PII: S0032-3861(97)00574-0

Polymer Vol. 39 No. 12, pp. 2551-2556, 1998

0032-3861/98/$19.00+0.00

Flory-Huggins interaction parameter of poly(ethylene oxide)/poly(epichlorohydrin) and poly(ethylene oxide)/ poly(epichlorohydrin-*co*-ethylene oxide) blends

Marcia A. Silva, Marco-A. De Paoli and M.Isabel Felisberti*
Instituto de Química — UNICAMP, Caixa Postal 6154, 13083-970, Campinas S.P., Brazil
(Accepted 3 July 1997)

Blends of poly(ethylene) oxide with poly(epichlorohydrin) and poly(epichlorohydrin-*co*-ethylene oxide) have been prepared by the freeze-drying method from benzene solutions of the polymer mixture at different compositions. The miscibility of the mixtures was studied by DSC. A single glass transition temperature is observed for all the blends studied. Measurement of the melting temperature (T_m) depression for the blends allowed determination of the Flory-Huggins interaction parameter (χ_{12}) of the two polymers in the melt using the Nishi-Wang equation. The Hoffman-Weeks extrapolation was applied to obtain equilibrium T_m data. The values of the χ_{12} obtained from T_m depression data were negative for all blends. This suggests the miscibility of the components of the blends. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene oxide); poly(epichlorohydrin); poly(epichlorohydrin-*co*-ethylene oxide))

INTRODUCTION

There have been many studies of polymer blends in recent years. The interest in novel structures and properties of blends still motivates extensive studies, as does the increasing importance in practical applications of new polymeric materials having a wide range of physical and/or physicochemical properties, without similar behavior in homopolymers[1]. Recently, interest has been attracted to systems in which at least one of the components is crystallizable. In this case, a melt point depression of the crystalline phase relative to its melting point (T_m) in a non-interacting medium provides additional evidence of miscibility[2]. The crystalline polymer poly(ethylene oxide), PEO, has a T_m at ca 65°C and glass transition in the temperature range from − 53 to − 45°C. Above the melting point it can be processed as a thermoplastic[1,3]. Blends of PEO with poly(methyl methacrylate), PMMA[4-7], poly(vinyl acetate), PVAc[8-10], poly(3-hydroxybutyrate), PHB[11], and others, have been studied with emphasis on phase behavior. In these blends, miscibility, crystallization kinetics, morphology and the phase behavior were studied[10,12-14]. Poly(epichlorohydrin), PECH, is a linear and amorphous elastomer, exhibiting a glass transition temperature at − 23°C. Epichlorohydrin copolymer rubber, P(ECH-*co*-EO), with equimolar amounts of epichlorohydrin, ECH, and ethylene oxide, EO, has been used in various branches of technology, such as in the automotive industry, in fuel, lubricating fluids, air and vacuum hoses and others[15]. There are few published papers on PECH and the majority of publications were about properties, characterization and chemical modification[16-18]. PECH has been studied in blends with PHB[19], polyacrylates[20] and aliphatic polyesters[21].

In this work, we investigate the miscibility of blends of PEO with PECH and with P(ECH-*co*-EO) using differential scanning calorimetry (DSC). The Flory-Huggins interaction parameter was determined by the PEO melting point depression method.

EXPERIMENTAL

Materials

The polymers used in this work are listed in *Table 1*.

The molar mass (*Mn*) were determined by gel permeation chromatography (GPC) on a Waters chromatograph (model II A) using three linear columns (Ultrastyragel molecular weight range from 2.0×10^3 to 4.0×10^6 g mol^{-1}) with a Waters differential refractometer (model 410) as detector.

Blends preparation

The blends were prepared by the freeze-drying method from benzene solutions of polymer mixtures at 5 wt% concentration. Blends with different compositions were prepared: 20, 40, 60, 80 wt% in PEO. The mixtures were dried under vacuum until constant weight and then stored in a desiccator. Films of the blends were obtained by pressing at 130°C for 5 min at 25 MPa and 10 min at 50 MPa.

Characterization of blends by DSC

The DSC curves for the homopolymers and the blends were obtained on a T.A. Instruments model 2100 coupled to a T.A. 2100 data analysis system. Sample weights were maintained in the range of 18-20 mg. All experiments were performed under nitrogen flow of 100 mL min^{-1}. The samples were first held at 100°C for 5 min to eliminate the thermal history. After cooling the samples to −100°C at a rate of 10°C min^{-1}, they were heated again to 100°C at a rate of 10°C min^{-1}. The DSC curves shown in this work and used to construct the phase diagrams correspond to the

---

* To whom correspondence should be addressed

Table 1 Polymers used in this study

Polymer	Code	Source	*Mn* (g mol^{-1})	*Mw*/*Mn*
poly(ethylene oxide)	PEO	Aldrich	1.0×10^5	2
poly(epichlorohydrin)	PECH	Aldrich	1.6×10^5	4
poly(epichlorohydrin-*co*-ethylene oxide)	P(ECH-*co*-EO)	Zeon Chemicals	2.8×10^5	4

heating scan. All DSC curves were normalised with respect to mass. The glass transition temperature and the melting temperature were assumed as the half height of the step and the maximum of the peak, respectively. Enthalpy of melting was obtained by integration of the peak area.

Determination of the equilibrium melting temperature

The isothermal crystallization was performed on the DSC equipment based on the Hoffman–Weeks method[22]. The weight of the PEO and the blends was maintained in the region of 12 mg. The isothermal crystallization experiment was carried out using the following procedure: the samples were heated to 100°C, kept at this temperature for 5 min, rapidly cooled (cooling rate > 40°C min^{-1}) to the desired crystallization temperature (T_c) and maintained at this temperature for 20 min. After the isothermal crystallization was completed, the samples were cooled to 20°C and heated to 100°C at a rate of 10°C min^{-1} for the measurement of the T_m. This procedure was repeated for different crystallization temperatures.

RESULTS AND DISCUSSION

Figure 1a shows DSC curves of PEO and its blends with PECH and *Figure 1b* with P(ECH-*co*-EO). PECH and P(ECH-*co*-EO) exhibit glass transition (T_g) at -23°C and -42°C, respectively. PEO exhibits T_g at -50°C and T_m at 68°C (*Table 2*). For P(ECH-*co*-EO) we also observed a reproducible crystallization peak followed by melting. In this case the crystalline phase is probably formed by organization of the ethylene oxide blocks present in the copolymer structure. A single T_g is observed for all blends studied. It does not change appreciably with the composition, showing values near to the T_g of the pure PECH or P(ECH-*co*-EO), suggesting that the amorphous phase is rich in elastomer. The blends show also a single endothermic peak corresponding to the melting of the PEO phase (*Table 2*). The T_m of PEO is depressed by the presence of the second component, PECH or P(ECH-*co*-EO), indicating a favourable polymer–polymer interaction, *Figure 2*. Blends of PEO/PECH only exhibit crystallinity above 20 wt% of PEO, while blends with P(ECH-*co*-EO) exhibit crystallinity

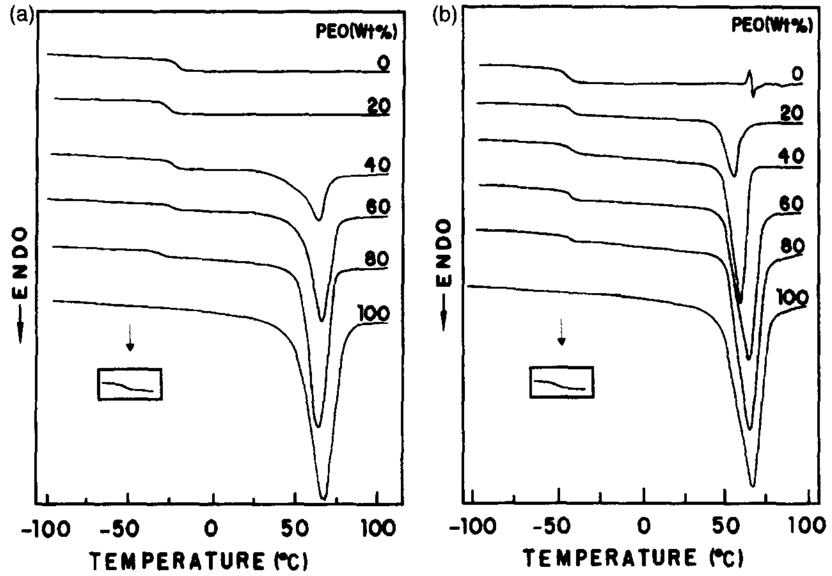

Figure 1 DSC curves for blends: (a) PEO/PECH and (b) PEO/P(ECH-*co*-EO). Heating rate = 10°C min^{-1}

Table 2 Glass transition temperature (T_g), melting point (T_m) and degree of crystallinity (X_c) of PEO/PECH and PEO/P(ECH-*co*-EO) blends

	PECH			P(ECH-*co*-EO)		
PEO (wt%)	T_g(°C)	T_m (°C)	X_c(%)	T_g(°C)	T_m(°C)	X_c(%)
0	-23 ± 3	-	-	-42 ± 3	65 ± 1	-
20	-27 ± 3	-	-	-42 ± 3	56 ± 1	15 ± 3
40	-27 ± 3	63 ± 1	18 ± 3	-42 ± 3	59 ± 1	24 ± 3
60	-26 ± 3	65 ± 1	33 ± 2	-43 ± 4	65 ± 1	47 ± 2
80	-32 ± 3	63 ± 1	51 ± 1	-44 ± 5	65 ± 1	60 ± 1
100	-50 ± 5	68 ± 1	73 ± 1	-50 ± 5	68 ± 1	73 ± 1

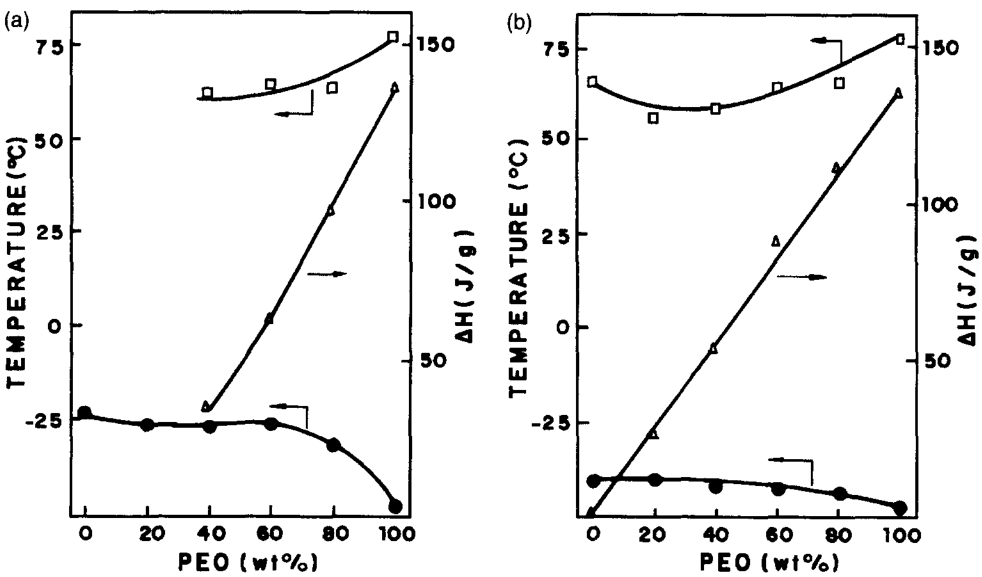

Figure 2 Phase diagrams for blends: (a) PEO/PECH and (b) PEO/P(ECH-*co*-EO). (□) melting point; (Δ) enthalpy of fusion; (●) glass transition temperature

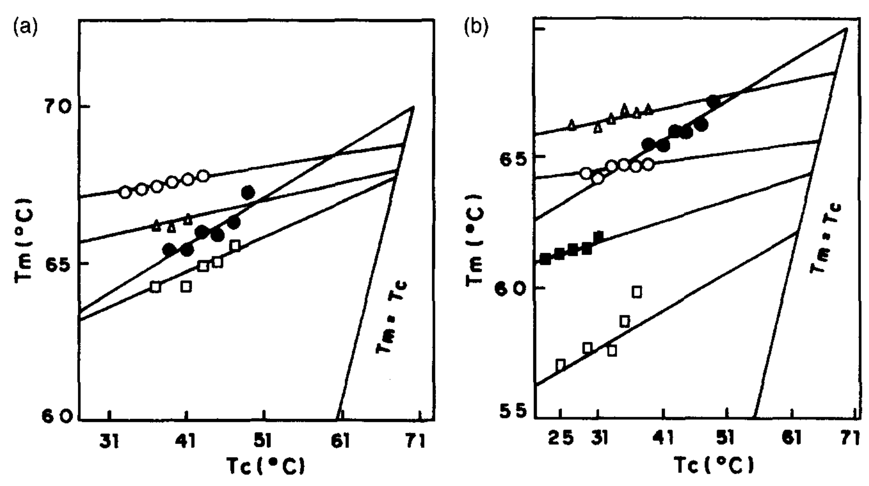

Figure 3 Hoffman–Weeks plots for isothermally crystallised blends: (a) PEO/PECH and (b) PEO/P(ECH-*co*-EO) blends. PEO (wt%): (●) 100; (Δ) 80; (○) 60; (□) 40; and (■) 20

for all studied compositions. The degree of crystallinity (X_c) of the PEO phase and of the blends are calculated using equation (1), where ΔH_f is the enthalpy of melting per gram of 100% crystalline PEO ($188\ \mathrm{J\ g^{-1}}$)[13] and ΔH_f^* is the apparent enthalpy of melting per gram of blend.

$$X_c = \Delta H_f^* / \Delta H_f \qquad (1)$$

The degree of crystallinity (X_c) of the blends decreases for all compositions with increase in concentration of PECH and P(ECH-*co*-EO). This effect is more pronounced for blends of PEO/PECH (*Table 2*) and it is not expected, because the molar mass of the copolymer is higher than the homopolymer (see *Table 1*), resulting probably in higher viscosity in the melt for the first system. The melting viscosity affects the crystallization kinetics and, for the same crystallization conditions, blends with P(ECH-*co*-EO) should achieve lower crystallization degrees in comparison to blends of PECH, in absence of other factors. However, the crystallization is favourable for blends of P(ECH-*co*-EO) suggesting that crystallizable ethylene oxide blocks in the copolymer act as crystallization nuclei depressing the activation barrier to the nucleation process. This results in an increase of the overall crystallization rate.

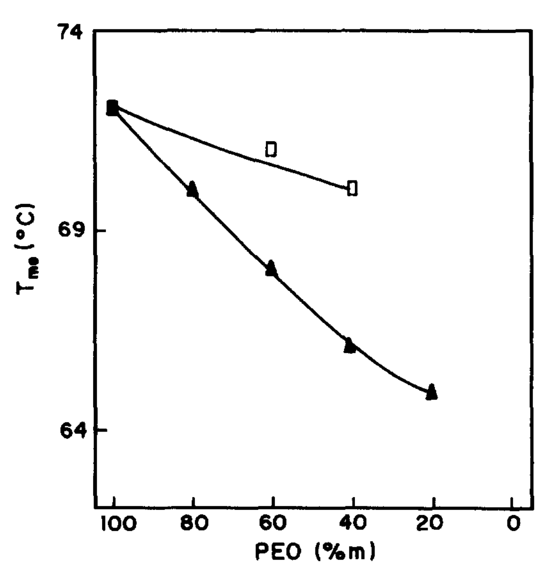

Figure 4 T_{me} as a function of blend composition: (□) PEO/PECH blends and (▲) PEO/P(ECH-*co*-EO) blends

Polymer–polymer interaction parameter

The DSC study has already revealed that the T_m of PEO is depressed systematically with the increase of PECH and P(ECH-*co*-EO) content in the binary blends. This phenomenon may be explained in terms of thermodynamic mixing, by the exothermic interaction between a crystalline and an amorphous polymer and in terms of kinetic or morphological factors. The kinetic effects result because crystals are formed at temperatures below the equilibrium melting and this can be avoided using equilibrium melting temperatures. Morphological effects are associated with changes in crystal perfection or geometry and with different thermal histories of the samples[23]. The contribution of such morphological effects can usually be removed by constructing a Hoffman–Weeks plot[22] using melting data for PEO and for blends isothermally crystallized at different temperatures (T_c). The equilibrium melting temperature (T_{me}) is determined by the extrapolation of the experimental curve of T_m versus T_c to the theoretical curve corresponding to $T_m = T_c$ (*Figure 3*) assuming that the crystals are perfect and of finite size and that no recrystallization takes place during the melting run.

A value of T_{me} of 70°C was obtained for pure PEO and melting point depressions were observed in blends with PECH and [P(ECH-*co*-EO)] (*Figure 4*). The copolymer is more efficient in depressing the melting point of the crystalline phase of PEO in comparison to the homopolymer. The melting point depression can be due to the decrease of the chemical potential of the crystallizable polymer caused by the addition of the miscible diluent. The expression to describe the dependence of the melting point depression due only to thermodynamic effects on the blends composition is given, according to the Flory–Huggins theory modified by Nishi–Wang[11,13,23,24] in equation (2).

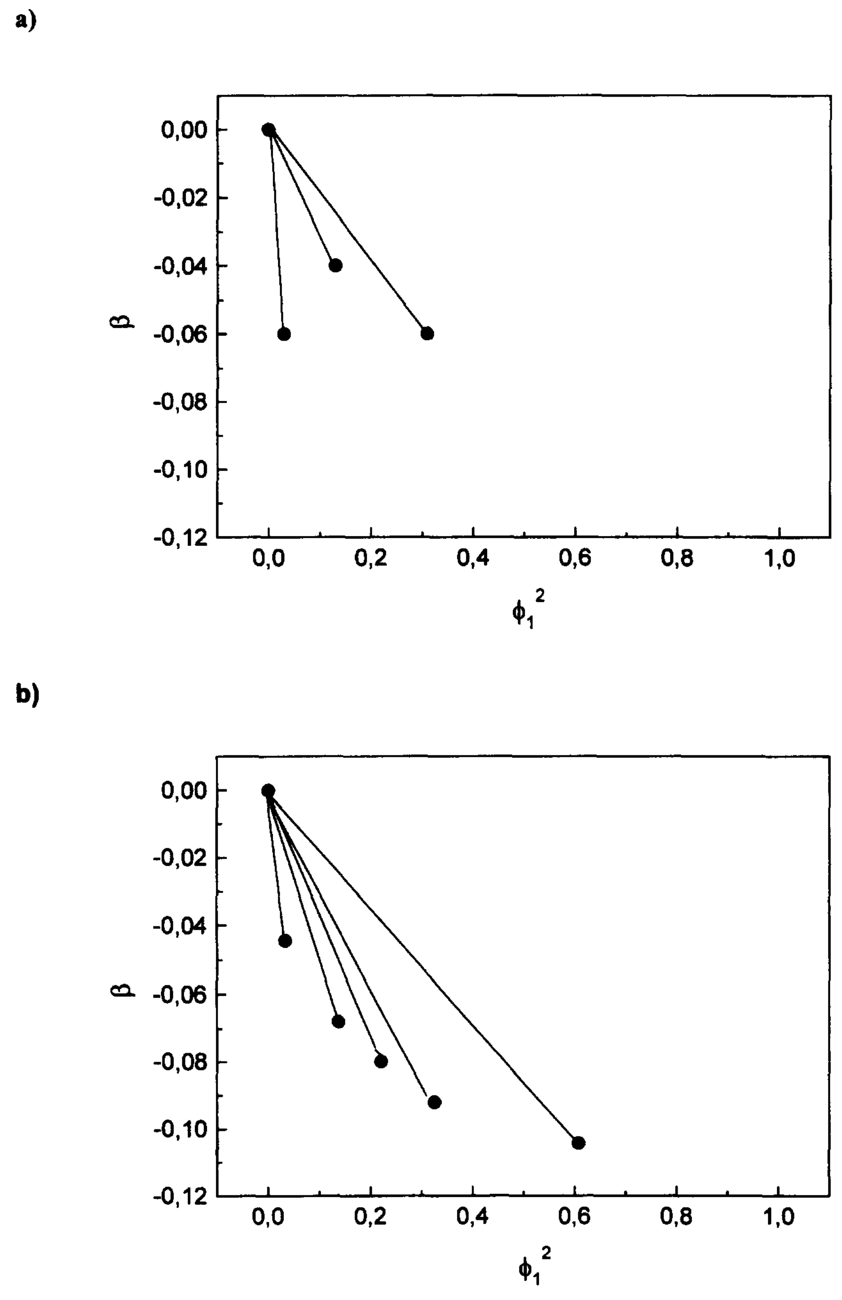

Figure 5 Plots of β versus ϕ_1^2 according to equation (3) for blends: (a) PEO/PECH and (b) PEO/ P(ECH-*co*-EO)

Table 3 Polymer–polymer interaction parameter (χ_{12}) for PEO/PECH blends and PEO/P(ECH-*co*-EO) blends

PEO (wt%)	PEO/PECH	PEO/P(ECH-*co*-EO)
20	-	−0.17 ± 0.03
40	−0.19 ± 0.03	−0.28 ± 0.04
60	−0.21 ± 0.01	−0.50 ± 0.02
80	−0.91 ± 0.02	−1.35 ± 0.02

$$(1/T_{me} - 1/T^{o}_{me}) = -(RV_{2u}/\Delta H_{2u}V_{1u})[\ln\phi_2/m_2 + (1/m_2 - 1/m_1)\phi_1 + \chi_{12}\phi_1^2] \qquad (2)$$

In equation (2), T_{me} and T^{o}_{me} are the equilibrium melting points of the blends and pure PEO, respectively. Subscript 1 identifies the polymer additive (P(ECH-*co*-EO) and PECH) and subscript 2 the crystallizable polymer (PEO). V_u is the molar volume of the repeating unit, ΔH_{2u} is the enthalpy of fusion per mole of repeating unit, m is the degree of polymerization, ϕ are the volume fractions, R is the universal gas constant and χ_{12} is the polymer–polymer interaction parameter. By rearranging the terms of equation (2) we obtain equation (3).

$$-[(\Delta H_{2u}V_{1u}/RV_{2u})(1/T_{me} - 1/T^{o}_{me})] - \ln\phi_2/m_2 - (1/m_2 - 1/m_1)\phi_1 = \beta = \chi_{12}\phi_1^2 \qquad (3)$$

A plot of β versus ϕ_1^2 should give a straight line passing through the origin if χ_{12} is assumed to be independent of the composition. The plots shown in *Figure 5* were obtained using the following parameters: $\Delta H_{2u} = 8.26\ \mathrm{KJ\ mol^{-1}}$; $R = 8.31\ \mathrm{J\ K^{-1}\ mol^{-1}}$; $V_{\mathrm{PECH}} = 67.6\ \mathrm{cm^3\ mol^{-1}}$; $V_{\mathrm{PEO}} = 38.9\ \mathrm{cm^3\ mol^{-1}}$; $V_{[\mathrm{P(ECH\text{-}co\text{-}EO)}]} = 53.7\ \mathrm{cm^3\ mol^{-1}}$; $m_{\mathrm{PECH}} = 1081$; $m_{\mathrm{PEO}} = 2273$; $m_{[\mathrm{P(ECH\text{-}co\text{-}EO)}]} = 4102$. For PEO/PECH blends the points are dispersed and for PEO/P(ECH-*co*-EO) blends β presents a logarithmic dependence on ϕ_1^2, suggesting a composition dependence of χ_{12}. In this case the interaction parameter, at different blend compositions (*Table 3*), can be obtained as the slope of the lines connecting each experimental point and the origin, as shown in *Figure 5*. The values of χ_{12} calculated according to this method are negative for all investigated compositions indicating miscibility of PEO with PECH and with P(ECH-*co*-EO) in the melt.

Min *et al.*[25] also studied blends of PEO and PECH and found that the χ_{12} parameter is not dependent on the composition ($\chi_{12} = -1.04$). But, in this case, materials with different molar mass and polidispersity were used and the blends were prepared by casting. These factors can be responsible for the observed behavior. The values of χ_{12} obtained for PEO/PECH and PEO/P(ECH-*co*-EO) blends were comparable to those described in the literature for other blends, as shown in *Table 4*.

Nishi and Wang attribute the dependence of χ_{12} on the blend composition to morphological and kinetics factors,

Table 4 Values of χ_{12} for blends described in the literature

Blends	χ_{12}	Reference
PEO($Mw = 4.0 \times 10^6\ \mathrm{g\ mol^{-1}}$)/PMMA($Mw = 4.0 \times 10^6\ \mathrm{g\ mol^{-1}}$)	−0.131	2
PEO($Mw = 3.65 \times 10^6\ \mathrm{g\ mol^{-1}}$)/PMMA($Mw = 9.36 \times 10^4\ \mathrm{g\ mol^{-1}}$)	−0.139	2
PEO($Mw = 2.0 \times 10^4\ \mathrm{g\ mol^{-1}}$)/aPMMA($Mw = 1.31 \times 10^5\ \mathrm{g\ mol^{-1}}$)	−0.29	13
PEO($Mw = 3.0 \times 10^5\ \mathrm{g\ mol^{-1}}$)/PVAc($Mw = 1.6 \times 10^5\ \mathrm{g\ mol^{-1}}$)	−0.30	14
PEO($Mw = 2.0 \times 10^3\ \mathrm{g\ mol^{-1}}$)/PHB($Mw = 2.79 \times 10^3\ \mathrm{g\ mol^{-1}}$)	[a]	11
PECH($Mw = 2.0 \times 10^4\ \mathrm{g\ mol^{-1}}$)/PEMA($Mw = 1.5 \times 10^5\ \mathrm{g\ mol^{-1}}$)	−1.08	23
PECH($Mw = 7.0 \times 10^5\ \mathrm{g\ mol^{-1}}$)/PHB($Mw = 1.5 \times 10^4\ \mathrm{g\ mol^{-1}}$)	[b]	19
PECH($Mw = 5.55 \times 10^5\ \mathrm{g\ mol^{-1}}$)/PEO($Mw = 3.0 \times 10^5\ \mathrm{g\ mol^{-1}}$)	−1.04	25
PECH($Mw = 7.0 \times 10^5\ \mathrm{g\ mol^{-1}}$)/PEO($Mw = 5.0 \times 10^4\ \mathrm{g\ mol^{-1}}$)	−0.172	26

[a] depends on the blend composition, varying from −0.21 to −2.0

[b] depends on the blend composition varying from −0.054 to −0.058

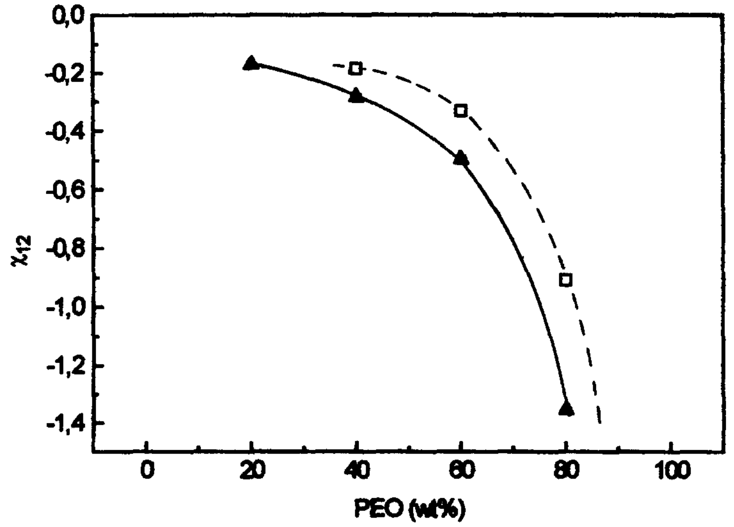

Figure 6 χ_{12} as a function of blend composition: (□) PEO/PECH blends and (▲) PEO/P(ECH-*co*-EO) blends. Dashed line represents χ_{12} as a function of the total ethylene oxide content in the PEO/P(ECH-*co*-EO) blends

such as recrystallization, phase segregation, etc.[11,14,19,27]. However, Painter *et al.*[28] proposed that this effect results from the strong interactions between the different components, such as hydrogen bonding observed in poly(vinyl phenol) and poly(ethylene-*co*-acrylic acid) blends. In the present work, the interaction between the blend components are mainly of the dipole–dipole type, which can also be responsible for the strong dependence of χ_{12} on the composition. It is very interesting to observe that χ_{12} decreases for rich PEO blends, and that, despite the higher molar mass of P(ECH-*co*-EO), its blends present lower χ_{12} values in comparison to blends of PECH, as can be observed in *Table 3*. The meaning of the first observation is a decrease of the interaction energy density or miscibility as the elastomer concentration increases. The second observation implies that the interaction energy density is higher for PEO/P(ECH-*co*-EO) in comparison with PEO/PECH. If we consider that only interaction between epichlorohydrin segments in both homopolymer and copolymer and ethylene oxide segments in PEO contribute effectively to the blend miscibility, the lower value for χ_{12} for blends containing copolymer can be understood as a simple dilution effect. Blends with the copolymer have lower epichlorohydrin concentration in comparison to the blends of the homopolymer at the same compositon. In *Figure 6* we show the dependence of χ_{12} on the blend composition. The dashed line represents χ_{12} values for PEO/P(ECH-*co*-EO) blends as a function of the total ethylene oxide segments in the blend and it fits the experimental data for PEO/PECH blends.

CONCLUSIONS

Binary blends of PEO with PECH and P(ECH-*co*-EO) obtained by the freeze-drying method are miscible, as demonstrated by the presence of only one glass transition temperature for all the compositions investigated and by the systematic depression of the melting temperature of PEO with an increase in PECH and P(ECH-*co*-EO) content. The observation of the thermal transitions enable us to reasonably conclude that the polymer pairs are thermodynamically miscible. The polymer–polymer interaction parameters obtained from thermodynamic melting temperature depression analysis are negative and exhibit dependence on the blend composition, decreasing for blends rich in PEO. PEO/P(ECH-*co*-EO) blends are more miscible than the corresponding PEO/PECH blends and this is attributed to the lower epichlorohydrin concentration in the blends of the copolymer.

ACKNOWLEDGEMENTS

Financial support of this work by FAPESP (process no. 93/1330-9) is gratefully acknowledged.

REFERENCES

1. Nishio, Y., Haratani, T. and Takahashi, T., *J. Polym. Sci., Polym. Phys.*, 1990, **28**, 355.
2. Cortazar, M. M., Calahorra, M. E. and Guzman, G. M., *Eur. Polym. J.*, 1982, **18**, 165.
3. McCormick, C. L., Bock, J. and Schulz, D. N., Water soluble polymers. In *Encyclopedia of Polymer Science and Engineering*, Vol. 17, ed. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, 2nd edn. John Wiley, New York, 1988, p. 755.
4. Marcos, J. I., Orlandi, E. and Zerbi, G., *Polymer*, 1899, **1990**, 31.
5. Venugopal, G., Krause, S. and Wnek, G. E., *Polymer*, 1993, **34**, 3241.
6. Nakafuku, C., *Polymer*, 1993, **34**, 4166.
7. Martuscelli, E., Pracella, M. and Yue, W. P., *Polymer*, 1984, **25**, 1097.
8. Jinghua, Y., Alfonso, G. C., Turturro, A. and Pedimonte, E., *Polymer*, 1993, **34**, 1465.
9. Silvestre, C., Karasz, F. E., Macknight, W. I. and Martuscelli, E., *Eur. Polym. J.*, 1987, **23**, 745.
10. Avella, M., Martuscelli, E. and Raimo, M., *Polymer*, 1993, **34**, 3234.
11. Avella, M. and Martuscelli, E., *Polymer*, 1988, **29**, 1731.
12. Vachom, C., Vasco, M., Perrier, M. and Prudhomme, J., *Macromolecules*, 1993, **26**, 4023.
13. Cimmino, S., Di Pace, E., Martuscelli, E. and Silvestre, C., *Makromol. Chem.*, 1990, **191**, 2447.
14. Kalfoglou, N. K., Sotiropoulou, D. D. and Margaritis, A. G., *Eur. Polym. J.*, 1988, **24**, 389.
15. Chujo, Y. and Saeusa, T., Polyether elastomers. In *Encyclopedia of Polymer Science and Engineering*, Vol. 6, ed. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, 2nd edn. John Wiley, New York, 1988, p. 308.
16. Biedron, T., Kubisa, P. and Penczek, S., *J. Polym. Sci. Polym. Chem.*, 1991, **29**, 619.
17. Cheng, H. N. and Smith, D. A., *Makromol. Chem.*, 1991, **192**, 267.
18. Zhang, X., Shimoda, M. and Toyoda, D., *J. Polym. Sci. Polym. Phys.*, 1994, **32**, 1399.
19. Paglia, E. D., Beltrame, P. L., Canetti, M., Seves, A., Marcandalli, B. and Martuscelli, E., *Polymer*, 1993, **34**, 996.
20. Fernandes, A. C., Barlow, J. W. and Paul, D. R., *J. Appl. Polym. Sci.*, 1986, **32**, 5481.
21. Fernandes, A. C., Barlow, J. W. and Paul, D. R., *J. Appl. Polym. Sci.*, 1971, **1984**, 29.
22. Hoffman, J. D. and Weeks, J. J., *J. Res. NBS Phys and Chem.*, 1962, **66**, 13.
23. Cimmino, S., Martuscelli, E., Silvestre, C., Canetti, M., De Lalla, C. and Seves, A., *J. Polym. Sci., Polym. Phys.*, 1989, **27**, 1781.
24. Nishi, T. and Wang, T. T., *Macromolecules*, 1975, **8**, 909.
25. Min, K. E., Chiou, J. S., Barlow, J. W. and Paul, D. R., *Polymer*, 1987, **28**, 1721.
26. Herrero, C. R. and Acosta, J. L., *J. Polym.*, 1994, **26**, 786.
27. Yoo, H. Y., Umemoto, S., Kikutani, T. and Okui, N., *Polymer*, 1994, **1**, 117.
28. Painter, P. C., Shenoy, S. L., Bhagwagar, D. E., Fisburn, J. and Coleman, M. M., *Macromolecules*, 1991, **24**, 5623.