Polymer Vol. 39 No. 20, pp. 4929–4935, 1998
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0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10352-4

Thermodynamics of blends of poly(ethylene oxide) with poly(methyl methacrylate) and poly(vinyl acetate): prediction of miscibility based on Flory solution theory modified by Hamada

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(Received 9 July 1997; revised 23 September 1997; accepted 21 November 1997)

Flory solution theory modified by Hamada *et al.* (*Macromolecules*, 1980, **13**, 729) was used to predict the miscibility of blends of poly(ethylene oxide) with poly(methyl methacrylate) (PEO-aPMMA) and with poly(vinyl acetate) (PEO–PVAc). Interaction parameters of a PEO–aPMMA blend with the weight ratio of PEO/aPMMA = 50/50 at the temperature range of 393–433 K and PEO-PVAc blends with different compositions and temperatures were calculated from the determined equation-of-state parameters based on Flory solution theory modified by Hamada *et al.* Results show that interaction parameters of the PEO–aPMMA blend are negative and can be comparable with values obtained from neutron-scattering measurements by Ito *et al.* (*Macromolecules*, 1987, **20**, 2213). Also, interaction parameters and excess volumes of PEO–PVAc blends are negative and increase with enhancing the content of PEO and the temperature. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: thermodynamics; blends; interaction parameter)

INTRODUCTION

Flory and co-workers[1,2] proposed the equation-of-state theory based on the free-volume concept. The advantage in applying this theory to polymer solution is that thermodynamic parameters can be evaluated from the measurable parameters such as specific volumes, thermal expansion coefficients and thermal pressure coefficients of each component and their blends; thus, theoretically evaluated values can be compared with experimental results in many polymer–solvent systems. This theory also can describe LCST and UCST phenomena[3]. McMaster[4] extended this theory from polymer–solvent systems to polymer–polymer blends and found that free-volume effects are of importance in polymer–polymer mixtures as well as in polymer–solvent systems. Since McMaster generalized the Flory theory when he applied it to polymer mixtures, equations developed by him are extremely complicated and of little utility for experimental verification. Patterson and Robard[5] used the Van der Waals dependence of the configuration energy on volume and developed a simplified version of Flory solution theory as extended by McMaster. By measuring heats of mixing of blends, thermal expansion and thermal pressure coefficients of components and blends, the interaction parameters can be calculated from the equations developed by Patterson. However, in Patterson's theoretical treatment the interaction parameter was assumed to be independent of compositions of blends. In fact, the miscibility extent of a polymer blend is strongly dependent upon compositions. Interaction parameters do change with compositions. In a sense their theoretical treatment is over-simplified, as admitted by themselves[5], and an accurate prediction of a critical solution temperature or a interaction parameter for some particular experimental situations cannot be expected.

In contrast to Patterson's theoretical treatment, the modified Flory's theory by Hamada *et al.*[6]. can evaluate accurately the dependence of interaction parameters on concentrations and the phase behavior of polymer solutions without specific interactions. Their modified theory was successfully used for several polymer blends, especially for poly(vinyl methyl ether)–polystyrene couple[6–9]. The dependence of the interaction parameters on the concentration and the temperature obtained by them was in agreement with those measured by neutron-scattering methods[10,11].

PEO can act as a proton acceptor and form miscible blends with a variety of proton-donating polymers[12], since it has partial negative charge on the oxygen atoms[13]. There is a partial positive charge on their carbonyl carbon atoms of

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aPMMA[13] and PVAc[14]. A number of researchers have offered experimental evidence to indicate that the blends of PEO with aPMMA[13,15–21] and PVAc[14,22–27] are miscible. Russell and co-workers[28] applied the neutron-scattering method to measure interaction parameters of PEO–aPMMA mixtures. They found very small negative values and suggested the possible interaction between two components should be very weak. The existence of a very weak specific interaction between PEO and aPMMA was also confirmed by Ramana Rao *et al.*[13] with vibration spectroscopy. They pointed out that the attractive forces between the negatively charged oxygen atoms of PEO and positively charged carbonyl carbon atoms of aPMMA are weakened by the repulsive forces offered by the negatively charged oxygen atoms of aPMMA. Similar situations should appear between PEO and PVAc, since PVAc has more or less similar carbonyl groups to aPMMA. Because of no strong interactions present between PEO and aPMMA (or PVAc) Flory solution theory might be used to predict the miscibility of PEO–aPMMA and PEO–PVAc blends. Cimmino *et al.*[29] and Pedemonte and co-workers[14,30] have applied the simplified Patterson's theory to calculate the interaction parameters of these two kinds of blend. Values obtained by them are negative and very close to zero. In this work, considering Flory solution theory modified by Hamada and co-workers is more precise to evaluate the interaction parameters and their dependence upon concentrations and temperature than Patterson's theoretical treatment, we chose this modified theory to treat our experimental data of PEO–aPMMA and PEO–PVAc blend systems. Then, we compared the results with those obtained from small-angle neutron-scattering experiments by Russell and co-workers[28] and values from Patterson's simplified equation.

THEORETICAL BACKGROUND

The specific interactions cannot be expressed by the van der Waals type interaction. Dudowicz and Freed[31] proposed a general lattice cluster theory which can be used to describe small-angle neutron-scattering measurements to deduce the specific interaction parameters. Painter *et al.*[32] developed the association models to describe the free energy changes related to hydrogen-bonding between components of binary polymer blends where one polymer self-associates while the second one does not, but is capable of forming a hydrogen bond with the first. Balazs and Sanchez[33] incorporated the specific interaction term into the lattice fluid theory. Brinke and Karasz[34] applied Vause's incompressible lattice-gas model to polymer blends with specific interactions. But some of the above models or theoretical treatments are of very little utility for experimental verification and others are not easy to use in our system. In fact, the specific interaction of PEO with PVAc or aPMMA is not so strong as mentioned in Section 1. The Flory-type equation-of-state theory may be adequate to this system. Other measurement techniques such as gas-liquid chromatography[35], osmotic pressure[36] and neutron-scattering measurements[37] perhaps can give further verification. Continuing work is being done by us.

In his solution theory Flory[1,2] assumed that segments of both molecules in the mixture were arbitrarily chosen to be of equal core volume. This assumption leads to linearity of the molecular core volume in the mole fraction. By considering the existence of the repulsive forces between segments Hamada and co-workers[6] assume the core volume of segments of mixtures as

$$v^* = \phi_1^2 v_1^* + 2\phi_1\phi_2 v_{12}^* + \phi_2^2 v_2^* \qquad (1)$$

where

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \text{ or } v_{12}^* = (v_1^* + v_2^*)/2 \qquad (2)$$

where ϕ_i (i = 1,2) is the segment fraction of component i, v_i* is the core volume per segment of component i.

Flory[1,2] also assumed that the number of external degrees of freedom, c, for a mixture was a linear function of the blend composition. By taking into consideration a departure from linearity Hamada and co-workers suggested the external degrees of freedom of segments for the mixture as

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \theta_2 c_{12} \qquad (3)$$

where θ_i is the site fraction of component i and c_{12} is the parameter characterizing the deviation from additivity of the external degrees of freedom, c.

The residual chemical potential, $(\mu_1 - \mu_1^0)^R$, of component 1 defined as

$$\mu_1 - \mu_1^0 = RT[\ln(1-\phi_2) + (1 - r_1/r_2)\phi_2] + (\mu_1 - \mu_1^0)^R \qquad (4)$$

and $(\mu_1 - \mu_1^0)^R$ can be expressed as

$$\begin{aligned}(\mu_1 - \mu_1^0)^R = &- 3/2 r_1 P_1^* v^* \bar{T}_1 \ln(m/m_1) \\ &+ 3r_1 RTc_{12}\theta_2^2 \ln K - 3/2[(m_1 - m_2)/m]P^* \\ &r_1 v^* \bar{T}\phi_2 + 3P_1^* r_1 v^* \bar{T}_1 \\ &\times \ln[(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] \\ &+ 3r_1 RTc_{12}\theta_2^2 \ln(\bar{v}^{1/3} - 1) \\ &+ P_1^* r_1 v^* (1/\bar{v}_1 - 1/\bar{v}) + r_1 v^* X_{12}\theta_2^2/\bar{v}\end{aligned} \qquad (5)$$

In equation (5) K and m are expressed as

$$K = (2\pi mkT/h^2)^{1/2}(gv^* e^3)^{1/3} \qquad (6)$$

$$m = \phi_1 m_1 + \phi_2 m_2 \qquad (7)$$

where r_i is the number of segments in molecule i, m_i is the mass per segment of component i, and X_{12} is the contact energy term. $\bar{P}$, $\bar{v}$ and $\bar{T}$ are the reduced parameters of pressure, volume and temperature, respectively, defined by their actual pressure, volume and temperature, P, v, T and hard core parameters, P^*, v^*, T^* as follows

$$\bar{P} = P/P^* \qquad (8)$$

$$\bar{v} = v/v^* \qquad (9)$$

$$\bar{T} = T/T^* \qquad (10)$$

g in equation (6) is the geometric factor[6]. If the coordination number z is assumed to be 12, g is taken as $(4\pi/3)2^{1/2}$, k and h in equation (6) are Boltzmann and Planck constants.

The characteristic temperature T^* for the mixture is given by

$$\begin{aligned}1/T^* = [&\phi_1 P_1^*(v_1^*/v^*)/T_1^* + \phi_2 P_2^*(v_2^*/v^*)/T_2^* \\ &- \phi_1\theta_2 k c_{12}/v^*]/P^*\end{aligned} \qquad (11)$$

The interaction parameter can be expressed as

$$\chi = (\mu_1 - \mu_1^0)^R/(RT\phi_2^2) \qquad (12)$$

The site fraction θ_i was defined as

$$\theta_i = s_i r_i N_i/(s_1 r_1 N_1 + s_2 r_2 N_2) \qquad (13)$$

in which s_i is the surface area of segment i. At infinite dilution

$$\begin{aligned}\chi_1 = \lim_{\phi_2 \quad 0} \chi &= 3P_1^* r_1 v^* \bar{T}_1 \{(m_2/m_1 - 1)[2(T_1^* P_2^* \\ &/T_2^* P_1^*) - (m_2/m_1 + 1) \\ &- 2(T_1^*/P_1^*)(s_2/s_1)(Rc_{12}/v^*)]/4 \\ &+ \ln[K_1(\bar{v}_1^{1/3} - 1)](s_2/s_1)^2(T_1^*/P_1^*)(Rc_{12}/v^*)\}/RT \\ &+ (P_1^* r_1 v^*/\bar{v}_1)(A^2\alpha_1 T/2 + Y_{12})/RT \qquad (14)\end{aligned}$$

where

$$\begin{aligned}A = (1 - T_1^*/T_2^*)(P_2^*/P_1^*) - (s_2/s_1)(X_{12}/P_1^*) \\ + (T_1^*/P_1^*)(s_2/s_1)(Rc_{12}/v^*) \qquad (15)\end{aligned}$$

$$Y_{12} = (s_2/s_1)^2(X_{12}/P_1^*) \qquad (16)$$

The heat of mixing per segment is expressed as

$$\begin{aligned}\Delta H^{\mathrm{M}} = \bar{r}N[-(3/2)\phi_1\theta_2 r_1 c_{12} RT + \phi_1 P_1^* v_1^*/\bar{v}_1 \\ + \phi_2 P_2^* v_2^*/\bar{v}_2 - P^* v^*/\bar{v}] \qquad (17)\end{aligned}$$

for

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1\theta_2 X_{12} \qquad (18)$$

where rN is the number of the total segments of $N_1 r_1$-mers and $N_2 r_2$-mers.

The ratio of the excess volume V^{E} to the sum V^0 of the volumes of the pure components is

$$V^{\mathrm{E}}/V^0 = \bar{v}/\bar{v}_0 - 1 \qquad (19)$$

in which

$$\bar{v}_0 = \phi_1\bar{v}_1 + \phi_2\bar{v}_2 \qquad (20)$$

EXPERIMENTAL SECTION

Materials

The source and the molecular characteristics of PEO–aPMMA and PVAc in this work are reported in *Table 1*. PEO and aPMMA were used as received. PVAc was fractionated before use. A detailed description of the fractionating procedure is presented elsewhere[14].

Sample preparation

A blend with the composition PEO/aPMMA = 50/50 (in weight) was prepared by freeze-drying the solution of the two polymers (4% in weight) at 0°C for 10 h. Benzene was used as the common solvent.

PEO–PVAc blends with compositions PEO/PVAc = 20/80, 39/61 and 66/34 (in weight) were prepared by the solution casting method. Chloroform was used as the common solvent.

Table 1 Molecular characteristics of PEO, aPMMA and PVAc measured by g.p.c.

Polymer	Source	M_w	M_n	M_w/M_n
PEO	Fluka	24 800	13 600	1.82
aPMMA	BDH	174 000	65 900	2.64
PVAc	Aldrich	41 800	20 800	2.00

Heats of mixing measurements

An indirect route according to a thermodynamic cycle based on Hess's law[31,32] was adopted to measure heats of mixing of PEO–aPMMA and PEO–PVAc blends. The measuring procedure and the adopted calorimeter were reported in our previous paper[14].

Thermal pressure coefficient measurements

A home-made apparatus was used to measure the thermal pressure coefficients of PEO, aPMMA and PVAc. The sketched figure and the measuring procedure were also reported elsewhere[14].

Thermal expansion coefficient measurements

Thermal expansion coefficient and specific volume measurements of PVAc were performed with a standard dilatometric technique. A detailed description of this experimental method and sample preparation was given in a previous work[33].

RESULTS AND DISCUSSION

PEO–aPMMA blend system

The measurement of the thermal pressure coefficients, γ, has an experimental uncertainty of ± 4%. The experimental results of γ (J cm^{-3}) in the temperature range of 373–403 K can be expressed by following two equations:

$$\gamma_{\mathrm{PEO,l}} = 3.58 - 5.90 \times 10^{-3}T - 1.09 \times 10^{-6}T^2 \qquad (21)$$

$$\gamma_{\mathrm{aPMMA}} = 1.63 - 0.71 \times 10^{-3}T - 0.81 \times 10^{-6}T^2 \qquad (22)$$

The thermal expansion coefficients of PEO, aPMMA and their blend with PEO/aPMMA = 50/50 (in wt) were taken from Refs. 29 and 30 and listed as follows, respectively.

$$\alpha_{\mathrm{PEO,l}} = 6.546 \times 10^{-4} + 9.70 \times 10^{-7} \times (T - 273) \qquad (23)$$

$$\alpha_{\mathrm{aPMMA,l}} = 5.182 \times 10^{-4} + 1.44 \times 10^{-6} \times (T - 273) \qquad (24)$$

$$\alpha_{\mathrm{blend,l}} = 5.996 \times 10^{-4} + 1.12 \times 10^{-6} \times (T - 273) \qquad (25)$$

The specific volumes of PEO and aPMMA were also taken from the work of Cimmino *et al.*[29] and presented in

$$\begin{aligned}v_{\mathrm{sp,PEO,l}} = 0.87812 + 5.6755 \times 10^{-4}(T - 273) \\ + 6.8174 \times 10^{-7}(T - 273)^2 \qquad (26)\end{aligned}$$

$$\begin{aligned}v_{\mathrm{sp,aPMMA,l}} = 0.81643 + 4.1374 \times 10^{-4}(T - 273) \\ + 8.1194 \times 10^{-7}(T - 273)^2 \qquad (27)\end{aligned}$$

where T is expressed in K.

The respective equation-of-state parameters which are needed to calculate various thermodynamic quantities of PEO, aPMMA and their blend can be calculated from the following reduced equation-of-state:

$$\bar{v}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \qquad (28)$$

$$\bar{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/1} \qquad (29)$$

$$P^* = \gamma \cdot T \cdot \bar{v}^2 \qquad (30)$$

The calculated equation-of-state parameters of PEO, aPMMA and their blend at different temperatures are

Table 2 Equation-of-state parameters of PEO

T (K)	$\tilde{v}$	$v^*_{sp,1}$ (cm^3 g^{-1})	T^* (K)	P^* (J cm^{-3})
393	1.2510	0.7642	6830	674
398	1.2550	0.7649	6850	664
403	1.2590	0.7652	6870	656
413	1.2667	0.7665	6900	636
423	1.2747	0.7677	6940	613
433	1.2828	0.7689	6970	587

Table 3 Equation-of-state parameters of aPMMA

T (K)	$\tilde{v}$	$v^*_{sp,1}$ (cm^3 g^{-1})	T^* (K)	P^* (J cm^{-3})
393	1.2291	0.7142	7270	730
398	1.2336	0.7140	7263	740
403	1.2381	0.7139	7260	751
413	1.2471	0.7139	7260	772
423	1.2562	0.7139	7260	793
433	1.2653	0.7140	7260	814

Table 4 Equation-of-state parameters of PEO–aPMMA Blend (50/50 in wt)

T (K)	$\tilde{v}$	T^* (K)
393	1.2410	7030
398	1.2451	7028
403	1.2491	7046
413	1.2573	7071
423	1.2658	7093
433	1.2740	7114

shown in *Tables 2–4*. These parameters changed with temperature, although they were defined as temperature-independent in the original Flory's solution theory. In this work we took the values obtained at 398 K, since the ΔH^M was measured at this temperature.

The average experimental calorimetric data determined in two complementary steps are shown in *Table 5*. The first step provides the total heat effect associated with dissolution of polymer 1 ($w_1\Delta H_1$), dissolution of polymer 2 ($w_2\Delta H_2$) and mixing of the resulting solutions (ΔH_3). In the second independent step, a heat effect associated with a dissolution of PEO–aPMMA blend (ΔH_4) was measured. And the parameter, ΔH^M (J g^{-1}) was calculated by using equation (17) and equation (18). The heat of mixing, ΔH^M, expressed in joules per total segments per mole listed in the last column of *Table 5* was converted from joules per total polymer weight to the value per segment by using

$$\Delta H^M \text{ (J mol}^{-1}) = \Delta H/(m_1 + m_2)/(w_1 v^*_{sp,1}/v^* + w_2 v^*_{sp,2}/v^*) \qquad (31)$$

where $v^*_{sp,i}$ is the specific core volume (cm^3 g^{-1}) of component i, and v^* is the core volume per mole segments of the blend.

As mentioned in Section 2, the interaction parameter, χ, can be calculated from equation (12) if the contact-energy term, X_{12}, and the parameter c_{12} are known. By using simultaneously equation (11) and equation (17) we obtain $P^* = 714$ J cm^{-3} and $c_{12} = 0.01$. Then we get $X_{12} = -10.9$ J cm^{-3} from equation (17) and equation (18). In these calculations the equation-of-state parameters at 398 K were used. The ratio of s_2/s_1 was taken as 0.53 which was calculated from Bondi's Table[38]. Here, the subscripts 1 and 2 indicate PEO and aPMMA, respectively. The temperature dependence of the interaction parameter per mole segment of PEO, χ/r_1, is shown in *Figure 1*.

In the temperature range used, χ/r_1 values are negative and their absolute values are quite small. It can be taken as another verification, from the theoretical point of view, that PEO and aPMMA are miscible. The miscibility extent should decrease with increase of the temperature, since the values of χ/r_1 increase with the temperature. Russel and co-workers[28] suggested the entropic contribution to the interaction parameter are more important. In our opinion LCST (lower critical solution temperature) is a common phenomenon of miscible polymer blends. Interaction parameters should change with temperature. Stein and co-workers[10] found the interaction parameter of poly(vinyl methyl ether)–polystyrene blends is dependent on the concentration and temperature from the neutron-scattering measurements. Usually, the absolute values of the interaction parameter determined from thermodynamic methods is larger than those from scattering methods[39]. The value of χ/r_1 obtained here at the same concentration and temperature is about one order magnitude larger than the data from neutron-scattering measurements by Russell and co-workers[28].

Due to the inevitable uncertainties of reference parameters, values of interaction parameters obtained here are different from those calculated by Cimmino *et al.*[29]. In our previous paper[30] some error occurred in calculating the reference pressure of aPMMA. Values of P^* of aPMMA was corrected in this paper. Therefore, P^* of aPMMA listed in this paper is different from the previous one. Their difference is about 12%. Calculation showed this difference had a very small influence on the values of interaction parameters of PEO–aPMMA. Compared with the previous work using Patterson's theoretical treatment, similar changing trends of interaction parameters with the temperature were observed. In previous work, interaction parameters were normalized by molar hard-core volume of PEO molecules (χ/v_1^*). Here, they were normalized by molar segment mass of PEO (χ/r_1). By simple calculation very near magnitudes of both interaction parameters, χ values were obtained. These features suggest that both Hamada and co-workers modified theory and Patterson's simplified theory may be acceptable to predict the miscibility of PEO–aPMMA blend with PEO/aPMMA = 50/50.

PEO–PVAc blend system

The measured thermal pressure coefficients (J cm^{-3}) of PVAc in the temperature range of 307–350 K is expressed as:

$$\gamma_{\text{PVAc,e}} = 3.30 - 6.03 \times 10^{-3} T \qquad (32)$$

Table 5 Heat of mixing for the PEO–aPMMA system at 398 K

PEO–aPMMA (wt%)	$w_1\Delta H_1 + w_2\Delta H_2 + \Delta H_3$ (J g^{-1})	ΔH_4 (J g^{-1})	ΔH^M (J g^{-1})	ΔH^M (J mol^{-1})
50/50	64.4	65.8	− 1.4	− 95.8

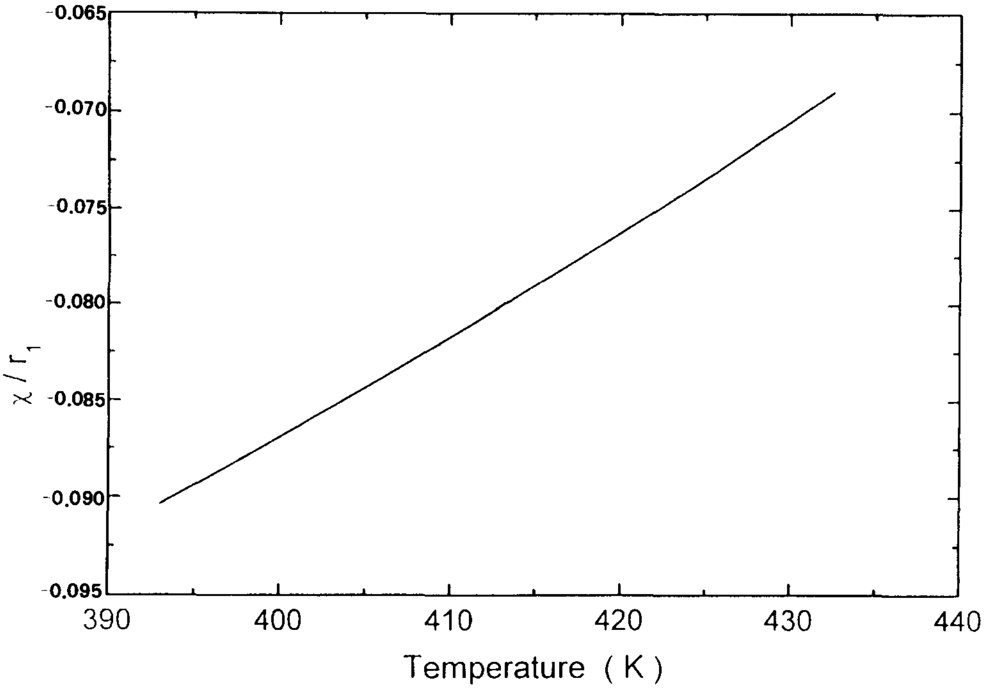

Figure 1 Interaction parameter per segment, χ/r_1, for the PEO–aPMMA blend (50/50 in wt) as a function of temperature

Table 6 Equation-of-state parameters of PEO and PVAc at 343 K

Parameter	PEO	PVAc
$\bar{v}$	1.2120	1.1968
$v^*_{sp,1}$ (cm^3 g^{-1})	0.7584	0.7193
T^*	6696	7064
P^*	726	611

The thermal expansion coefficient and volume–temperature coefficient of PVAc determined in the temperature range of 303–373 K are listed, respectively, as follows:

$$\alpha_{\mathrm{PVAc,e}} = 8.1468 \times 10^{-4} - 4.4288 \times 10^{-7}T \qquad (33)$$

$$v_{\mathrm{sp,PVAc,e}} = 0.8210 + 5.7047 \times 10^{-4}T \qquad (34)$$

The calculated equation-of-state parameters of PEO and PVAc at 343 K are shown in *Table 6*. The average experimental calorimetric data determined in two complementary steps and the calculated heats of mixing with different compositions at 343 K are reported in *Table 7*.

The contact-energy term, X_{12} and the parameter c_{12} were calculated from equations (17) and (18) by using the experimental heats of mixing, ΔH^{M}. Here $X_{12} = -19.2$ J cm^{-3} and $c_{12} = 0.013$, which were the average of three experimental values, were taken. The site fraction at different compositions, θ_2, was calculated from equation (13) using $s_1/s_2 = 0.53$ evaluated from Bondi's Table[38]. In this part the subscripts 1 and 2 indicate PEO and PVAc, respectively.

The concentration dependence of the interaction parameter per segment, χ/r_1, is shown in *Figure 2*. It increases

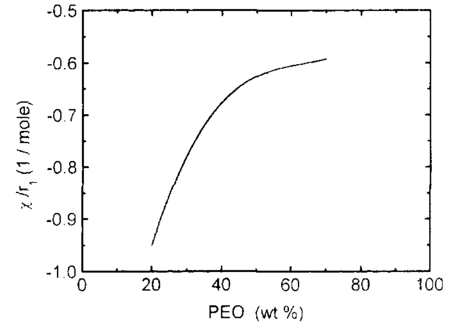

Figure 2 Interaction parameter per segment, χ/r_1, for the PEO–PVAc system at 343 K as a function of blend composition

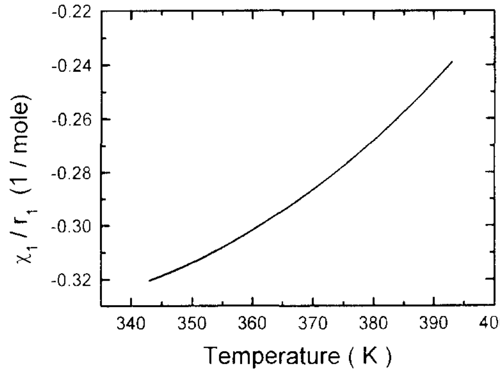

Figure 3 Interaction parameter, χ_1/r_1, for the PEO–PVAc system as a function of temperature

Table 7 Heats of mixing for the PEO–PVAc system at 343 K

PEO/PVAc (wt%)	$w_1\Delta H_1 + w_2\Delta H_2 + \Delta H_3$ (J g^{-1})	ΔH_4 (J g^{-1})	ΔH^{M} (J g^{-1})	ΔH^{M} (J mol^{-1})
20/80	16.9	21.4	− 4.5	− 324.6
39/61	16.8	20.1	− 3.3	− 206.2
66/34	16.0	18.4	− 2.4	− 125.8

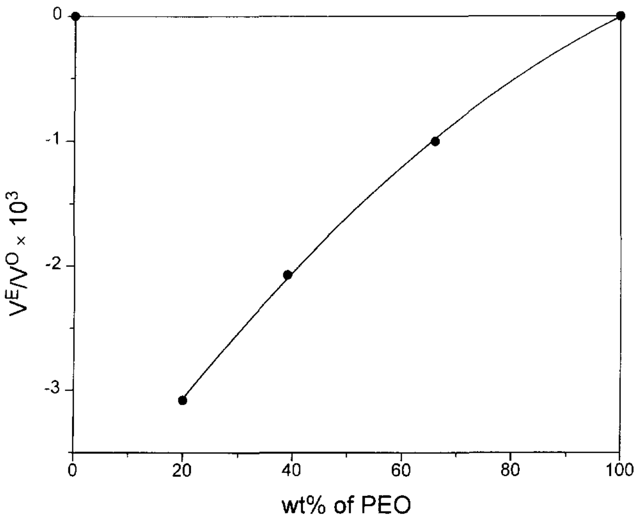

Figure 4 Excess volume ratios, V^E/V^0, for the PEO–PVAc system at 343 K as a function of blend composition

with increasing the concentration of PEO, which means that the miscibility decreases with increasing PEO content in blends. *Figure 3* shows the temperature dependence of χ/r_1 extrapolated to $\phi_{PVAc} = 0$, and calculated using equation (14). The parameter χ_1/r_1 increases monotonically with temperature. This feature predicts that an LCST may exist for this system. Similar trends were also observed by using Patterson's theoretical treatment for the blend with PEO/PVAc = 50/50 (mole ratio)[14]. The calculated curve of V^E/V^0 also has a concentration dependence as shown in *Figure 4*.

In this work, measured thermal expansion coefficient and volume–temperature coefficient of PVAc are taken from those published in the literature, equation-of-state parameters listed in *Table 6* are different from the previous paper. The difference is limited to 0.5% which has little influence on the absolute value of the interaction parameters, and comparisons with Patterson's previous treatment can still be valid. By simple calculation it can be shown that there is nearly same order magnitude of χ in both works when the blend has a similar composition. However, as shown in this mixture, interaction parameters are strongly concentration dependent. In a sense, the theory modified by Hamada and co-workers is preferable to the theory developed by Patterson.

As shown in this work, negative interaction parameters and contact-energy terms were obtained in both PEO–aPMMA and PEO–PVAc systems. They suggest that some extent of specific interaction is present in these two systems.

CONCLUSIONS:

(1) Negative values of heats of mixing for PEO–aPMMA (50/50, wt%) and PEO–PVAc (20/80, 39/61, 66/34, wt%) blends were obtained. These features offer us an absolute and direct evidence to confirm the miscibility of the two blending systems.

(2) Interaction parameters χ/r_1 and χ_1/r_1 of these two systems were evaluated by means of Flory solution theory modified by Hamada *et al.* These values are a little larger than the data determined by using the neutron-scattering method.

(3) χ/r_1 values of PEO–aPMMA are negative and increase with the temperature. LCST phase behavior might be present for this couple. χ/r_1 and χ_1/r_1 for PEO–PVAc blends are negative too. They increase with increasing the content of PVAc and temperature. This can be tentatively explained as the miscibility extent of this system depends mainly upon the content of PVAc. Its phase behavior might be similar to the PEO–aPMMA system. This behavior could be attributed to the fact that, on increasing PEO content, more and more PEO molecules packed and crystallized with a very high reduction of free energy.

(4) Due to the fact that there is no strong specific interaction, such as hydrogen bonding, the equation-of-state theory developed by Flory *et al.* and modified by Hamada could be used to predict or describe thermodynamic properties of PEO–aPMMA and PEO–PVAc systems.

ACKNOWLEDGEMENTS

This research has been carried out in the framework of Academia Sinica–C.N.R. (Italy) Cooperation Agreement. Both institutions are gratefully acknowledged. This work is also supported by Chinese National Natural Sciences Foundation Committee.

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