Elasticity Dominated Surface Segregation of Small Molecules in Polymer Mixtures

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We study the phenomenon of migration of the small molecular weight component of a binary polymer mixture to the free surface using mean field and self-consistent field theories. By proposing a free energy functional that incorporates polymer-matrix elasticity explicitly, we compute the migrant volume fraction and show that it decreases significantly as the sample rigidity is increased. A wetting transition, observed for high values of the miscibility parameter can be prevented by increasing the matrix rigidity. Estimated values of the bulk modulus suggest that the effect should be observable experimentally for rubberlike materials. This provides a simple way of controlling surface migration in polymer mixtures and can play an important role in industrial formulations, where surface migration often leads to decreased product functionality.

Introduction.—When a polymer mixture having mobile components of different molecular weights and with an interface that is free to the atmosphere is left to equilibrate, the small molecular weight component migrates to the surface [1–3]. Several industrial formulations, e.g., chocolate [4], food packaging [5], etc., suffer from this ubiquitous problem. While many experimental [1,2,6] and theoretical studies [7] of this phenomenon exist, a good quantitative agreement between theoretical predictions and experiments is still lacking [1]. Further, experimental strategies to control the amount of material migrating to the surface is in a nascent stage of development.

In this Letter we ask how the elasticity of the polymer matrix influences surface migration of small molecules in polymer mixtures. We propose a free energy functional that incorporates elasticity of the polymer mixture explicitly, a feature that has been ignored in previous surface segregation studies. Using a Schmidt-Binder mean field theory (SB) and self-consistent field theory (SCFT) we show that as the sample rigidity is increased (i) the migrant fraction decreases, and (ii) a wetting transition can be avoided (demonstrated by a geometric construction [8,9]). These results are of paramount importance in industrial product formulations where surface migration of small molecular weight component results in decreased functional performance of the product.

Surface migration.—For a binary mixture, the component with the lower surface energy will migrate to the interface. A balance between loss of translational entropy and gain in surface energy dictates the equilibrium morphology of such systems. This is shown in Fig. 1 with a high migrant (black) concentration close to the interface ($z = 0$) of a mixture of low and high (red) molecular weight polymers. The migrant concentration decreases

monotonically to the bulk concentration ϕ_∞ as $z \to \infty$. A crucial parameter that dictates the thermodynamics of the system is χN, where χ is the miscibility parameter and N the molecular weight of the migrant. As χN increases, a wetting transition characterized by a macroscopic wetting layer is observed (Fig. 1, inset) [1].

Surface migration was first observed using x-ray photo-emission spectroscopy [10] and the resolution of the depth profile of the migrant concentration was improved significantly using neutron reflectivity [11]. Further studies concentrated on the theoretical aspects of the migration
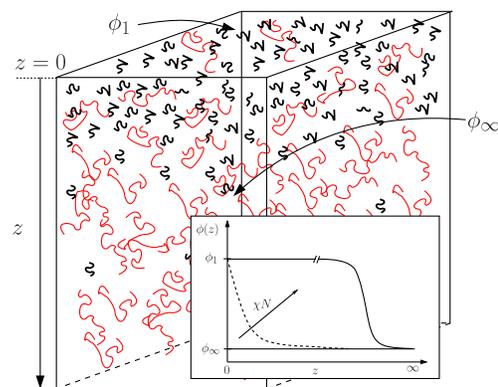
FIG. 1. Schematic figure showing a mixture of low (black) and high (red) molecular weight polymers, with the low molecular weight component migrating to the free interface $z = 0$. A semi-infinite geometry is assumed. The volume fraction of the migrant in bulk and at the surface is denoted by ϕ_∞ and ϕ_1, respectively. Inset shows migrant concentration profiles for different values of χN. For low values of χN a monotonically decreasing concentration profile is observed (dashed line). As χN increases, a wetting transition characterized by a macroscopically thick migrant layer (solid line with a break) is observed.

by Schmidt and Binder [12] and, subsequently, a comparison between theory and experiments [13]. The wetting transition of polymer mixtures at the air-mixture interface was first demonstrated by Steiner *et al.* [14]. Experimental and theoretical developments of this phenomenon have recently been reviewed by a few authors [2,6].

Flory-Huggins theory.—The thermodynamics of mixing of two chemically different polymers is well described by Flory-Huggins (FH) theory [15]. Assuming the same volume for the two monomers, and using it as a volume unit, the mixing free energy per unit volume is given by

$$\frac{F_{fh}[\phi]}{k_B T} = \frac{(1-\phi)}{N_B}\log(1-\phi) + \frac{\phi}{N_A}\log(\phi) + \chi\phi(1-\phi),$$

(1)

where χ is the miscibility parameter, and N_A and N_B are the degree of polymerization of A and B polymers, respectively. The volume fractions of the A ($\phi_A = \phi$) and B ($\phi_B = 1 - \phi$) polymers in Eq. (1) thus satisfy the incompressibility constraint $\phi_A + \phi_B = 1$. The phase behavior of such systems is well known [15]. Below a critical value of the miscibility parameter $\chi < \chi_c = 1/(2N_A) + 1/(2N_B) + 1/(\sqrt{N_A N_B})$ the equilibrium phase is a homogeneous mixture of A and B polymers. For $\chi > \chi_c$ (e.g., caused by changing temperature) phase segregation occurs with the system separating into A and B rich regions. Depending on the parameters, a first or second order transition might be observed. This is schematically shown in the inset of Fig. 2 (solid line).

Schmidt-Binder formalism.—While FH free energy describes the phase separation process in bulk it cannot be directly applied to study segregation close to an interface
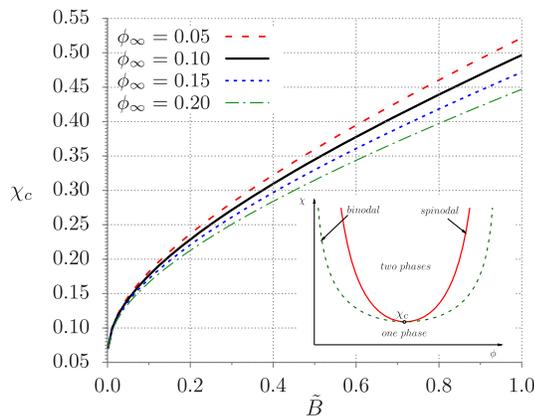
FIG. 2. The variation of χ_c on the elastic modulus $\tilde{B}$ of a phase separating the binary mixture with elastic interactions for different values of the bulk migrant volume fraction ϕ_∞. Main figure shows χ_c increases with $\tilde{B}$ (as $\sim\sqrt{\tilde{B}}$) indicating that softer systems are more susceptible to phase separation and decreases with ϕ_∞ for a fixed $\tilde{B}$. Inset shows phase diagram of polymer mixtures without elastic interactions (see text).

that is exposed to atmosphere. Cahn's [8] seminal work provides a cue in this case. This framework offers a way of calculating the concentration profile of a fluid near a wall, given a limiting fluid concentration, using the calculus of variations. The Flory-Huggins as well as Cahn's theory have successfully been combined into a single mean field description to describe the surface segregation of binary polymer mixtures by Schmidt and Binder [12] (referred as SB henceforth). The SB free energy functional for a semi-infinite system ($z > 0$) with a surface that is selectively attractive to component A having area A at $z = 0$ is given by

$$\frac{F_{SB}[\phi]}{A k_B T} = \int_0^\infty dz \left\{ \frac{F_{fh}[\phi]}{k_B T} + k(\phi)\left(\frac{d\phi}{dz}\right)^2 - \Delta\mu\phi \right\} + F_s(\phi_1),$$

(2)

where $k(\phi) = [a^2/36\phi(1-\phi)]$ is the coefficient associated with the energetic cost of creating a concentration gradient (obtained within the random phase approximation [12,13,16]), and $\Delta\mu$ models the exchange chemical potential. The SB functional also incorporates the surface free energy gain of the migrant $F_s(\phi_1)$ expressed as a polynomial expansion of the migrant volume fraction at the surface, [$\phi_1 = \phi(z = 0)$] and is given by $F_s(\phi_1) = -\phi_1\mu_1 - (g/2)\phi_1^2$, where μ_1 is the surface chemical potential and the coefficient g characterizes the change in bulk interactions due to the surface [12,17]. Within the gamut of square gradient theory the free energy functional in Eq. (2) can be minimized $\delta F_{SB}[\phi]/\delta\phi = 0$, to yield an integral expression for $z(\phi)$, which can be inverted to obtain the concentration profile of the migrant $\phi(z)$ [12]. For small values of χN an exponentially decaying profile shows reasonable agreement with experimental data [1].

Elastic Flory-Huggins theory.—We now explore the role of polymer matrix elasticity in the small molecule migration process. If one component (B polymer in our case) forms an elastic network as in cross-linked gels (reticulated permanent network), then its entropic contribution to the FH mixing free energy would be negligible in comparison to that of the migrant. Assuming the Flory-Rehner form of free energy [18] describing the energy cost of a migrating oligomer as it pushes its way through the matrix, the Flory Huggins elastic free energy F_{fhe} can be written as

$$\frac{F_{fhe}}{k_B T} = \frac{\phi\log(\phi)}{N_A} + \chi\phi(1-\phi) + \frac{F_{el}}{k_B T},$$

(3)

where $F_{el} = \tilde{B}(n/2)[\lambda^2 + (2/\lambda) - 3]$, modeling uniaxial network deformation [15,19,20], with λ representing the relative chain extension ($\lambda = (1 - \phi/1 - \phi_\infty)$), n the number density of chains in the network ($n = 1 - \phi_\infty$) [20], and $\tilde{B}$ the elastic modulus. The free energy that describes the small molecule migration through a matrix where elastic effects have been explicitly incorporated is therefore given by

$$\frac{F_{\text{tot}}[\phi]}{Ak_BT} = \int_0^\infty dz \left\{ \frac{F_{fhe}}{k_BT} + k(\phi)\left(\frac{d\phi}{dz}\right)^2 - \Delta\mu\phi \right\} + F_s(\phi_1),$$

$$(4)$$

where F_{fhe} is the elastic Flory Huggins functional in Eq. (3) and the gradient, exchange chemical potential, and surface contributions to the free energy is the same as the SB free energy functional in Eq. (2).

The role of elasticity in the phase separation of binary polymer mixtures where both species are cross-linked has been investigated earlier [21–23]. Such a system shows microphase separation and is different from the functional proposed here [Eq. (4)].

Before discussing the surface segregation process, we consider the bulk thermodynamic behavior of the system described by Eq. (3). This can be obtained easily by minimizing the elastic FH free energy with respect to ϕ. The minimization procedure leads to a relation between ϕ and χ, which for bulk concentration ϕ_∞ corresponds to the binodal curve $\chi = [1 - \log(\phi_\infty) - N_A\Delta\mu]/[N_A(1 - 2\phi_\infty)]$. It is interesting to note that the χ parameter does not depend on the elastic modulus $\tilde{B}$. The critical value of χ_c above which the mixed phase is unstable, obtained from the relation $\partial^3 F_{fhe}/\partial\phi^3 = 0$, however, increases with increasing $\tilde{B}$. This is shown in Fig. 2 with $\chi_c \sim \sqrt{\tilde{B}}$ for different values of ϕ_∞. As shown in Fig. 2 χ_c decreases with increasing ϕ_∞ for a fixed $\tilde{B}$. This can be understood as follows. As the volume fraction of the migrant increases, the available free volume decreases and, hence, entropy decreases. Since a balance between entropic and enthalpic contributions dictates the equilibrium, a lower value of enthalpy (and hence lower χ) is required to bring about the phase separation. With χ_c increasing with $\tilde{B}$ the single phase region of a rigid system is stable for larger values of χ in comparison to polymer mixtures without elastic interactions. The phase behavior of the binary polymer mixture without matrix elasticity is shown in the inset of Fig. 2.

Surface segregation for elastic FH theory.—The SB formalism outlined earlier can be used to compute the concentration profile of the migrant $\phi(z)$ close to the interface for the phenomenological free energy functional described by Eq. (4). Figure 3 shows migrant concentration profiles for both systems, a symmetric binary polymer mixture having a bulk concentration $\phi_\infty = 0.05$ with and without elastic interactions. The inset shows $\phi(z)$ as a function of depth z for different values of χ for $N_A = N_B = 10$ in the absence of elasticity [obtained by minimizing Eq. (2)]. For smaller values of χ [−0.78 (red dashed line)] an approximate exponentially decaying profile is observed. As χ increases, migrant concentration reaching the surface increases monotonically ($\chi = 0.320, 0.325$) and beyond a critical value $\chi_c = 0.327$ a macroscopic wetting layer is observed. In contrast, when elastic interactions are included (main panel Fig. 3), the migrant fraction for the same value
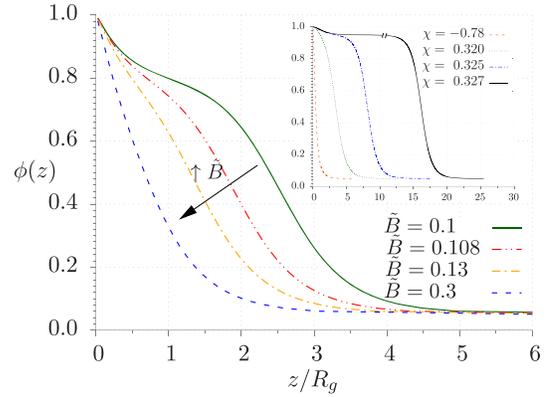
FIG. 3. Migrant concentration profiles $\phi(z)$ for the SB model including the elasticity obtained by minimizing Eq. (4) for ($\chi = 0.320$ and $N_A = 10$) and increasing $\tilde{B}$. A wetting transition is not observed in this model. Inset shows concentration profiles for the SB model without elasticity for the symmetric case $N_A = N_B = 10$ with increasing χ. The black solid line with a break indicates the formation of a macroscopic wetting layer.

of miscibility parameter χ (0.320), obtained by integrating the area under the curve $\phi(z)$ decreases monotonically with increasing $\tilde{B}$. For lower values of the modulus, $\tilde{B} = 0.1$, 0.108 a shoulder (reminiscent of a rounded wetting transition) is observed. For higher values of $\tilde{B}$ (0.13, 0.3) an exponentially decaying profile is obtained, suggesting elastic interactions severely inhibiting migration.

While physically intuitive and relatively straightforward to implement, the SB model has some disadvantages. First, the surface migrant fraction ϕ_1 is an additional input and cannot be calculated from the model. In order to establish our main result, namely, that elastic interactions inhibit surface migration as the matrix rigidity is increased, we employ a self-consistent field theoretic approach where this limitation does not exist. However, both the SB model and the SCFT framework suffers from the limitation that the bulk volume fraction ϕ_∞ is held constant, no matter how much material flows to the surface. Modifications to the SB and SCFT framework that do not suffer from this drawback will be reported elsewhere [24].

Self-consistent field theory.—First introduced in the context of polymers by Edwards [25], self-consistent field theory (SCFT) has been successfully employed to solve equilibrium behavior of polymeric systems [26]. We employ the SCFT formalism developed for end absorbed polymer brushes in polymer matrices [27,28] and adapt it to our situation (see Supplemental Material [20]).

The concentration profile of the migrant as a function of distance from the surface (in units of R_g) obtained from the SCFT calculation is shown in Fig. 4 for a miscibility parameter $\chi = 0.22$ and surface energy $F_s = -2.0$. The migrant polymer has a Kuhn length $a = 1$ and a degree of polymerization $N_A = 10$. As the elastic modulus of the matrix $\tilde{B}$ is increased (from 0.001 to 0.11) the amount of
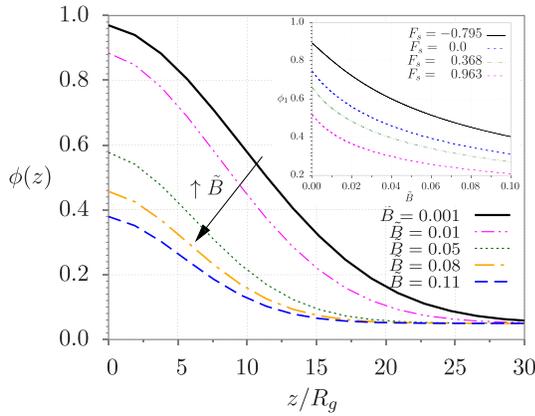
FIG. 4.   Migrant concentration profiles $\phi(z)$ for different elastic moduli $\tilde{B}$ of the polymer matrix. The amount of material flowing to the surface decreases with increasing $\tilde{B}$. The dependence of the surface fraction ϕ_1 as a function of $\tilde{B}$ for different surface free energy F_s is shown in the inset. As expected, the volume fraction decreases for system with higher F_s.

FIG. 5.   Cahn construction showing first order wetting transition for the Flory Huggins free energy functional, F_{fh} [Eq. (1)]. An intersection between $F_{fh}(\phi_1)$ and $F'_s(\phi_1)$ at three points demarcate areas S_1 and S_2, such that $S_1 > S_2$ indicates a first-order wetting transition. A similar graphical construction for the elastic Flory-Huggins functional F_{fhe} [Eq. (3)] with $\tilde{B} = 0.17$ shows one intersection, indicating the absence of the wetting transition.

material migrating to the surface decreases monotonically. In contrast to the SB model where ϕ_1 is an additional input, [($\phi_1 = 1.0$) in Fig.(3)], it can be calculated within the SCFT framework. Figure 4 shows ϕ_1 decreasing monotonically with increasing $\tilde{B}$. The inset in Fig. 4 shows the variation of the migrant concentration at the surface ϕ_1 as a function of $\tilde{B}$ for different values of the surface energy F_s. The effect of elasticity on the migrant fraction ϕ_1 is more pronounced for low values of $\tilde{B}$, ($\approx 0 - 0.02$). As expected, ϕ_1 decreases with increasing surface free energy F_s for a given value of $\tilde{B}$. For the elastic systems considered here, a wetting transition is not observed. A direct comparison between the parameters in the SB model and a variant of the SCFT method presented here [29] is currently underway.

Cahn construction.—A geometric way of demonstrating the absence of a wetting transition has been proposed by Cahn [8,9] and applied in the context of binary polymer mixtures [30]. A calculation of the surface migrant concentration ϕ_1 involves solving the equation

$$F'_s(\phi_1) = \sqrt{k(\phi_1)F(\phi_1)}, \qquad (5)$$

where $k(\phi)$ has the same meaning as Eq. (4), and $F(\phi_1)$ refers to the F_{fh} for the SB model and F_{fhe} when elastic interactions are present. A graphical method of solving Eq. (5) is shown in Fig. 5, plotting the surface $F'_s(\phi_1)$ (blue solid line) for $\mu_1 = -0.5$ and $g = 0.4$, and bulk free energy contributions $\sqrt{k(\phi_1)F(\phi_1)}$ as a function of ϕ_1 for a system with (red dashed line) and without (green dash dotted line) elastic interactions. In the absence of elasticity $\tilde{B} = 0$ the curves intersect at three points, demarcating areas S_1 and S_2. The area difference is related to the spreading coefficient $S = S_1 - S_2$, such that $S_1 > S_2$

indicates the formation of a complete wetting layer. For a finite value of $\tilde{B}$ (0.17 in Fig. 5) the wetting transition is absent [8,9].

Conclusion.—In conclusion, we have analyzed the role of matrix elasticity on the surface migration of small molecules in binary polymer mixtures (with the matrix being a reticulated gel), proposing a phenomenological free energy functional and using mean field and self-consistent field theories. We have shown that increasing the rigidity of the matrix leads to significant reduction of the migrant fraction on the surface. Further, by increasing the elastic modulus of the polymer matrix a wetting transition can be avoided for systems having miscibility parameters in the range that would otherwise have led to it. This provides a novel way of controlling surface migration in complex industrial formulations such as adhesives in hygiene products where surface migration leads to decreased product functionality. To the best of our knowledge, the only experimental system (despite significant differences) related to the theory presented here investigates segregation processes in polystyrene networks [31]. A theoretical formalism that starts from a microscopic Hamiltonian incorporates long-ranged elastic interactions in heterogeneous matrices and employs field theoretic techniques to arrive at a coarse-grained free energy functional similar to the one proposed is beyond the scope of the current work and will be pursued elsewhere. We hope that our theoretical work will prompt more theoretical and experimental studies in this direction.

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[1] R. A. L. Jones and R. W. Richards, *Polymers at Surfaces and Interfaces* (Cambridge University Press, Cambridge, England, 1999).

[2] A. Budkowski, Adv. Polym. Sci. **148,** 1 (1999).

[3] Y. Lipatov, Prog. Polym. Sci. **27,** 1721 (2002).

[4] P. Lonchampt and R. W. Hartel, Eur. J. Lipid Sci. Technol. **106,** 241 (2004).

[5] K. Bhunia, S. S. Sablani, J. Tang, and B. Rasco, Compr. Rev. Food Sci. F **12,** 523 (2013).

[6] M. Geoghegan and G. Kraush, Prog. Polym. Sci. **28,** 261 (2003).

[7] K. Binder, Acta Polym. **46,** 204 (1995).

[8] J. Cahn, J. Chem. Phys. **66,** 3667 (1977).

[9] P.-G. de Gennes, Rev. Mod. Phys. **57,** 827 (1985).

[10] D.-K. Pan and W. M. Prest, J. Appl. Phys. **58,** 2861 (1985).

[11] R. A. L. Jones *et al.*, Europhys. Lett. **12,** 41 (1990).

[12] I. Schmidt and K. Binder, J. Phys. II (France) **46,** 1631 (1985).

[13] R. A. L. Jones, E. J. Kramer, M. H. Rafailovich, J. Sokolov, and S. A. Schwarz, Phys. Rev. Lett. **62,** 280 (1989).

[14] U. Steiner, J. Klein, E. Eiser, A. Budkowski, and L. J. Fetters, Science **258,** 1126 (1992).

[15] M. Rubinstein and R. Colby, *Polymer Physics*, 1st ed. (Oxford University Press, New York, 2009).

[16] P.-G. de Gennes, *Scaling Concept in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[17] R. A. L. Jones, Phys. Rev. E **47,** 1437 (1993).

[18] P. J. Flory and J. Rehner, J. Chem. Phys. **11,** 521 (1943).

[19] L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed. (Clarendon Press, Oxford, 2005).

[20] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.116.208301 for detailed derivation of the elastic free energy, and the self consistent field theory.

[21] P.-G. de Gennes, J. Phys. (Paris) **40,** L69 (1979).

[22] D. J. Read, M. G. Brereton, and T. C. B. McLeish, J. Phys. II (France) **5,** 1679 (1995).

[23] N. Clarke, T. C. B. McLeish, S. Pavawongsak, and J. Higgins, Macromolecules **30,** 4459 (1997).

[24] J. Krawczyk, S. Croce, and B. Chakrabarti (to be published).

[25] S. F. Edwards, Proc. Phys. Soc. London **85,** 613 (1965).

[26] G. Fredrickson, *Equilibrium Theory of Inhomogeneous Polymers*, 1st ed. (Oxford University Press, New York, 2006).

[27] K. R. Shull and E. J. Kramer, Macromolecules **23,** 4769 (1990).

[28] K. R. Shull, J. Chem. Phys. **94,** 5723 (1991).

[29] J. Genzer, A. Faldi, and R. J. Composto, Phys. Rev. E **50,** 2373 (1994).

[30] A. Budkowski, F. Scheffold, J. Klein, and L. J. Fetters, J. Chem. Phys. **106,** 719 (1997).

[31] M. Geoghegan, F. Boué, A. Menelle, F. Abel, T. Russ, H. Ermer, R. Brenn, and D. G. Bucknall, J. Phys. Condens. Matter **12,** 5129 (2000).