cm^{-3})
 m_i = degree of polymerization of species i
 M = molecular weight (g mol^{-1})
 N = total number of molecules in mixture
 N_i = amount of substance of species i
 P = pressure (J cm^{-3})
 P_i^* = characteristic pressure of species i (J cm^{-3})
 \bar{P}_i = reduced pressure of species i (dimensionless)
 P^* = characteristic pressure of mixture (J cm^{-3})
 \bar{P} = reduced pressure of mixture (dimensionless)
 Q_{12} = interaction entropy parameter ($\text{J cm}^{-3} \text{K}^{-1}$)
 R = gas constant ($\text{J cm}^{-3} \text{K}^{-1}$)
 r_i = number of segments in chain molecule i
 \bar{r} = average number of segments in mixture
 S_i = number of contact sites per segment in species i
 t = temperature ($^{\circ}\text{C}$)
 T = temperature (K)
 T_c = crystallization temperature
 T_i^* = characterization temperature of species i (K)
 \bar{T}_i = reduced temperature of species i (dimensionless)
 T^* = characteristic temperature of mixture (K)
 \bar{T} = reduced temperature of mixture (dimensionless)
 t_g = glass transition temperature
 V_i^* = characteristic hard-core molar volume of species i ($\text{cm}^3 \text{mol}^{-1}$)
 v_i^* = characteristic hard-core volume of species i ($\text{cm}^3 \text{g}^{-1}$)
 \hat{v}_i = reduced volume of species i (dimensionless)
 v^* = characteristic hard-core volume of mixture ($\text{cm}^3 \text{g}^{-1}$)
 v = specific volume ($\text{cm}^3 \text{g}^{-1}$)
 V = molar volume ($\text{cm}^3 \text{mol}^{-1}$)
 V_u = molar volume of repeat unit ($\text{cm}^3 \text{mol}^{-1}$)
 w_i = weight fraction of species i (dimensionless)
 X_{12} = interaction energy term (J cm^{-3})
 α = thermal expansion coefficient (K^{-1})
 γ = thermal pressure coefficient ($\text{J cm}^{-3} \text{K}^{-1}$)
 δ = solubility parameter ($(\text{cal cm}^{-3})^{1/2}$)
 χ_{12} = Flory-Huggins interaction parameter (dimensionless)
 $(\chi_{12})_{cr}$ = critical value of interaction parameter (dimensionless)
 Φ_i = segment fraction of species i (dimensionless)
 Θ_i = site fraction of species i (dimensionless)