Miscibility and kinetics of phase separation in blends of poly(ethylene oxide) and poly(ether sulphone)

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The miscibility and kinetics of phase separation in mixtures of poly(ethylene oxide) (PEO) and poly(ether sulphone) (PES) were studied. The mixture was found to have a lower critical solution temperature which, in contrast to observations by other authors, is higher than the glass transition temperatures of the mixtures. Using a light scattering technique the spinodal decomposition temperatures of the mixture were also obtained. The Cahn–Hillard theory was found to be capable of predicting qualitatively the behaviour of phase separation in one mixture (PES/PEO, 10/90). Quantitative description of the spinodal decomposition behaviour would require knowledge of the effects of thermal fluctuation and of non-instantaneous temperature jumps on the experimental results.

(Keywords: poly(ethylene oxide); poly(ether sulphone); spinodal decomposition; miscibility; phase separation; blends)

INTRODUCTION

The widespread potential applications for polymer blends have led in recent years to an increasing research effort on miscibility[1,2] and on the phase separation process, especially its kinetics[3-5]. The miscibility of poly(ether sulphone) (PES) and poly(ethylene oxide) (PEO) was first suggested in two patents[6,7]. From the patents it was clear that miscibility of PES/PEO was dependent on the solvent used to dissolve the polymers and that the miscible blends have a lower critical solution temperature (LCST). Later Singh[8] studied the miscibility of this blend in detail. A phase diagram of the blend was obtained and the interaction between PES and PEO was investigated using the permeation method and observation of melting point depression.

In this paper we have studied the miscibility of this blend using light scattering techniques, and have also investigated the spinodal decomposition at different temperatures. The results are compared with those of Singh and analysed using the Cahn–Hillard kinetic theory.

THEORIES

According to the Flory–Huggins lattice model[9] the free energy of mixing, ΔG_m, for a polymer blend is determined by the entropy ($T\Delta S$) and the enthalpy (ΔH) of the system. Due to the high molecular weights of polymers, the entropic effects of the system play a minor role in determining miscibility of a polymer blend.

At a certain temperature a polymer blend can reduce its free energy of mixing by separating into two phases. The phase separation process can proceed by spinodal decomposition or by the nucleation and growth mechanism. The nucleation and growth mechanism is

possible only in the region between the spinodal and the binodal of a phase diagram. At the binodal the chemical potentials of the two coexisting phases are equal. The spinodal is defined by the points of inflexion where the second derivative of the ΔG_m with respect to the composition of the mixture $(\partial G^2/\partial^2\phi)$ equals zero. Spinodal decomposition is the most widely studied separation process in polymer blends due to its simplicity and resulting interconnected structure. One of the most widely used theories on spinodal decomposition is the Cahn–Hillard theory.

Cahn and Hillard[10] derived a diffusion equation for a spinodal decomposition process:

$$\partial\phi/\partial t = M(\partial^2 G/\partial\phi^2)\nabla^2\phi - 2MK + \text{non-linear terms} \tag{1}$$

where M is the diffusional mobility of the system and the term K arises from the free energy in the concentration gradients and can be determined[11] from the statistical segment length of the component polymers.

If the non-linear terms are ignored, equation (1) can be solved in terms of the growth rate $R(Q)$ in amplitude, of each Fourier component of the concentration fluctuations:

$$R(Q) = -M(\partial^2 G/\partial\phi^2)Q^2 - 2MKQ^4 \tag{2}$$

The function has a maximum at:

$$Q_m = 1/2[(-\partial^2 G/\partial\phi^2)/K]^{1/2} \tag{3}$$

and for values of $Q > Q_c$ ($= 2^{1/2}Qm$), $R(Q)$ becomes negative so that short wavelength fluctuations are damped out.

The scattered intensity from such a system grows exponentially with time as:

$$S(Q, t) = S(Q, 0)\exp[2R(Q)t] \tag{4}$$

Comparing equation (2) with the normal diffusional equation $(\partial\phi/\partial t = D\nabla^2\phi)$ the coefficient of the first term

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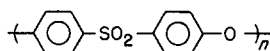* To whom correspondence should be addressed

on the right hand side of equation (1) is identified as the Cahn–Hillard diffusion coefficient D_{app}.

The early stages of the spinodal decomposition are observed as an exponentially increasing scattered intensity which develops a maximum at Q_m. During the early stages Q_m is not time-dependent. D_{app} can be obtained from the intercept of a plot of $R(Q)/Q^2$ versus Q^2 following equation (2). These values extrapolate to zero at the spinodal temperature where $\partial^2 G/\partial \phi^2 = 0$.

EXPERIMENTAL

Materials

PES is a high temperature engineering plastic with a repeat unit:

$$\text{---}\hspace{-2pt}\langle\bigcirc\rangle\hspace{-2pt}\text{---SO}_2\text{---}\hspace{-2pt}\langle\bigcirc\rangle\hspace{-2pt}\text{---O}\text{---}_{\overline{n}}$$

PES used in this study was kindly supplied by ICI (Victrex 200p). It has a quoted reduced viscosity of $0.41 \text{ cm}^3 \text{ g}^{-1}$ in a 1% solution of dimethylformamide (DMF) at 25°C, a density of 1.37 g cm^{-3} at 25°C, a refractive index of 1.65 and a glass transition temperature of 226°C. The quoted number-average molecular weight was 1765 g mol^{-1} and thus the degree of polymerization was approximately 76. It was dried in an oven before use (150°C for 5 h).

PEO is a liquid or wax at low molecular weight and a crystalline low melting point solid at higher molecular weight. It has a repeat unit of $(-CH_2-CH_2-O-)$. The PEO used in this work was obtained from BP Chemicals (Carbowax M20) with a quoted molecular weight of $15\,000$ to $20\,000 \text{ g mol}^{-1}$ and a density of 1.065 g cm^{-3}.

Preparation of polymer blends

Before the preparation, PES and PEO were dried under vacuum for several days. Dried PES and PEO were dissolved in DMF in appropriate quantities to form a 5% solution. The solution was centrifuged for 30 min. Several drops of the centrifuged solution were placed on cover slips which were put inside a Petri dish. Due to the high adsorption of moisture by PEO, which could result in cloudy films, the Petri dish was directly transferred into a vacuum oven at 60°C for 3 days in order to exclude moisture and to dry the film. The typical thickness of a dried film is 0.2 to 0.3 mm.

Determination of glass transition temperature

The blends were examined by differential scanning calorimetry (d.s.c.) (Perkin-Elmer DSC-II) in order to obtain their glass transition temperatures T_g. The samples weighed about 10 mg. A nitrogen flow was maintained through the sample chamber. The sample was scanned from −50 to 250°C. The T_g was arbitrarily taken to be the temperature at which the change in heat capacity was one half of the transition. For each composition three samples were run and the average of the three runs was obtained. The estimated error in the value was ±2°C. For all the experiments reported a heating rate of 20°C min⁻¹ was used.

Determination of phase boundaries

Phase boundaries of PES/PEO blends were obtained by measuring scattered light intensity from the sample.

Details of the equipment and the experimental procedure are described elsewhere[5].

The scattered light intensity of the blends was also examined as a function of time at a constant temperature. Difference in scattering behaviour in nucleation and growth, and spinodal decomposition were utilized to roughly determine the spinodal temperature of the system. The temperature was varied by intervals of 0.5°C. The temperature at which the transition from gradual intensity increase (nucleation and growth mechanism) to exponential increase occurs was taken as the spinodal temperature. The observed temperature may vary within ±1°C due to experimental errors.

In kinetic experiments 10% PEO blend was used. Dried films of the blend were preheated at 75°C for 10 min and then quickly transferred into the sample block of the light scattering equipment. The temperature of the sample block was controlled within a range of 0.5°C. The time required to reach the phase separation temperature from the preheating temperature was estimated to be 5 s. The region from 5 to 30 s on the intensity versus time plots was thus taken as the early stage of spinodal decomposition.

The wave vector, Q, was calculated from the equation:

$$Q = 4\pi n \sin(\theta/2)/\lambda \qquad (5)$$

with $\lambda = 6328 \text{ Å}$ and the refractive index of the mixture $n = 1.58$. $\theta/2$ is the scattering angle.

RESULTS AND DISCUSSION

Miscibility of the blend

In observing the clarity of films made from the blend it is seen that films with PEO concentration <50% are clear at room temperature, while those with PEO concentration >50% are cloudy. This is due to the crystallization of PEO in the blend with higher PEO content. The existence of crystals in the film at room temperature is confirmed by the observation of spherulite crystal structure under an optical microscope and by the fact that films with higher PEO content become clear when the temperature of the film is over 65°C where crystals have melted. Transparency of the film usually indicates that PES and PEO are miscible.

Since film clarity alone is not a sufficient criterion to confirm miscibility, glass transition temperatures of the blends were also measured. The results are presented in *Figure 1* where glass transition temperatures intermediate
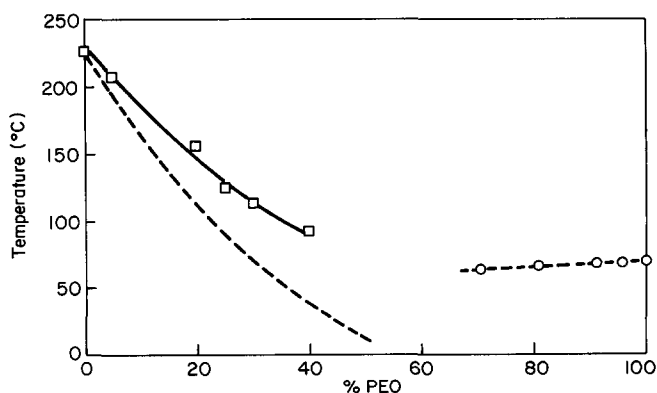
Figure 1 Plots of glass transition temperatures (□) and melting temperatures (○) of the mixture; ----, Fox equation

between those of the component polymers are observed for all blends. Due to crystallization of PEO, the glass transition temperatures of blends with PEO concentration $>50\%$ were not obtained. The broken line in the figure is drawn using the Fox equation[12]:

$$1/T_{\mathrm{g}} = w_1/T_{\mathrm{g}1} + w_2/T_{\mathrm{g}2} \tag{6}$$

where $T_{\mathrm{g}i}$ is the glass transition temperature of component i and w_i the weight fraction of component i. A value of $-75°C$ for PEO is used in the calculation. The positive deviation of the experimental results from the prediction of equation (6) may suggest the existence of specific interactions between the two components[2].

Also included in *Figure 1* is the melting temperature of mixtures having a PEO concentration $>50\%$. Crystallization of PEO in mixtures having a PEO concentration $<50\%$ is not observed by d.s.c. experiments.

The cloud point curve of the mixture obtained is depicted in *Figure 2*. A minimum point is found in the 90% PEO blend, in agreement with Singh's observation[8]. Differences between this result and those of Singh are observed in the high PES concentration range. In contrast to Singh's observation, cloud points higher than the glass transition temperature of the mixture are found. This is in logical agreement with the fact that polymer molecules are immobilized below T_{g}. Also plotted in *Figure 2* are the spinodal decomposition temperatures measured by observing the development of scattered intensity with time at successive temperatures. A typical plot of this kind is shown in *Figure 3*.

Kinetics of phase separation

Preliminary experiments have shown that phase separation of PES/PEO is in the Q range accessible by the light scattering equipment. Within the phase boundary of the 90% PEO blend plots of scattered intensity change exponentially with time (*Figure 4*) and the corresponding ln(intensity) *versus* time plot is linear in the initial stage (*Figure 5*). A maximum in the $I(Q)$
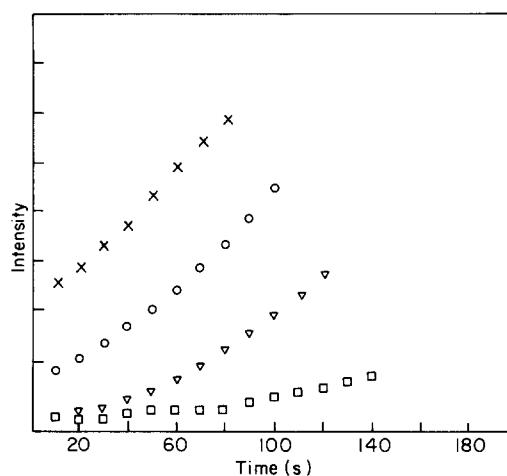

Figure 3 Typical plot of intensity *versus* time for spinodal decomposition and for the nucleation and growth mechanism: $\times$, 84°C; $\bigcirc$, 83°C; $\triangledown$, 82.5°C; $\square$, 81°C
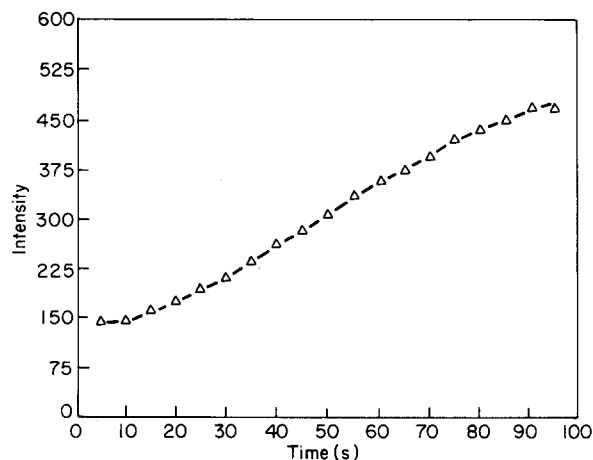

Figure 4 Typical plot of scattered intensity *versus* time for PES/PEO (10/90) mixture during phase separation at 87.7°C
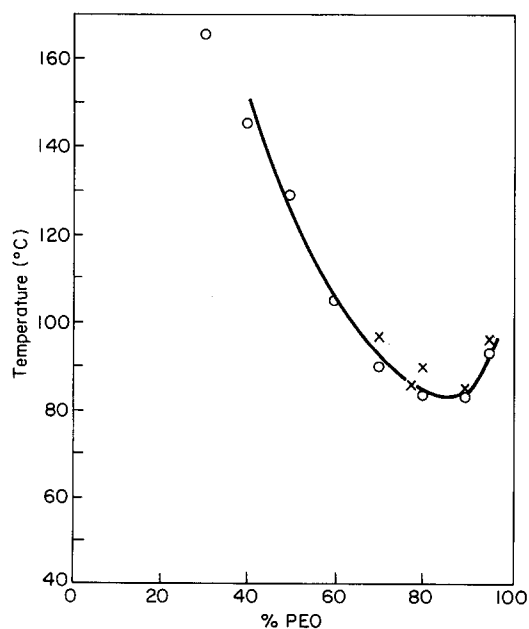

Figure 2 The phase boundary of PES/PEO blend: $\bigcirc$, cloud point; $\times$, spinodal decomposition temperature
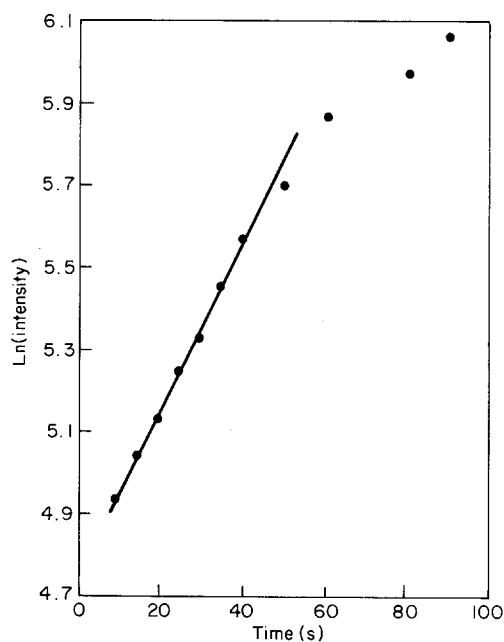

Figure 5 Plot of ln(intensity) *versus* time for the plot shown in *Figure 4*

versus Q plot also appears to be time-independent in the region where linear $\ln I$ *versus* time is found, and moves to smaller Q as phase separation continues. The movement of Q_m to smaller Q may be caused by ripening and coalescence mechanisms in the later stages of phase separation.

Growth rates, $R(Q)$, obtained from slopes of $\ln(\text{intensity})$ *versus* time at different temperatures as a function of Q are plotted in *Figure 6*. A broad peak is observed in the plot and moves to high Q as temperature increases. The increase of Q_m with increasing temperature is caused by increase of $\partial^2 G/\partial\phi^2$ as the phase separation moves away from the spinodal temperature[13]. The values of Q_m obtained at different temperatures are tabulated in *Table 1*.

In agreement with previous experiments[3,4,14,15] $R(Q)/Q^2$ *versus* Q^2 shows a marked deviation from linearity, especially in the low Q range (*Figure 7*). The curvature of $R(Q)/Q^2$ *versus* Q^2 plots has been attributed to: (1) the omission of the non-linear terms in the simple Cahn–Hillard theory, as considered by Langer[16]; (2) the possible wave vector dependence of the diffusional coefficient, M, discussed by Pincus[17] and Binder[18]; (3) the effects of slowly relaxing variables associated with glass transitions of the components. These effects have been discussed by Binder *et al.*[19]; (4) the thermal
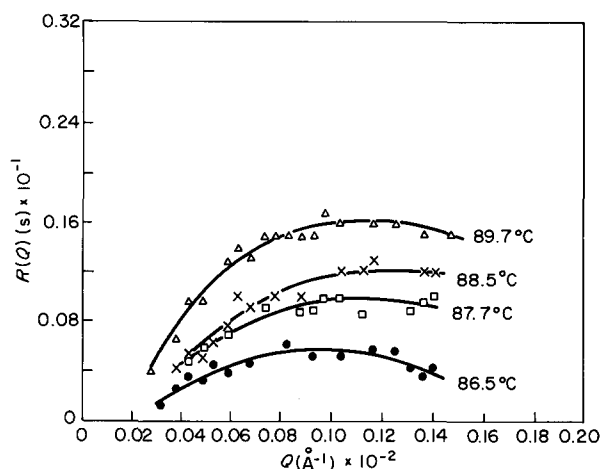
Table 1 Experimental data of phase separation of PES/PEO (10/90) mixture at different temperatures

Temperature (°C)	D_{app} (cm² s⁻¹) ×10⁻¹³	$Q_m{}^a$ (cm⁻¹) ×10⁵	$Q_m{}^b$ (cm⁻¹) ×10⁵
86.5	9.27	1.14	1.0
87.7	16.0	1.23	1.2
83.5	19.3	1.21	>1.4
89.7	24.0	1.24	>1.4

^{a}From $R(Q)/Q^2$ *versus* Q^2 plots
^{b}From $R(Q)$ *versus* Q plots

fluctuation force occurring in the phase separation process discussed by Cook[20] and others[21,22].

The first two possibilities are very unlikely to be important here since the data presented meet the two requirements of $2R(Q_m)t > 1$ and $R_g Q \ll 1$, set respectively for linearity of behaviour, and Q-independent diffusional coefficients. The third possibility is considered less important, at least until others are ruled out, because the phase separation takes place well above the T_g of the mixture.

Camesin[23], via computer simulation, has demonstrated that a non-instantaneous temperature quench will result in a non-linear $R(Q)/Q^2$ *versus* Q^2 plot. Because long wavelength fluctuations are amplified during the continuous quench, the resulting peak would be broadened. The broad peak observed in the $R(Q)$ *versus* Q plot in *Figure 6* may indicate the existence of such effects.

The effects of thermal fluctuation force have been vigorously pursued both experimentally and theoretically. Okada and Han[24] claimed that such effects have been observed in the spinodal decomposition of polystyrene/poly(vinyl methyl ether) mixtures when the quench depth ΔT is $<0.48°C$. Higgins and co-workers[5,25] have stated that the disagreement between the simple Cahn–Hillard theory and the experimental results for poly(methyl methacrylate)/styrene-*co*-acrylonitrile and tetramethyl polycarbonate/polystyrene may be due to thermal fluctuations. Although the quench depth in this study, ranging from 1 to 8°C, is much greater than 0.48°C, as used in the polystyrene/poly(vinyl methyl ether) system, thermal fluctuations may still be present in this case, since a limit on the quench depth below which the effects of thermal fluctuations are apparent may be a system-dependent parameter. In fact, it is not so much ΔT, as $\partial^2 G/\partial\phi^2$ that matters, i.e. the rate of change of $\partial^2 G/\partial\phi^2$ with ΔT will determine quench depth below which thermal fluctuation can be ignored.

Thus the data presented above apparently obey qualitatively the predictions of the Cahn–Hillard theory of spinodal decomposition. In detail, however, there are a number of predictions which are not observed and which show up the quantitative inadequacies of the simple theory. The apparent mutual diffusion coefficient, D_{app}, has been calculated from the intercept of the straight line drawn in the high Q range of $R(Q)/Q^2$ *versus* Q^2 plots and the calculated values of D_{app} at different temperatures are presented in *Table 1*. The values of D_{app} (of the order of 10^{-12} to 10^{-13} cm² s⁻¹) are comparable with values obtained for other systems[3,24,25]. Considering that phase separation temperatures are far below the T_g of PES and far above the T_g of PEO, it would be most probable that the phase separation in this mixture is

Figure 6 Plots of growth rate $R(Q)$ *versus* Q for the PES/PEO (10/90) mixture at different temperatures: $\triangle$, 89.3°C; ×, 88.5°C; $\square$, 87.7°C; $\bullet$, 86.5°C
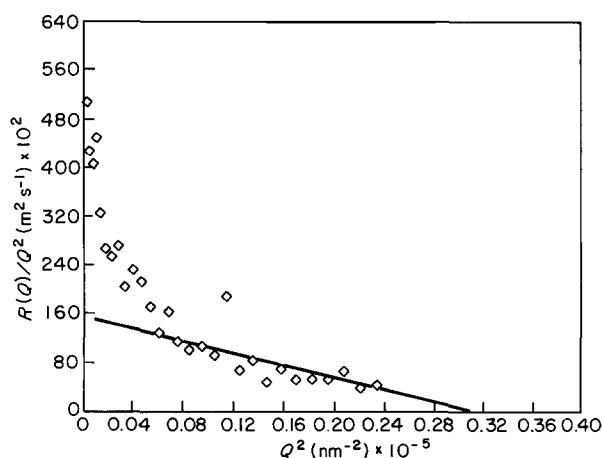

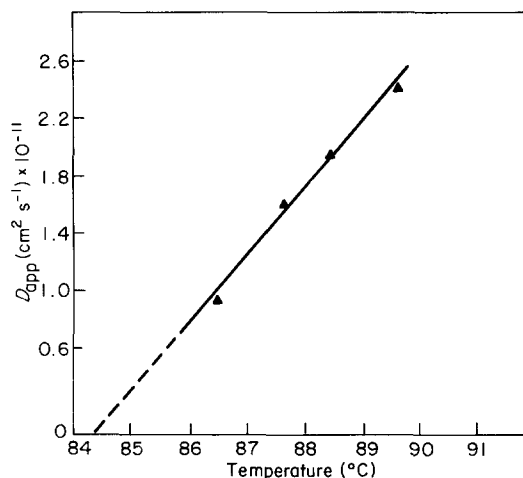**Figure 7** Typical plot of $R(Q)/Q^2$ *versus* Q^2 at 87.7°C

Figure 8 Apparent diffusion coefficient D_{app} *versus* the temperature of phase separation

mainly controlled by the fast moving component, PEO, which has an estimated diffusion coefficient of about 2.5×10^{-10} cm^2 s^{-1} (ref. 26)*.

If the mobility of polymers does not change significantly with temperature in the experimental region, and the phase separation is brought about by the entropy term in the free energy, the plot of D_{app} *versus* temperature should be linear and extrapolate to the spinodal temperature at $D_{app} = 0$. Such a plot for the values of D_{app} obtained is shown in *Figure 8*. A least-squares fit to these data extrapolates to a spinodal temperature of 85°C which agrees well with the value of 84°C obtained from the static experiments described earlier.

Provided that K, the energy gradient term in the Cahn–Hillard theory, is known, the values of Q_m may be used to calculate $\partial^2 G / \partial \phi^2$, the thermodynamic driving force of spinodal decomposition. K is obtained from the equation:

$$K = M_A / 6 \{ [(R_g^2 / M_w) / \phi_A] + [M_B (R_g^2 / M_w) / (\phi_B M_A)] \} \tag{7}$$

where M_A and M_B are the mass of monomer components A and B and ϕ_A and ϕ_B are the volume fraction of the same components. A value of 34.7 Å for K is calculated using $(R_g^2 / M_w) = 0.310$ for PES and $(R_g^2 / M_w) = 0.263$ for PEO taken from ref. 27. Since no data are available for PES in the literature a value for poly(sulphophenyl ethylene) is taken instead[27]. According to equation (3) a value of -2.14×10^{-4} is obtained for $\partial^2 G / \partial \phi^2$ at a temperature of 89.8°C. This value is comparable with those found for other polymer blend systems[1]. However, it is much smaller than the value calculated[28] from the

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* The diffusion coefficient of PEO used in the present study is calculated from the relation of $D \propto M^{-2}$ describing the molecular weight effects on D. The D value estimated from Figure 2(b) of ref. 26 is about 2×10^{-7} cm^2 s^{-1} at 88–103°C

equation of state[29] using parameters such as X_{12}, Q_{12} and S_2 / S_1 from the work of Singh[8]. Such disagreement may be attributed to the different methods of measurement. The use of the melting point depression method for measurement of the interaction parameter between components in polymer blends has often been criticized for making various assumptions and for its lack of accuracy in measurements[1,2,30].

CONCLUSIONS

Clear evidence for spinodal decomposition has been observed in the PES/PEO blends. The Cahn–Hillard theory qualitatively predicts the behaviour of the spinodal decomposition in the early stages.

Additional factors, such as the thermal fluctuation force and the speed of the temperature jump, should be included in the detailed theoretical treatment of the spinodal decomposition for this blend.

REFERENCES

1 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
2 Paul, D. R. and Newman, S. (Eds) 'Polymer Blends', Academic Press, New York, 1978
3 Synder, H. L. and Meakin, P. *J. Polym. Sci., Polym. Symp.* 1985, **73**, 217
4 Hashimoto, T., Itakura, M. and Hasegawa, H. *J. Chem. Phys.* 1986, **85**, 6773
5 Guo, W. and Higgins, J. S. *Polymer* 1990, **31**, 699
6 ICI plc, Newton, A. B. European Patent Application EP37181, 1981; *Chem. Abstr.* 1982, **96**, 7553
7 Kararay Co. Ltd, Suenka, A. and Hamamoto, Y. Japanese Patent 8235906, 1982; *Chem. Abstr.* 1982, **97**, 25085
8 Singh, B. PhD Thesis, Imperial College, London, UK, 1985
9 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660
10 Cahn, J. W. *Trans. Met. Soc. AIME* 1968, **242**, 169
11 Schichtel, T. E. and Binder, K. in press
12 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **2**, 1123
13 Van Aartsen, J. J. *Eur. Polym. J.* 1970, **5**, 919
14 Hashimoto, T., Kumaki, J. and Kawai, H. *Macromolecules* 1983, **16**, 641
15 Hill, R. PhD Thesis, Imperial College, London, UK, 1985
16 Langer, J. S. *Phys. Rev. A* 1975, **7** (4), 1414
17 Pincus, P. *J. Chem. Phys.* 1981, **75**, 1996
18 Binder, K. *J. Chem. Phys.* 1983, **79**, 6387
19 Binder, K., Frisch, H. L. and Jäckle, J. *J. Chem. Phys.* 1986, **85**, 1505
20 Cook, H. E. *Acta Metal.* 1970, **18**, 297
21 Park, W. W., Cooper, A. R. and Hener, A. H. *Scripta Met.* 1975, **9**, 321
22 Binder, K. *J. Chem. Phys.* 1983, **79**, 6387
23 Camesin, H. O., Heermann, D. W. and Binder, K. *J. Chem. Phys.* 1983, **79**, 5588
24 Okada, M. and Han, C. C. *J. Chem. Phys.* 1985, **85**, 5317
25 Higgins, J. S., Fruitwala, H. and Tomlins, P. E. *Macromolecules* 1989, **22**, 5674
26 Fytas, G. *Macromolecules* 1987, **20**, 1431
27 Bohn, L. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), Wiley, New York, 1975
28 Guo, W. PhD Thesis, Imperial College, London, UK, 1989
29 McMaster, L. P. *Macromolecules* 1973, **6**, 760
30 Rim, P. B. and Runt, J. P. *Macromolecules* 1984, **17**, 1520