Morphology and Macroscopic Properties of Conducting Polymer Blends

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Morphological features of blends, the organizations of their domains, and the nature and form of their interfacial zones strongly influence macroscopic properties. The solid-state morphology of polymer blends has been well characterized by scanning electron microscopy techniques and more recently by confocal laser scanning microscopy.[1−3] Despite this characterization, properties of polymer blend systems are often correlated with component selection and component ratio variation rather than related to morphological features. One reason for this is the lack of a suitable representation of blend morphology. An approach originally due to Cahn[4] to simulate morphology influenced by spinodal decomposition in isotropic two-phase systems gives a realistic description of cocontinuous blend morphology. We show that an extension of this approach[5] provides a model morphology for an interfacial film or coating contiguous to the two blend phases. This is a natural description for several blend morphologies, in particular morphologies exhibited by low volume fraction conducting polymer blends.[6−9] From a statistical description of the morphology,[10,11] effective transport and elastic properties of the blend morphology are predicted. This allows for comparison with experiment.

The electrical conductivity of polymer blends can be increased by dispersing a conductive filler throughout the polymer matrix or by blending of soluble conducting polymers in solution with insulating polymers. The critical amount of filler necessary to build up a continuous conductive network and to make the material macroscopically conductive is referred to as the percolation threshold.[12] Classic percolation theory for a three-dimensional network of conducting hard-core spheres embedded in an insulating matrix predicts a percolation threshold at volume fraction $p \simeq 0.16$ and macroscopic conductivity given by $\sigma = \sigma_0(p - p_c)^t$, where σ_0 is the conductivity of the spheres, and the conductivity exponent $t = 2.0$ in three dimensions.[12] This threshold and conductivity behavior has been observed in several blends. Suppression of the percolation threshold is desirable in conducting polymer blends as an excessive amount may often distort other properties of the matrix material. Polymer blends have recently been reported to conduct at a much lower volume fraction of conducting component than expected theoretically for a random binary mixture of conducting and insulating hard spheres.[6−13] In one set of experiments, Gubbels et al.[6,7] decrease the percolation threshold of carbon black (CB) particles in polymers by selectively localizing carbon black within the multiphase material. In Table 1 we summarize their results for the percolation threshold and conductivity exponent for carbon black localized in one phase of a binary polyblend and then localized at the interface of the binary blend. Remarkably, in the latter case a percolation threshold of less than 0.5% is obtained.

Table 1

CB dispersed	exptl threshold (%)	conductivity exponent
within a single phase	3	1.5 ± 0.2
along the interface of two phases	<0.5	1.3 ± 0.2

A common explanation for the low threshold of conducting polymers is based on a double-percolation picture.[14,15] In this picture, the connectivity is heirarchical—based on a connected path within a connected path, the last of which is conducting. To two levels in the heirarchy, critical volume fractions of conducting phase in the blend of less than 3% can be realized. This is in agreement with experimental data in Table 1 for CB dispersed within the PE phase. To account for the much lower volume fractions of conducting phase (<1%), it was imaginatively proposed that the double-percolation picture be extended to multiple percolation.[15] While the argument readily gives critical volume fractions in agreement with that observed experimentally, the model is unnecessarily artificial. Moreover, it is difficult to reconcile the model with the reported experimental CB results as the experiments only consider *binary* polyblends with filler. In this Communication we show that the approach due to Cahn and its extensions provides a natural and quantitatively accurate description of the morphologies and properties exhibited by these low volume fraction conducting polymer blends.

Cahn's approach[4] 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,[4] one associates an interface between two material phases of uniform density with a level set (or contour) of a random standing wave $y(r)$, composed of N sinusoids with fixed wavelength $\lambda = 2\pi/k$ but random directions $\mathbf{k}_n$, phase constants ϕ_n, and amplitudes A_n, $y(r) = (1/N^{1/2}) \sum_n A_n \cos(k\mathbf{k}_n \cdot \mathbf{r} + \phi_r)$. As $y(r)$ is as positive as often as it is negative, a 50/50 (isometric) blend coincides with the zero set of $y(r)$. The resultant morphology is characterized by an undulating interface of consistent curvature and exhibits two similar phase structures (see Figure 1). The resultant morphology is evocative of the morphology of two-component blends as imaged by micrographic techniques. Blend ratios other than 50/50 can be easily defined within the model by varying the position of the level cut. The model structures exhibit a wide range of random cocontinuous morphologies similar to phase-separated liquids and porous glasses.[4]

Cahn's approach has been extended[5] to a description of the interspace between a pair of interfaces associated with two nearly level sets of the same wave. The volume between a pair of interfaces associated with two level sets of the same wave, say the level cuts $\alpha \le y(r) \le \beta$, is considered to be phase 1, while the two regions contiguous to this ($y(r) < \alpha$; $y(r) > \beta$) define a complementary bulk phase. Defining $\alpha \simeq -\epsilon$ and $\beta \simeq \epsilon$ with ϵ small, one has a natural description for an interfacial film or coating between the two isometric phases ($y(r) = 0$).[16] The resultant morphology exhibits a ribbon- or sheet-like structure and is characterized by a high degree of interconnectivity (see Figure 2). In the low conducting threshold systems of Gubbels et al.,[6,7] the CB phase remains locally at the interface between the binary polyblend. The model therefore qualitatively

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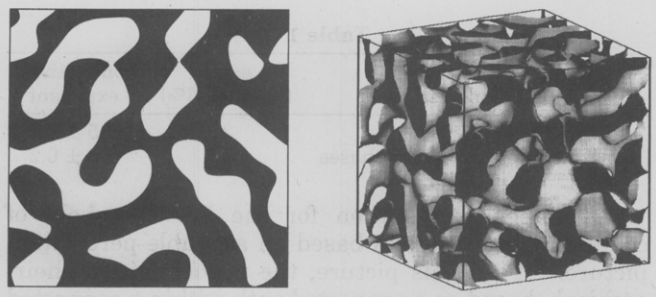

Figure 1. Model morphology given by Cahn's approach: (a) two-dimensional cut; (b) three-dimensional image.

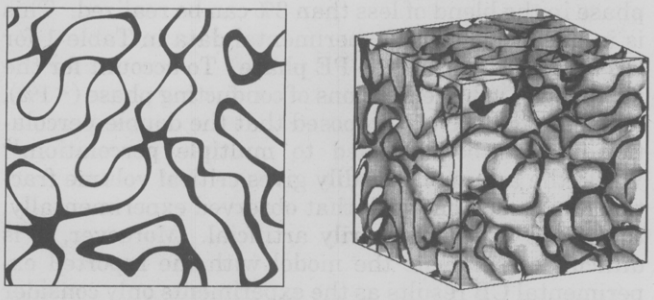

Figure 2. Model morphology given by extended Cahn's approach: (a) two-dimensional cut; (b) three-dimensional image. Note that the generating function for both (a) and (b) is the same as for the morphology illustrated in Figure 1. Now the interface between the two phases in Figure 1 is shown as one phase, the remainder as the second phase.

replicates the morphology of the blends with CB localized at the interface (see Figure 3 of ref 6 and Figure 10 of ref 7). Varying the position of the cuts for α and β, one can vary both the volume fractions of the two bulk phases and the volume fraction of the interfacial phase.

The volume fraction of conducting polymer required to coat the model interface is simply given as $(1/2)(S/V)d$, where S/V is the surface-to-volume ratio of the interfacial region and d is the film thickness. The surface-to-volume ratio is easily derived for any level cut of our field and is given by $S/V = (2/\pi)(\langle k^2 \rangle/3)^{1/2}(e^{-\alpha^2/2} + e^{-\beta^2/2})$.[17] From the micrographs in Gubbels et al.,[6] we estimate the characteristic wavelength $\lambda = 2\pi/k \simeq 10$ μm. Assuming a uniform CB film thickness of $d \simeq 100$ Å, we predict a critical volume fraction of the film phase to be $(S/V)d \simeq 0.15\%$. The value of the threshold from this simple argument is consistent with the experiments of Gubbels et al.[6,7]

From a statistical description of the morphology,[10,18] bounds on mechanical and transport properties can be derived[19] and computer simulation data for transport properties used to test the analytic predictions. We first consider the conductive properties of our model blend. In Figure 3 we show the predicted conductivity of a 50/50 insulative blend with a conductive filler at the interface (morphology of Figure 2) as a function of the concentration of filler.[20] From this figure the conductivity exponent t is measured and found to be 1.2 ± 0.2, again in agreement with experiment (Table 1) and consistent with percolation theory.

Other properties of the model blend can be derived over the full range of filler concentration for the identical morphology. For example, bounds on the mechanical properties of polymer morphologies are derived.[11,21] In Figure 3 we also show bounds on the bulk modulus κ_{eff} for the polymer blend assuming the bulk phases have modulus $\kappa_0 = 1$ and the filler localized at the interface has a $\kappa_1 = 0$.[20] Extrapolating to very low volume

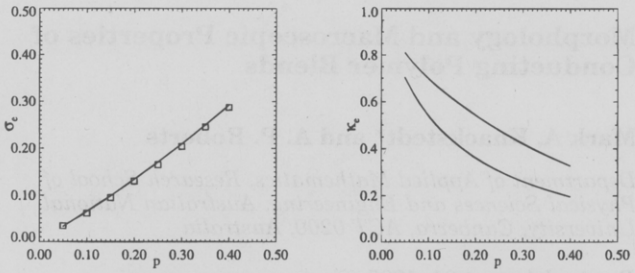

Figure 3. Prediction of conductivity σ_e and bulk modulus κ_e for the model morphology given in Figure 2 as a function of conductive filler concentration p. (a) Conductivity of blend, assuming conductivity of bulk polymer blend $\sigma_{bulk} \simeq 0$, and of conductive filler $\sigma_{CB} = 1.0$. The line corresponds to the upper bound and the squares denote simulation data. (b) Bounds on the bulk modulus of the blend assuming $\kappa_{bulk} = 1.0$ and $\kappa_{CB} = 0.05$.

Table 2

model	model threshold (%)	conductivity exponent
double percolation[15]	≥3	2.0–4.0
multiple percolation[15]	≥0.5	2.0–6.0
two-cut Gaussian	0.15	1.2 ± 0.2

fraction p of filler, we note that a small fraction of filler will have a minimal effect on the mechanical properties of the blend. This has been observed experimentally.

Until now, relating a realistic (complex) morphology of a polymer blend to observed macroscopic properties has seemed overwhelmingly difficult. In this Communication we have shown that simple, physically plausible model of the morphology of an interfacial film partitioning two bulk polymer phases can account for the very small observed conductivity transitions in carbon black filled polymer blends without the need to resort to unnecessarily artificial morphologies. The model also gives a conductivity exponent in agreement with experiment. Transport and mechanical properties across a large range of filler concentration have been derived. Mechanical, transport, and optical properties for a wider range of morphologies and component properties can also be derived via this method.[17]

References and Notes

(1) Verhoogt, H.; van Dam, J.; de Boer, A. P.; Draaijer, A.; Houpt, P. *Polymer* **1993**, *34*, 1325.
(2) Li, L.; Sosnowski, S.; Chaffey, C. E.; Balke, S. T.; Winnik, M. A. *Langmuir* **1994**, *10*, 2495.
(3) Jinnai, H.; Nishikawa, Y.; Koga, T.; Hashimoto, T. *Macromolecules*, submitted.
(4) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(5) Berk, N. F. *Phys. Rev. Lett.* **1987**, *58*, 2718.
(6) Gubbels, F.; Jerome, R.; Teyssie, P.; Vanlathem, E.; Deltour, R.; Calderone, A.; Parente, V.; Bredas, J. *Macromolecules* **1994**, *27*, 1972.
(7) Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Brouers, F.; Teyssie, P. *Macromolecules* **1995**, *28*, 1559.
(8) Wang, Y.; Rubner, M. *Macromolecules* **1992**, *25*, 3284.
(9) Reghu, M.; Yoon, C.; Yang, C.; Moses, D.; Heeger, A.; Cao, Y. *Macromolecules* **1993**, *26*, 7245.
(10) Roberts, A.; Teubner, M. *Phys. Rev. E* **1995**, *51*, 4141.
(11) Roberts, A.; Knackstedt, M. A. *Phys. Rev. E*, submitted.
(12) Stauffer, D.; Aharony, A. *Introduction to Percolation Theory*, 2nd ed.; Taylor and Francis: London, 1992.
(13) Fizazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, S.; Smith, P.; Heeger, A. *Phys. Rev. Lett.* **1990**, *64*, 2180.
(14) Sumita, M.; Sakata, K.; Hayakawa, Y.; Asai, S.; Miyasaka, K.; Tanemura, M. *Colloid Polym. Sci.* **1993**, *270*, 134.
(15) Levon, K.; Margolina, A.; Patashinsky, A. *Macromolecules* **1993**, *26*, 4061.

(16) This approach is similar to that proposed by Suzuki et al.,[22] who explained volume fraction conducting blends in terms of a film or coating on the surface of an interconnected insulating surface of fibrillar and lamellar crystals. In this model, they assumed the conducting polymer adsorbed onto a network with a rod and pancake morphology.
(17) Knackstedt, M.; Roberts, A., preprint, 1995.
(18) Teubner, M. *Europhys. Lett.* **1991**, *14*, 403.
(19) Torquato, S. *Appl. Mech. Rev.* **1991**, *44*, 37.
(20) Finite size effects preclude us from obtaining results at volume fractions less than 5%.
(21) Roberts, A. Diffusion-Controlled Growth and Transport in Random Composites. Ph.D. Thesis, Australian National University, June 1995.
(22) Suzuki, Y.; Heeger, A. J.; Pincus, P. *Macromolecules* **1990**, *23*, 4730.

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