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# Morphology, Cocontinuity, and Conductive Properties of Anisotropic Polymer Blends

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Blending of polymers is a common method to produce engineering materials with novel property profiles. It is well-established that properties depend crucially on morphology, which in turn depends on flow conditions during blending and subsequent processing. An appreciation of the influence of morphology on polymer blend properties is a major element in providing a better framework within which to predict, control, and change macroscopic properties via polymer blending technology. In the processing of polymer blends, two steps are involved: the first step is melt blending of the two polymers using a batch mixer or continuous extruder, and the second step is shaping using fabrication equipment such as an injection moulding machine. Invariably, the morphology of the resultant blend is effected by the processing conditions; in particular, the blend exhibits an anisotropic structure due to shear during the melt mixing and final moulding. Numerous studies of polymer blends have addressed the problem of morphology development, with emphasis on rheological and thermodynamic considerations (see e.g., Utracki[1]). In contrast, the properties of polymer blend systems have been correlated simply with component selection and composition ratio variation rather than morphological features. One reason for this has been the lack of a suitable model representation of blend morphology. In a recent paper,[2] we showed that an approach originally due to Cahn[3] and its extensions[4] provides a natural description of the morphology of isotropic cocontinuous blends and for interfacial films contiguous to the blend phases. In this paper, we extend our previous work to the generation of realistic *anisotropic* blend morphologies. We report the percolation thresholds and evaluate the anisotropic conductive properties of model two-phase blends as a function of component volume fraction. We show that the interpretation of dual-phase continuity from two-dimensional images is flawed. We show a simple theory for conductive properties which provides a good approximation to the observed behavior for blend morphologies.

Cahn's approach[3] was originally developed to describe the morphologies associated with spinodal decomposition. It is therefore a natural choice for describing the morphology of polymer blends generated by phase separation. In the original scheme due to Cahn,[3] one associates an interface between two material phases of uniform density with a level set (or isosurface) of a random standing wave $y(\mathbf{r})$, composed of $N$ sinusoids with fixed wavelength $\lambda = 2\pi/k$ but random directions $\hat{\mathbf{k}}_n$, phase constants $\phi_n$ and amplitudes $A_n$, $y(\mathbf{r}) = (N)^{-1/2}\sum_n A_n \cos(k\hat{\mathbf{k}}_n\cdot\mathbf{r} + \phi_r)$. As $y(\mathbf{r})$ is positive as often as it is negative, a 50/50 (isometric) blend coincides with the zero set of $y(\mathbf{r})$. The resultant morphology is characterized by an undulating interface of consistent curvature and exhibits two similar phase structures.[3,5]

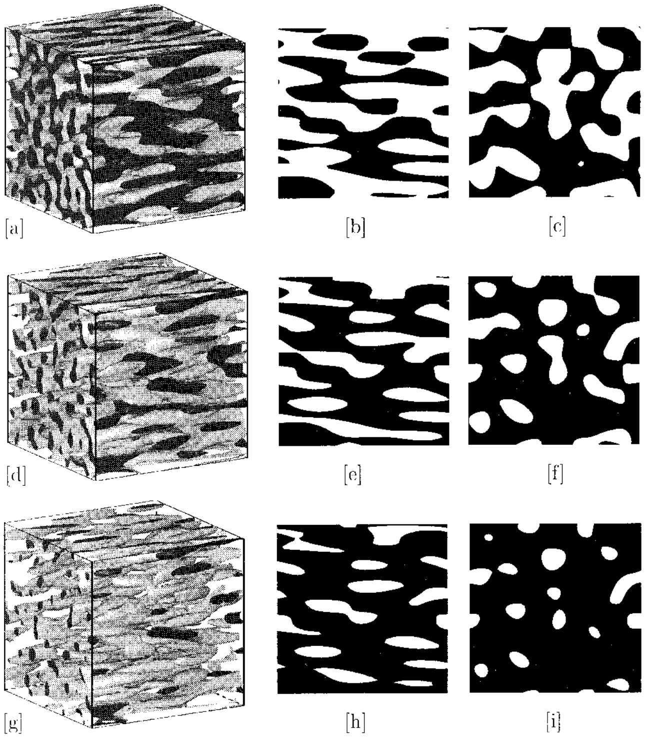

**Figure 1.** Three dimensional model morphology and two-dimensional projections for the anisotropic model. (a−c) 50/50 blend. (d−f) 30/70 blend. (g−i) 15/85 blend. Parts b, e, and h are projections along the extrusion plane. Parts c, f, and i are projections perpendicular to the plane. Comparison of parts a and g with experimental images (e.g., Figures 5 and 6 of Verhoogt[6]) gives an excellent qualitative match. Note, however, the difficulty in interpreting cocontinuity from two-dimensional images. In parts e and h, it is not obvious from the 2D images whether the system is cocontinuous. The full 3D rendering shows that the system is certainly cocontinuous.

Anisotropic media are developed by either shortening or elongating the period of the wave along one axis by a stretching factor $A$. An example of a 50/50 blend with a stretching factor of 4.0 is shown in Figure 1a. The morphology of processed polymer blends has been characterized in three dimensions by confocal laser scanning microscopy.[6] The structure shown in Figure 1a qualitatively replicates the morphology of these blends (compare to Figure 5 of Verhoogt et al.[6]). Varying the position of the level cut allows one to vary the blend ratios of the two phases; in Figure 1, we show the morphologies of the model at different blend ratios in three dimensions and in two dimensions along and perpendicular to the stretched axis (the extrusion plane). The model morphologies give a realistic representation of polymer blend morphology in both three[6] and two dimensions.[7−12]

The continuity of phases has a great impact on the resultant macroscopic properties of blends. At a critical blend ratio, the morphology changes from a three-

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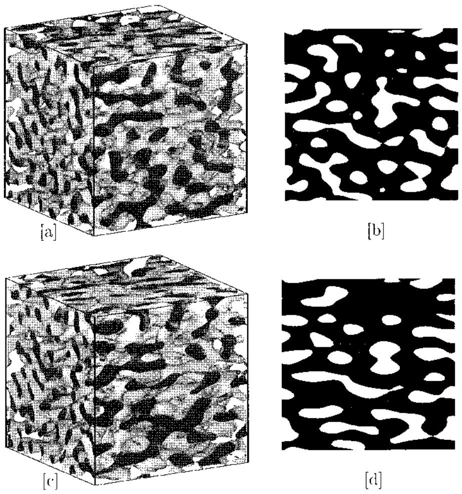

**Figure 2.** Comparison of 30/70 blends in 3- and 2D for different anisotropy ratios. (a) and (b), $A = 1.5$. (c) and (d) $A = 2$. Again, it is not obvious from the 2D images whether the minority phase is cocontinuous.

dimensional cocontinuous network to discrete inclusions of one phase dispersed within another. A key morphological factor in determining physical properties of binary blends is the position of the percolation threshold $\phi_c$ ; the volume fraction at which one component first forms a continuous phase. We evaluate[13] the values of $\phi_c$ in the directions parallel and perpendicular to the extrusion axis. The threshold for both directions is given by $\phi_c = 12.7 \pm 0.5\%$; i.e., stretching does not alter the connectivity of the model.

From the morphology of the *two*-dimensional cuts shown in Figure 1, one would perhaps not expect such low phase fractions to exhibit cocontinuous morphologies. For example, in Figure 1h, one would interpret the 2D morphology *clearly* to be that of ellipsoids of the minority phase dispersed in the majority phase. However, from the three-dimensional image and the value of $\phi_c$, we find that the system is *cocontinuous* along each axis. This would be difficult to discern from the 2D images alone. Clearly, interpretation of dual-phase continuity is difficult from 2D images.

Similarly, consider the two-dimensional images of a model 30/70 blend at different stretching factors $A$ (Figures 1e,f and 2b,d). These morphologies for different $A$ compare well to micrographs of 30/70 blends from the literature; e.g., compare to Figures 3−5 of Yang and Han[11] and Figure 1 of Heeschen.[14] In all cases the morphology is made up of discrete *two*-dimensional domains of the minority phase in a continuous majority matrix. Based on these 2D images, the experimental blend morphology in 3D has been interpreted as dispersed minority phase.[11,14] However, in all cases for the model morphology, the blends are *strongly* cocontinuous (see Figures 1d and 2a,c). The full 3D rendering of the image illustrates this high degree of interconnectivity and macroscopic cocontinuity of the system. This result highlights the caution required when interpreting dual-phase continuity from 2D images and the advantages of full 3D images of blend morphologies.

Knowledge of the dual-phase threshold may help in the design of blended materials. The percolation threshold is particularly important in the design of conducting polymer composite materials. Percolation of a continuous conducting phase in an insulating matrix is required to achieve conductivity throughout the sample. The electrical conductivity of polymer blends can be increased by dispersing a conductive filler throughout the polymer matrix or by blending soluble conducting polymers in solution with insulating polymers. Furthermore, the suppression of the percolation threshold is desirable in conducting polymer blends, as an excessive amount of filler may often distort other properties of the matrix material. Anisotropy also has a strong influence on the conductivity; specifically, the conductivity is increased along the direction of the extrusion axis, thereby reducing the volume fraction of the conductive filler necessary to achieve a desired conductivity. Quantitative studies of the interplay between the percolation threshold, anisotropy, and conductivity may assist in the design and development of blends with *macroscopically* anisotropic properties.

To date, frameworks for the prediction of conductive properties of polymer blends have been based on simple theoretical models that correlate the conductivity to the blend ratio. Depending on the detail of the composite microstructure, different theories may be needed to obtain good agreement with measured conductive properties. We compare some simple theories to measured properties on our model morphologies.

We begin with a discussion of isotropic morphologies. In the simplest case for cocontinuous blends, the conductivity of the resultant blend is assumed to be either a parallel or series combination of the individual conductivities of the matrix and filler $\sigma_m$ and $\sigma_f$;

$$\sigma_{\text{eff}} = \phi_f \sigma_f + \phi_m \sigma_m \tag{1}$$

$$\frac{1}{\sigma_{\text{eff}}} = \frac{\phi_f}{\sigma_f} + \frac{\phi_m}{\sigma_m} \tag{2}$$

This simplistic model was used to correlate conductivity with morphology of an experimental blend of polymers with strongly varying resistivity.[7] Assuming the two phases are cocontinuous for 70/30 and 50/50 mixtures they used eq 1 to model the data. At 30/70, they assume the minority phase is discontinuous and use eq 2. Their fit to the data is poor. At best, eqs 1 and 2 represent primitive bounds on properties. A simple and convenient framework for the prediction of conductive properties of disordered materials is based on the effective medium theory[15] (EMA). In the EMA, spherical grains of conductivities $\sigma_m$ and $\sigma_f$ are assumed to be embedded in an unspecified medium of conductivity $\sigma_{\text{eff}}$. The choice of the conductivity of the effective medium is such that the average field acting on a grain of one phase due to all other phases averages to zero; the two components are treated in a symmetric manner and the effective conductivity is given by the following equation:

$$\phi_f \frac{\sigma_f - \sigma_{\text{eff}}}{\sigma_f + 2\sigma_{\text{eff}}} + \phi_m \frac{\sigma_m - \sigma_{\text{eff}}}{\sigma_m + 2\sigma_{\text{eff}}} = 0 \tag{3}$$

We show in Figure 3 a comparison of the conductivity of our model isotropic blend with prediction of eqs 1−3 for two different conductivity contrasts (10/1 and 10000/1). The EMA gives an excellent fit over all volume fractions at low contrast. At higher contrasts, the EMA gives a better fit than eqs 1 and 2 but is unfortunately restricted to media which percolate over the limited range $^1/_3 < \phi < ^2/_3$. Accordingly, since $\phi_c \simeq 0.13$ for the isotropic field, the prediction of the theory for higher contrast ratio is less satisfactory at concentrations $\phi < ^1/_3$.

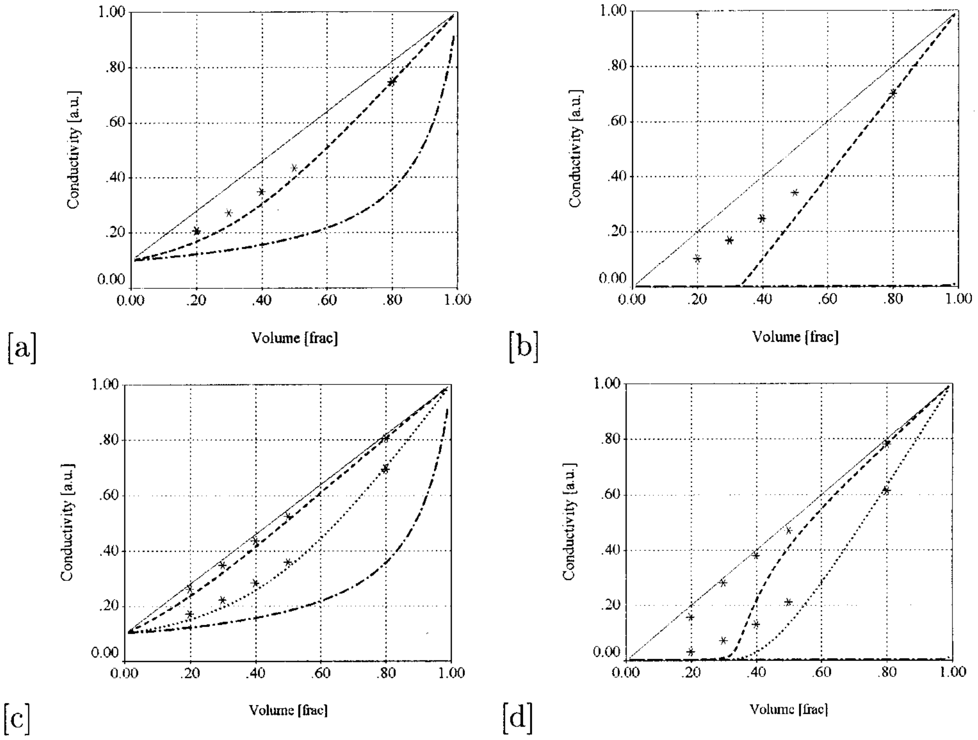

**Figure 3.** Prediction of series and parallel approximations and the EMA for different anisotropy factors and different phase contrasts. (a) Isotropic, $\sigma_1/\sigma_2 = 10$ and (b) isotropic, $\sigma_1/\sigma_2 = 10^4$. The thin solid line is eq 1, the dot-dashed line is eq 2, the dashed line is eq 3, and data points are from simulation. (c) Anisotropic ($A = 4$), $\sigma_1/\sigma_2 = 10$. (d) Anisotropic ($A = 4$), $\sigma_1/\sigma_2 = 10^4$. The dashed and dotted lines give predictions for eq 4 parallel and perpendicular to the extrusion axis, respectively.

Generalizing EMA to anisotropic media yields[16]

$$\frac{\phi_{\mathrm{m}}(\sigma_{\mathrm{m}} - \sigma_i)}{1 + \Lambda_i(\sigma_{\mathrm{m}} - \sigma_i)} + \frac{\phi_{\mathrm{f}}(\sigma_{\mathrm{f}} - \sigma_i)}{1 + \Lambda_i(\sigma_{\mathrm{f}} - \sigma_i)} = 0 \qquad (4)$$

where $\Lambda_i = L_i/\sigma_i$ and $2L_2 = 1 - L_1$. $L_1$ and $L_2$ depend on the ratio $\alpha = \sigma_2/\sigma_1$, with $\sigma_1$ and $\sigma_2$ the effective conductivities parallel and perpendicular to the extrusion axis. The relevant equations are eccentricity $e = [1 - \alpha(a/b)^2]^{1/2}$ and $L_2 = [(1 - e^2)/2e^3]\{\log[(1 + e)/(1 - e)] - 2e\}$. As in the isotropic case, the conductivity vanishes as $\phi \rightarrow {}^1/_3$. We show in Figure 3c,d the EMA prediction for anisotropic media with a stretching factor of 4.0. The EMA again shows good agreement at low contrasts and less satisfactory agreement at higher contrasts and low volume fractions due to the EMA's poor estimate of $\phi_c$. For high contrast, the conductivity parallel to the stretched axis fits the upper bound (eq 1) well. In general, however, the use of the EMA provides a better estimate of blend conductivity than the approximation in eqs 1 and 2.

Relating the realistic *complex* morphology of a polymer blend to observed macroscopic properties has appeared overwhelmingly difficult. In this communication, we have shown that a simple, physically plausible model allows one to generate realistic anisotropic morphologies for extruded two-phase blends. The percolation thresholds of the model morphologies have been evaluated. We have illustrated the problems associated with the quantitative interpretation of dual-phase continuity from two-dimensional images and derived anisotropic conductivities. We have shown that the EMA provides a good approximation to the observed conductive properties for model morphologies of two-phase blends. The general strategy outlined here is not limited to conductive properties; we are currently considering the mechanical and optical properties of these model morphologies. The aim is an understanding of the influence of morphology on various macroscopic properties to help provide a framework within which to predict and control properties of polymer blends.

## References and Notes

(1) Utracki, L. A. Polymer Blends and Alloys: Thermodynamics and Rheology; Hanser: Munich, Germany, 1989.
(2) Knackstedt, M.; Roberts, A. P. *Macromolecules* **1996**, *29*, 1369.
(3) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(4) Berk, N. F. *Phys. Rev. Lett.* **1987**, *58*, 2718.
(5) Roberts, A. P.; Knackstedt, M. *Phys. Rev. E* **1996**, *54*, 2313.
(6) Verhoogt, H.; van Dam, J.; de Boer, A. P.; Draaijer, A.; Houpt, P. M. *Polymer* **1993**, *34*, 1325.
(7) Ray, I.; Khastgir, D. *Polymer* **1993**, *34*, 2030.
(8) Hung, C.-C.; Carson, W. G.; Bohan, S. P. *Polym. Sci. B: Polym. Phys.* **1994**, *32*, 141.
(9) Li, L.; Sosnowski, S.; Chaffey, C. E.; Balke, S. T.; Winnik, M. A. *Langmuir* **1994**, *10*, 2495.
(10) Jinnai, H.; Nishikawa, T.; Hashimoto, T. *Macromolecules* **1995**, *28*, 4782.
(11) Yang, K.; Han, C. D. *Polymer* **1996**, *37*, 5795.
(12) Brown, G. M.; Butler, J. H. *Polymer* **1996**, *38*, 3937.
(13) The evaluation of $\phi_c$ for the model fields is dependent on the size of the system considered.[5,17] We evaluate $\phi_c$ for fields of side length $L = 32$, 48, 64, 96,and 128. Extrapolation to $L \rightarrow \infty$ gives the asymptotic value of $\phi_c$ in each case.
(14) Heeschen, W. A. *Polymer* **1995**, *36*, 1835.
(15) Kirkpatrick, S. *Rev. Mod. Phys.* **1973**, *45*, 573.
(16) Schwartz, L. *Phys. A* **1994**, *207*, 131.
(17) Roberts, A. P. Ph.D. Thesis, Australian National University, Canberra, ACT, 1995.

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