The surface composition of miscible polymer blends

R. A. L. Jones*
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

and E. J. Kramer
Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA

(Received 24 October 1991; revised 25 March 1992)

Simple, analytical expressions are derived for the surface composition and surface excess (adsorbed amount) of the lower surface energy component of a miscible polymer blend at equilibrium. In practical cases, the total surface excess is predicted to depend more strongly on the value of the Flory–Huggins interaction parameter between the segments of the two polymers than on the difference in surface energies between the components of the blend.

(Keywords: polymer surfaces; polymer blends; surface segregation)

INTRODUCTION

A number of technologically important properties of polymer blends are controlled by the surface composition of the blend; examples are the contact angle with water and other liquids, and the weatherability and frictional properties of the material. Experiments show that in many cases the polymer blend surface has a different composition from the bulk[1–5], and some recent experiments[3,6] show good agreement with the predictions of mean field theories[7,8]. While these theories seem to work reasonably well, to predict the equilibrium surface volume fraction ϕ_1 and the integrated surface excess z^* requires the numerical solution of non-linear equations. It would be desirable to have simple approximate analytical expressions for ϕ_1 and z^* which would allow trends with the many possible variables to be explored. We have succeeded in deriving such expressions for the case when the components have the same degree of polymerization, N. In this simple case, we show that to a good approximation the equilibrium surface volume fraction of a polymer blend is a function of the bulk volume fraction and a single reduced variable. This variable combines the effects of the difference in surface energy between the two components, the degree of polymerization and the Flory–Huggins interaction parameter χ. For the values of these parameters usually encountered in polymer blend systems, our prediction is that total enrichment—an equilibrium surface volume fraction of the lower surface energy species close to one—should be nearly universally observed. It follows from this prediction that the integrated surface excess saturates for a relatively small value of the surface energy difference, and in most practical cases the major factor in influencing the surface excess will be the bulk thermodynamics of the blend, not the value of the difference in surface energy between the components.

MEAN FIELD THEORY

If one component of any binary fluid mixture has a lower surface energy than the other then the system as a whole may save free energy by having a surface composition of the lower surface energy component which is higher than the bulk composition. On the other hand, there is a free energy cost associated with creating a surface layer with a different composition to the bulk; moreover there is an additional unfavourable free energy associated with the interface between the surface layer and the bulk material. The equilibrium surface composition and near surface composition profile are given by the minimization of the overall system free energy; the theory of this has been given for polymer blends by Schmidt and Binder[7] and Pincus and Nakanishi[8]. These authors adapted the treatment of the surface of liquid mixtures due to Cahn[9], which itself was an adaptation of the work of Van der Waals[10,11]. Here we summarize the results of this theory, using the notation of Schmidt and Binder[7].

In general the composition profile $\phi(z)$ which describes the way in which the composition changes from surface to bulk will decay from a surface composition ϕ_1 to the bulk composition ϕ_∞ over some characteristic length λ (*Figure 1*). One can write the appropriate thermodynamic potential in the grand canonical ensemble as a function of the composition profile $\phi(z)$, and find the $\phi(z)$ which minimizes the thermodynamic potential, by the standard methods of the calculus of variations. One finds that the surface composition is given by the solution of the equation:

$$-\frac{\mathrm{d}f_s}{\mathrm{d}\phi_1}=\mu_1+g\phi_1=\pm\frac{a}{3}\sqrt{\frac{Q(\phi_1,\phi_\infty)}{\phi_1(1-\phi_1)}} \tag{1}$$

Here $Q(\phi,\phi_\infty)$ is the function:

$$Q(\phi,\phi_\infty)=G(\phi)-G(\phi_\infty)-\Delta\mu(\phi-\phi_\infty) \tag{2}$$

where $G(\phi)$ is the free energy of mixing of the blend per

---

*To whom correspondence should be addressed

0032-3861/93/010115-04

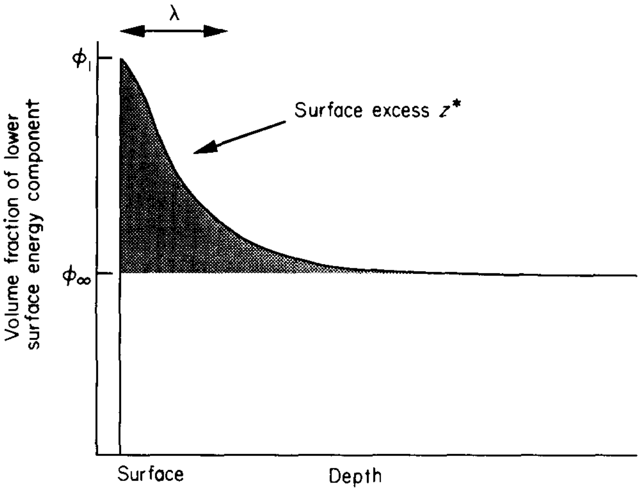

Figure 1 Schematic diagram of the surface of a polymer blend

lattice site, a is the statistical segment length and $\Delta\mu$ is the exchange chemical potential $(\partial G/\partial\phi)$ evaluated at the bulk volume fraction ϕ_∞. The effect of the surface is represented by a bare surface energy $f_s(\phi_1)$; this is conventionally expressed as:

$$f_s(\phi_1) = -\mu_1\phi_1 - \frac{g}{2}\phi_1^2 \tag{3}$$

The difference in surface energy between the two components is given by $\mu_1 + g/2$ (in units of kT) for a Flory–Huggins lattice cell, where μ_1 represents a surface chemical potential favouring component 1 at the surface. The parameter g expresses the way in which interactions between components of the blend are modified by the surface; a simple lattice argument[12] suggests that $g \sim -b\chi$, where b is the size of the Flory–Huggins lattice cell and χ is the Flory interaction parameter (per segment). For the chemically different polymer blends we are dealing with here, the actual surface energy difference should be much larger than this, and we may neglect g entirely.

The composition profile is given by:

$$z = \frac{a}{6}\int_{\phi_\infty}^{\phi(z)} \frac{\mathrm{d}\phi}{[\phi(1-\phi)Q(\phi,\phi_\infty)]^{0.5}} \tag{4}$$

Note that the shape of the composition profile is entirely determined by bulk thermodynamics; the difference in surface energy between the components affects only the surface composition.

The integrated surface excess z^*, defined by the expression:

$$z^* = \int_0^\infty [\phi(z) - \phi_\infty]\,\mathrm{d}z \tag{5}$$

can be directly calculated as:

$$z^* = \frac{a}{6}\int_{\phi_\infty}^{\phi_1} \frac{\mathrm{d}\phi(\phi-\phi_\infty)}{[\phi(1-\phi)Q(\phi,\phi_\infty)]^{0.5}} \tag{6}$$

This theory is complete in the sense that equations (1) and (3) may be used to calculate numerically the surface volume fraction and near surface depth profile of any system of interest, if the difference in surface energies and the bulk blend thermodynamics are known. Our aim in the rest of this paper is to obtain simple, analytical expressions for the surface volume fraction and for the integrated surface excess. The resulting expressions will be easier to use in practice, and more transparent in form, allowing us to draw some general conclusions about the nature of the surface of a polymer blend.

SURFACE COMPOSITION AND INTEGRATED SURFACE EXCESS FOR MISCIBLE POLYMER BLENDS

We assume the use of the Flory–Huggins form for the free energy of mixing $G(\phi)$, and assume equal degrees of polymerization N:

$$G(\phi) = \frac{\phi}{N}\ln(\phi) + \frac{1-\phi}{N}\ln(1-\phi) + \chi\phi(1-\phi) \tag{7}$$

We now introduce the variable χ_b, the value of the Flory–Huggins interaction parameter χ on the coexistence curve, which is given by the expression:

$$\chi_b = \frac{1}{N(1-2\phi_\infty)}\ln\left(\frac{1-\phi_\infty}{\phi_\infty}\right) \tag{8}$$

We stress again that this expression is valid only for the case of equal molecular weights. Using equations (7) and (8) we can rewrite equation (2) to yield:

$$Q(\phi,\phi_\infty) = (\chi_b - \chi)(\phi - \phi_\infty)^2 + \frac{1}{N}f(\phi,\phi_\infty) \tag{9}$$

where

$$f(\phi,\phi_\infty) = \phi\ln\phi + (1-\phi)\ln(1-\phi) - \ln(1-\phi_\infty) + \frac{\phi(1-\phi)-\phi_\infty^2}{(1-2\phi_\infty)}\ln\frac{(1-\phi_\infty)}{\phi_\infty} \tag{10}$$

If $|\chi|N$ is large, as is often the case in miscible polymer blends, and ϕ_∞ is not too close to 0 or 1, the second term in equation (9) may be neglected. This leads to the following much simpler expression for $Q(\phi,\phi_\infty)$:

$$Q(\phi,\phi_\infty) = (\chi_b - \chi)(\phi - \phi_\infty)^2 \tag{11}$$

This step allows us to evaluate explicitly equations (1) and (6), for the surface volume fraction and the surface excess, respectively.

We start with the expression for the surface volume fraction. Substituting from equation (11) into equation (1) and solving the resulting quadratic equation gives us the following expression for the surface volume fraction ϕ_1, in terms of the bulk volume fraction ϕ_∞, and a new reduced variable t:

$$\phi_1 = \frac{\phi_\infty + t}{1 + t} \tag{12}$$

Here t is a measure of the driving force for surface segregation, a reduced surface energy difference, and is given by:

$$t = 9\left(\frac{\mu_1}{a}\right)^2 \frac{1}{\chi_b - \chi} \tag{13}$$

Thus the surface volume fraction ϕ_1 may be expressed in terms of the bulk volume fraction ϕ_∞ and a single reduced parameter, t, which accounts for the difference in surface energies between the two polymers, their molecular weight and, via the interaction parameter χ, their thermodynamics of mixing.

Moving now to the surface excess z^*, substituting equation (11) into equation (6) yields the following

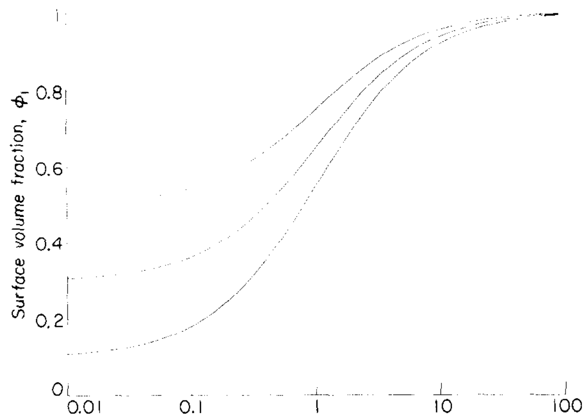

Figure 2 Surface volume fraction ϕ_1 as a function of the reduced surface energy difference t for different values of the bulk volume fraction ϕ_∞, as calculated from equation (12)

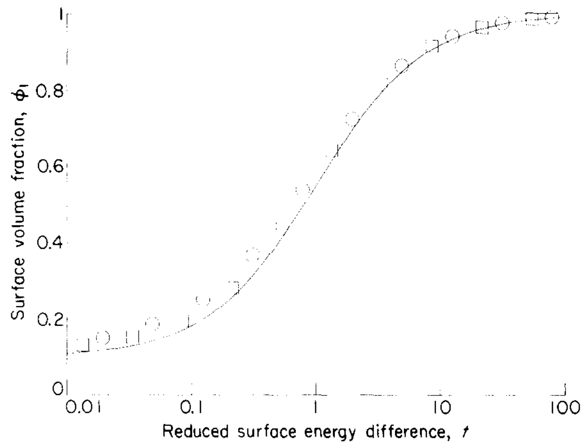

Figure 3 Surface volume fraction ϕ_1 as a function of the reduced surface energy difference t for a value of the bulk volume fraction $\phi_\infty=0.1$. The solid line is the approximation of equation (12), whereas the symbols are the exact solutions of equation (1) for degree of polymerization $N=1000$, Flory–Huggins parameter $\chi=-0.001$ (□) and $\chi=-0.1$ (○), in each case calculated for a variety of different surface energy differences

expression for z^*:

$$z^*=\frac{a}{6}\frac{1}{\sqrt{\chi_b-\chi}}\int_{\phi_\infty}^{\phi_1}\frac{d\phi}{\sqrt{\phi(1-\phi)}} \tag{14}$$

The integral may be done analytically to yield the final expression for z^*:

$$z^*=\frac{a}{3}\frac{1}{\sqrt{\chi_b-\chi}}(\arcsin\sqrt{1-\phi_\infty}-\arcsin\sqrt{1-\phi_1}) \tag{15}$$

MODEL CALCULATIONS AND DISCUSSION

To use these equations for real situations one must obtain the value of μ_1 from known values of the surface energy difference $\Delta\gamma$. The quantities are related by the equation:

$$\mu_1=\frac{b^3}{kT}\Delta\gamma \tag{16}$$

where b is the size of the Flory–Huggins lattice cell (which is not, in general, the same as the step length a). Taking polystyrene as an example this gives the relation $\Delta\gamma=3.54\mu_1$ (where $\Delta\gamma$ is in mJ m^{-2} and μ_1 is in Å).

Figure 2 shows the relation between surface volume fraction and the reduced variable t for a variety of different values of the bulk volume fraction, as found from equation (12). To investigate the validity of the approximations used we compare in *Figure 3* the results of equation (12) with the complete, numerically evaluated solutions of equation (1) for a variety of values of μ_1, N and χ. Even for quite small values of χ, the simple expression works well.

In *Figure 4a* the solid curves show values of the surface excess z^*, as calculated from equations (12) and (15), as a function of the surface energy difference for a variety of values of the interaction parameter χ. We have plotted the surface energy in experimental units (mJ m^{-2}) assuming that the Flory–Huggins interaction parameter is calculated for a lattice cell appropriate for a polystyrene monomer. Again, for comparison the points represent the results of the full numerical evaluation of equation (6). Once again, the agreement is very good, with the discrepancy being largest for small values of χ. In *Figure 4b*, we plot the surface volume fraction ϕ_1 for the same conditions as those in *Figure 4a*. Except for the most miscible blend ($\chi=-0.1$) for surface energy differences $>\sim 2$ mJ m^{-2} both the surface excess and the surface volume fractions ϕ_1 are extremely insensitive to the value of the surface energy difference. Under these conditions both z^* and ϕ_1 are determined almost entirely by the

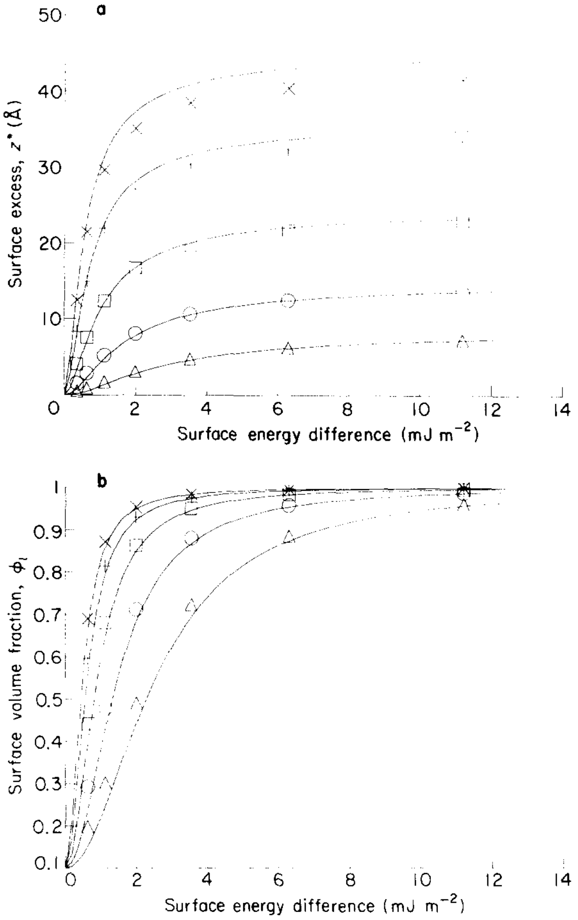

Figure 4 (a) surface excess z^* and (b) surface volume fraction ϕ_1 as a function of surface energy difference for various values of the Flory–Huggins χ parameter, as calculated from the approximate expressions equations (12) and (15) (solid lines), and as calculated from equation (5) (symbols): (△) $\chi=-0.1$; (○) $\chi=-0.0316$; (□) $\chi=-0.01$; (+) $\chi=-0.00316$; (×) $\chi=-0.001$. In all cases the bulk volume fraction $\phi_\infty=0.1$ and the degree of polymerization $N=1000$

bulk thermodynamics, that is by the value of the interaction parameter χ. Most practical polymer blends have surface energy differences much greater than $2\,\mathrm{mJ\,m^{-2}}$ [for example the difference in surface energy between polystyrene and poly(vinyl methyl ether) is nearly $8\,\mathrm{mJ\ m^{-2}}$]^2 and thus will be in this bulk thermodynamics dominated regime. This result is the most important conclusion of this work.

In conclusion, we have derived simple expressions for the surface composition and surface excess of the lower surface energy polymer in a miscible polymer blend at equilibrium. We have shown that surface enrichment in polymer blends is likely to be almost a universal phenomenon. The reason for this universality lies with the unusual nature of the thermodynamics of polymer blends, and specifically their very small entropy of mixing. To form a surface enriched layer in a polymer blend in general costs very little free energy, and so even a small surface energy difference will drive a large surface segregation. In fact, the usual situation, for a surface energy difference of $1\,\mathrm{mJ\,m^{-2}}$ or so, will be that the surface is essentially completely covered by the low surface energy polymer. It follows that the amount of segregated polymer will be determined by the bulk thermodynamics of the blend rather than by the difference in surface energies between the components.

ACKNOWLEDGEMENTS

RALJ is supported at Cambridge by a grant from ICI plc; at Cornell University this work was supported by the NSF-DMR Polymer Program grant DMR-8719123.

REFERENCES

1 Pan, D. H. and Prest, W. M. *J. Appl. Phys.* 1985, **58**, 2861

2 Bhatia, Q. S., Pan, D. H. and Koberstein, J. T. *Macromolecules* 1988, **21**, 2166

3 Jones, R. A. L., Kramer, E. J., Rafailovich, M. H., Sokolov, J. and Schwarz, S. A. *Phys. Rev. Lett.* 1989, **62**, 280

4 Schmidt, J. J., Gardella Jr, J. A. and Salvati Jr, L. *Macromolecules* 1989, **22**, 4489

5 Clark Jr, M. B., Burkhardt, C. A. and Gardella Jr, J. A. *Macromolecules* 1989, **22**, 4495

6 Jones, R. A. L., Norton, L. J., Kramer, E. J., Composto, R. J., Stein, R. S., Russell, T. P., Mansour, A., Karim, A., Felcher, G. P., Rafailovich, M. H., Sokolov, J., Zhao, X. and Schwarz, S. A. *Europhys. Lett.* 1990, **12**, 41

7 Schmidt, I. and Binder, K. *J. Phys.* 1985, **46**, 1631

8 Nakanishi, H. and Pincus, P. *J. Chem. Phys.* 1983, **79**, 997

9 Cahn, J. W. *J. Chem. Phys.* 1977, **66**, 3367

10 Van der Waals, J. D. *Zeitschrift Phys. Chem.* 1894, **13**, 657

11 Rowlinson, J. S. and Widom, B. 'Molecular Theory of Capillarity', Clarendon Press, Oxford, 1982

12 Jones, R. A. L., Kramer, E. J., Rafailovich, M. H., Sokolov, J. and Schwarz, S. *Mater. Res. Soc. Symp. Proc.* 1989, **153**, 133