The wetting transition for polymer mixtures

R. A. L. Jones
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
(Received 17 June 1993)

The location of the wetting transition in symmetric polymer blends is calculated as a function of the degree of incompatibility and the difference in surface energy between the pure components, using mean-field (square-gradient) theory, coupled with a lattice model for the bare surface energy. The conditions for second-order wetting are discussed.

(Keywords: surfaces; blends; wetting)

INTRODUCTION

Consider the two coexisting phases of an immiscible polymer blend in contact with a free surface or an inert wall. Two situations are possible: (i) the two phases may meet at the surface or wall with a finite contact angle; or (ii) a layer of the phase with lower surface or wall energy may separate the other phase from the surface or wall, forming a wetting layer. Which situation occurs at equilibrium is determined by the classical Young–Dupre equation, which gives an expression for the contact angle, θ_c, in terms of the surface energies of the two phases, σ_A and σ_B, and the interfacial energy, σ_{AB}:

$$\sigma_{AB} + \sigma_A \cos\theta_c = \sigma_B \qquad (1)$$

When this contact angle is equal to zero, we have complete wetting (see *Figure 1*). Cahn pointed out[1] that, as one approaches a critical point, the interfacial energy goes to zero more quickly than the difference in the surface energy between the two phases; thus there will always be a transition between the non-wet and the wet state—this is a thermodynamic phase transition known as the wetting transition. Such transitions have been observed in a variety of small-molecule liquid mixtures, and there has now been a wealth of theoretical work in this area[2]. However, the importance of wetting phenomena has not yet been widely recognized in the area of polymer mixtures, despite their relevance to a wide range of commercially important areas, for example the nature of the interphase in composite materials[3], self-stratification in coatings based on polymer mixtures[4] and the dynamics of polymer film coating processes. The original Cahn argument applies as well to polymer mixtures as to small-molecule liquid mixtures, but there are two important new features in the polymer case. First, in small molecules the transition occurs rather close to the critical point (hence a common term for the phenomenon is 'critical-point wetting'); in polymers, however, because the interfacial tension between immiscible polymer phases is always rather small, the wetting transition is usually expected to occur a long way from criticality (this point was first recognized by Schmidt and Binder[5]). The second new feature is that in polymers we have two extra variables at our disposal, namely the molecular weights of the polymers. This means that we can have a wetting transition as a function of molecular weight in immiscible polymer mixtures. This may well have important consequences when one is attempting to achieve desirable wetting properties for a coating, in that control of wetting properties by molecular weight may well be more practically realizable than, for example, control by temperature or the strength of the surface interaction.

The emphasis of this paper is on the use of well established, and relatively simple, theory to calculate the location of the wetting transitions and to present the results in a form that can easily be used by experimentalists. The theory used is an adaptation of the van der Waals/Cahn theory[1], using Flory–Huggins theory to describe the bulk thermodynamics, and a square-gradient coefficient derived from the random-phase approximation[6]. This type of theory has been already been used by Nakanishi and Pincus[7] and Schmidt and Binder[5] to make calculations of the wetting phase diagram of polymer blends. The aim of this paper is threefold. First, I will present the results of explicit calculations of the location of the wetting transition in two-component polymer mixtures with equal molecular weights, at a level of approximation that neglects the effect of the surface in modifying bulk interactions; this is valid in the limit of high molecular weight. At this level of approximation a single curve locates the wetting transition at a given degree of incompatibility for a given reduced surface-energy difference. I then use a simple lattice model, which has already been used to account for surface segregation in polymer blends in the one-phase regime[8], to relax this approximation. Finally, I will use the same lattice-based model to explore the question of the order of the wetting transition, explicitly calculating the line of tricritical points that separate those conditions in which the transition is first-order from those in which it is second-order. It is hoped that these calculations may guide the experimental search for second-order wetting, which has still not been definitively observed in any system, polymer or non-polymer.

0032-3861/94/10/2160–07