Thermodynamics of poly(ethylene oxide)–poly(methyl methacrylate) blends: prediction of miscibility based on the corresponding-states theory

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The compatibility of the poly(ethylene oxide)–atactic poly(methyl methacrylate) (PEO–aPMMA) system has been studied using Patterson's theory of polymer–polymer miscibility. Specific volumes and thermal pressure coefficients for both polymers have been accurately determined; the characteristic parameters V^*, T^* and P^* are obtained from the experimental results. Experimental heat-of-mixing data were used to calculate the interaction energy between the two components. The shape of the curve of χ_{12}/V_1^* *versus* temperature indicates that PEO–aPMMA mixtures are miscible in the liquid state over all the composition and temperature range explored.

(Keywords: miscibility; poly(ethylene oxide); poly(methyl methacrylate))

INTRODUCTION

A body of experimental evidence (a detailed collection of the most important of which can be found in refs. 1 and 2) shows that poly(ethylene oxide)–atactic poly(methyl methacrylate) (PEO–aPMMA) mixtures are miscible in the liquid state.

Ramana Rao *et al.*[3], investigating the nature of intermolecular interactions by vibrational spectroscopy, confirmed the existence of weak specific interactions between PEO and aPMMA due to the presence of attractive and repulsive forces between atoms.

Yin Jinghua *et al.*[4] have shown, using molecular models, that the possible dipole–dipole interaction between the oxygen atom of PEO and the carbonyl atom of PMMA is weakened by the repulsive forces offered by the negative end of the carbonyl dipole of PMMA.

In a previous paper, Cimmino *et al.*[2] have applied Patterson's theory to the PEO–aPMMA system. In that work the contact energy term, X_{12}, was computed by using the literature values of the Flory–Huggins interaction parameter, χ_{12}, and the thermal pressure coefficients were calculated from the solubility parameters. Applying the theory in this way, a prediction of miscibility for the two components from 0 to 200°C was obtained.

The aim of this work is again to apply Patterson's theory to the PEO–aPMMA system, but by using experimental and accurate values of heat of mixing and thermal pressure coefficient measured from 120 to 160°C, in order to check the validity of the predictions obtained previously.

THEORETICAL BACKGROUND

The extent of polymer–polymer interactions can be qualified by means of a thermodynamic interaction parameter.

In the last 20 years the Prigogine corresponding-states theory (CST)[5] has attracted attention, particularly in the modified form of Flory[6,7], which leads to a correct expression of the interaction parameter of polymer–solvent systems. McMaster[8] applied this theory to polymer mixtures, but the derived equations are too complex and of little utility for experimental verification.

Patterson[9–11] elaborated a simplified version of the CST, which leads to the following expression for the interaction parameter:

$$\frac{\chi_{12}}{V_1^*}=\frac{P_1^*}{RT_1^*}\left[\underset{\text{interaction}}{\frac{\tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3}-1}\left(\frac{X_{12}}{P_1^*}\right)}+\underset{\text{free volume}}{\frac{\tilde{V}_1^{1/3}}{2(4/3-\tilde{V}_1^{1/3})}\tau^2}\right] \quad (1)$$

Equation (1) is composed of an interactional and a free-volume term.

The interaction term is characterized by X_{12}/P_1^*; the contact energy term, X_{12}, is a measure of the interchange energy between unlike units and can be positive or negative, depending on whether dispersion forces or specific interactions are dominating in the mixture,

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respectively. $X_{12} > 0$ implies unfavourable mixing; $X_{12} < 0$ must normally be fulfilled to obtain a thermodynamically stable mixture of the polymer couple.

The second term of equation (1) reflects differences in free volume between the components through the parameter:

$$\tau = 1 - (T_1^*/T_2^*) \tag{2}$$

and gives an unfavourable contribution to polymer–polymer miscibility, always being positive. It becomes increasingly important at higher temperatures.

In the CST the basic quantities characterizing a liquid are the reduced temperature ($\tilde{T}$), volume ($\tilde{V}$) and pressure ($\tilde{P}$), defined by:

$$\tilde{T} = T/T^* \tag{3a}$$

$$\tilde{V} = V/V^* = v/v^* \tag{3b}$$

$$\tilde{P} = P/P^* \tag{3c}$$

The quantities carrying an asterisk are constant reference parameters. V^* and v^* are sometimes called hard-core volumes; they are the molar and specific volumes, respectively, at 0 K ($V^* = Mv^*$, where M is the molecular weight of the component). The reduced volume ($\tilde{V}$) and temperature ($\tilde{T}$) are related to the thermal expansion coefficient (α) through the equations:

$$\tilde{V}^{1/3} - 1 = \alpha T/[3(1 + \alpha T)] \tag{4}$$

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{5}$$

where

$$\alpha = (\partial \ln V/\partial T)_P \tag{6}$$

The reference parameters T^* and V^* are calculated by equations (3a) and (3b). The reference pressure (P^*) can be calculated by the following relation:

$$P^* = \gamma T \tilde{V}^2 \tag{7}$$

where

$$\gamma = (\partial P/\partial T)_V$$

is the thermal pressure coefficient.

The contact energy X_{12} can be obtained in two ways: (a) from ΔH_{mix}, the heat of mixing of polymers[12,13]:

$$\Delta H_{\text{mix}} = w_1 P_1^* v_1^* (1/\tilde{V}_1 - 1/\tilde{V}) + w_2 P_2^* v_2^* (1/\tilde{V}_2 - 1/\tilde{V}) + w_1 v_1^* \theta_2 X_{12}/\tilde{V} \tag{8}$$

where w_i is the weight fraction of i; and (b) from T, the reduced temperature of the mixture:

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}) \tag{9}$$

The parameters ϕ_i (segmental fraction) and θ_2 (site fraction) in equations (8) and (9) are defined as:

$$\phi_2 = 1 - \phi_1 = x_2/(x_2 + x_1 r_1/r_2) \tag{10}$$

$$\theta_2 = \phi_2(\phi_2 + \phi_1 S_1/S_2) \tag{11}$$

where

$$r_1/r_2 = V_1^*/V_2^* \tag{12}$$

$$S_1/S_2 = (V_1^*/V_2^*)^{-1/3} \tag{13}$$

with x_1 and x_2 the mole fractions of components 1 and 2 respectively.

The critical value of χ_{12}/V_1^*, beyond which phase separation occurs, is given by the following expression:

$$\left(\frac{\chi_{12}}{V_1^*}\right)_{\text{crit}} = \frac{1}{2}\left(\frac{1}{(V_1^*)^{1/2}} + \frac{1}{(V_2^*)^{1/2}}\right)^2 \tag{14}$$

EXPERIMENTAL

Materials

The molecular characteristics of the polymers used are reported in *Table 1*. Binary blends (50–50) were prepared by freeze-drying solutions in benzene of the two polymers (4% in weight) at 0°C for 10 h. Mixtures were then dried in a vacuum oven at 30°C for 24 h to complete the removal of the solvent.

Dilatometry

The measures of the specific volume and thermal expansion coefficient for pure polymers were presented in a previous paper[2]; here the same measurements for the blends are reported. Instrumentation and mathematical elaborations of data are as previously indicated[2].

Thermal pressure coefficient measurements

The apparatus made in our own laboratories sketched in *Figure 1* was used to measure the thermal pressure coefficient of PEO and aPMMA[14–16]. The whole apparatus was connected to a pressure balance (Budemberg balance) and placed in an oil thermostat, with a temperature control at ±0.002°C. The parameter γ was obtained from the slope of the pressure *versus* temperature plot[16].

Heat-of-mixing measurements

It is impossible to measure directly the heat of mixing for polymer–polymer systems, owing to the very small heat exchange and to the slow interdiffusion of both components.

A convenient approach is to follow an indirect route, according to the following thermodynamic cycle based on Hess's law[17,18]:

$$\begin{tikzcd}
\text{PEO}(1) & +\,\text{aPMMA}(2) \arrow[r, "\Delta H_{\text{mix}}"] & \text{Mixture}(1+2) \\
+\ \text{Solvent} \arrow[d, "\Delta H_1"] & +\ \text{Solvent} \arrow[d, "\Delta H_2"] & +\ \text{Solvent} \arrow[d, "\Delta H_4"] \\
\text{Solution } 1\,+ & \text{Solution } 2 \arrow[r, "\Delta H_3"] & \text{Solution } 1+2
\end{tikzcd}$$

From the above cycle ΔH_{mix} is calculated from:

$$\Delta H_{\text{mix}} = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 \tag{15}$$

The ΔH_{mix} values were obtained practically from the difference between $\Delta H_1 + \Delta H_2 + \Delta H_3$ (the heat of solution of a mechanical mixture of pure polymers, cut into

Table 1 Molecular characteristics of polymers

Polymer	Source (trade name)	M_w	M_n	M_w/M_n
Poly(ethylene oxide) (PEO)[a]	Fluka AG (PEO2)	24 800	13 600	1.82
Atactic poly(methyl methacrylate) (aPMMA)[b]	BDH	174 000	65 900	2.64

[a] G.p.c. in tetrahydrofuran (THF) at 25°C
[b] G.p.c. in chloroform ($CHCl_3$) at 25°C

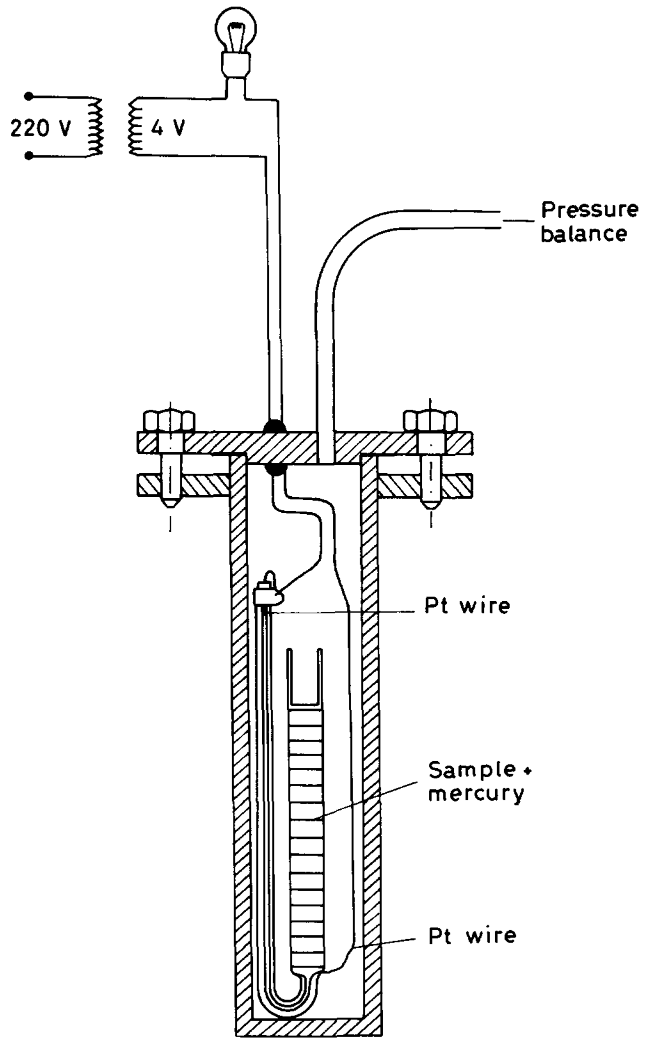

Figure 1 Apparatus made in our own laboratories and used for thermal pressure measurements

small pieces and mixed in the proper ratio) and ΔH_4 (the heat of solution of a blend).

Heat-of-solution measurements on mechanical mixtures and blends were carried out by means of a Setaram C80D calorimeter, using cyclohexanone as common solvent. In order to get the heat of mixing of components in the liquid state, the measurements were performed at 125°C, a temperature higher than the glass transition of aPMMA (113°C) and the melting point of PEO (65°C).

RESULTS

The thermal expansion coefficients for the pure polymers and the 50–50 blend are respectively:

$$\alpha_{\mathrm{PEO,l}} = 6.546 \times 10^{-4} + 9.70 \times 10^{-7} T \qquad (16)$$

$$\alpha_{\mathrm{aPMMA,l}} = 5.182 \times 10^{-4} + 1.44 \times 10^{-6} T \qquad (17)$$

$$\alpha_{\mathrm{Blend,l}} = 5.996 \times 10^{-4} + 1.12 \times 10^{-6} T \qquad (18)$$

in which T is expressed in K and α in K^{-1}; the letter l indicates that the value applies to the liquid state; the relative average error is $\pm 8 \times 10^{-7}\,\mathrm{K}^{-1}$.

The determination of γ presents an experimental uncertainty of ±4%. The experiments suggest, in the temperature range explored, the following relations between $\gamma\,(\mathrm{J\,cm^{-3}})$ and temperature (K):

$$\gamma_{\mathrm{PEO,l}} = 3.58 - 5.90 \times 10^{-3} T - 1.09 \times 10^{-6} T^2 \qquad (19)$$

$$\gamma_{\mathrm{aPMMA,l}} = 16.11 - 6.97 \times 10^{-3} T - 8.01 \times 10^{-6} T^2 \qquad (20)$$

Several measurements of the heat of solution have been performed on mechanical mixtures and on blends of the polymers prepared according to the procedure mentioned. The mean values are:

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = 64.4\,\mathrm{J\,g^{-1}}$$

$$\Delta H_4 = 65.8\,\mathrm{J\,g^{-1}}$$

and using equation (15):

$$\Delta H_{\mathrm{mix}} = -1.4\,\mathrm{J\,g^{-1}}$$

The average error on ΔH_{mix} is about ±10%.

TREATMENT OF DATA AND DISCUSSION

From the relations (16), (17) and (18), using the equations (3a), (3b), (4) and (5), it is possible to calculate the reduced and characteristic temperatures and volumes as functions of temperature. Similarly from (19) and (20), by equation (7), it is possible to obtain P^* as a function of temperature.

Tables 2, 3 and *4* show the values of the reference parameters for the liquid states of PEO, aPMMA and a 50–50 blend of the two polymers. They change with temperature, although the theory defines them as temperature-independent.

This behaviour has previously been observed for other polymers[16,19]. Brunacci *et al.*[16] suggest bypassing this

Table 2 Reduced volume ($\tilde{V}$) and reference parameters (v^*, T^*, P^*) of PEO computed in the range of temperature from 120 to 160°C

T (°C)	$\tilde{V}$	v^* ($\mathrm{cm^3\,g^{-1}}$)	T^* (K)	P^* ($\mathrm{J\,cm^{-3}}$)
120	1.251	0.764	6830	674
130	1.259	0.766	6870	656
140	1.267	0.767	6900	636
150	1.275	0.768	6940	613
160	1.283	0.769	6970	587

Table 3 Reduced volume ($\tilde{V}$) and reference parameters (v^*, T^*, P^*) of aPMMA computed in the range of temperature from 120 to 160°C

T (°C)	$\tilde{V}$	v^* ($\mathrm{cm^3\,g^{-1}}$)	T^* (K)	P^* ($\mathrm{J\,cm^{-3}}$)
120	1.229	0.714	7270	644
130	1.238	0.714	7260	629
140	1.247	0.714	7260	628
150	1.256	0.714	7260	637
160	1.265	0.714	7260	651

Table 4 Reduced volume ($\tilde{V}$) and reference parameter (T^*) of a 50–50 blend computed in the range of temperature from 120 to 160°C

T(K)	$\tilde{V}$	T^*(K)
120	1.241	7030
130	1.249	7046
140	1.257	7071
150	1.266	7093
160	1.274	7114

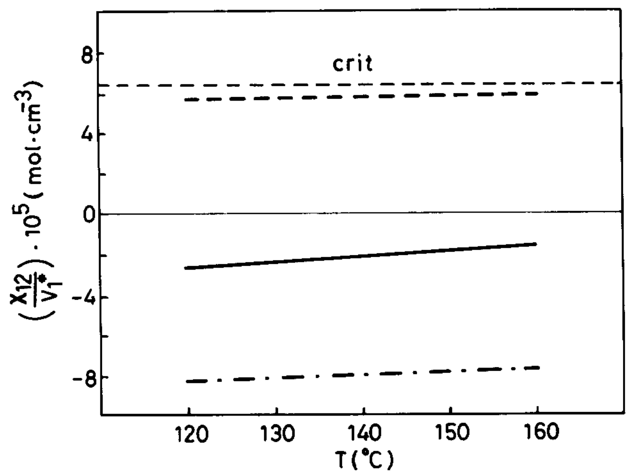

Figure 2 Plots of χ_{12}/V_1^* parameter (——), interaction term (—·—) and free-volume term (– – – –) as a function of temperature for PEO–aPMMA system. The broken horizontal line at the top corresponds to the critical value of χ_{12}/V_1^* ($=6.45 \times 10^{-5}$ mol cm^{-3})

problem by choosing average values, within the range of temperature studied. The average parameters relating to individual components PEO and aPMMA are presented here by the indices 1 and 2 respectively:

$$P_1^* = 633\ \mathrm{J\,cm^{-3}} \qquad P_2^* = 638\ \mathrm{J\,cm^{-3}}$$

$$T_1^* = 6900\ \mathrm{K} \qquad T_2^* = 7260\ \mathrm{K}$$

$$V_1^* = 0.767\ \mathrm{cm^3\,g^{-1}} \qquad V_2^* = 0.714\ \mathrm{cm^3\,g^{-1}}$$

Using simultaneously equations (10), (11), (12) and (13) it is possible to calculate:

$$\theta_2 = 0.34 \qquad \phi_1 = 0.52 \qquad \phi_2 = 0.48$$

The contact energy term, X_{12}, obtained from the reduced temperature of the mixture, using equation (9), is $X_{12} = -0.54\ \mathrm{J\,cm^{-3}}$, in good agreement with the prediction concerning the interactions between the two homopolymers. The contact energy term calculated by equation (8), using the measured value of ΔH_{mix}, is $X_{12} = -11.7\ \mathrm{J\,cm^{-3}}$. It is worth noting that the negative sign means a thermodynamically stable mixture, in accordance with the observed behaviour of the blend, but the absolute value is nevertheless too large for the weak interactions between these polymers. For this reason we are currently investigating this discrepancy and intend to discuss future results as soon as they become available.

As regards to this work, the value of X_{12} obtained from equation (9) is judged to be more reliable. In *Figure 2*, χ_{12}/V_1^*, calculated by equation (1), is plotted against temperature; the broken line represents the critical value (calculated by equation (14)) beyond which phase separation occurs; the interactional and free-volume terms are also shown in this figure. The PEO–aPMMA system is predicted to be miscible in the liquid state up to 160°C, according to the previous results of Cimmino *et al.*[2].

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