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Random copolymers as effective compatibilizing agents

Dilip Gersappe and Anna C. Balazs
Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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We introduce a mean field model that allows us to determine the interfacial behavior of *AB* random copolymers. Through this model, we calculate the reduction in interfacial tension γ that occurs when the random copolymers localize at the interface between immiscible homopolymers *A* and *B*. We also isolate the conditions under which the random copolymers are most efficient at reducing γ and therefore act as efficient compatibilizers. The calculations are useful in designing low-cost copolymer additives that significantly improve the properties of polymer blends.

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A fundamental problem in fabricating high-strength polymer blends is that different homopolymers are normally immiscible and, as a result, phase separate into distinct, macroscopic domains. In order to improve the adhesion between the homopolymer phases, copolymer "compatibilizers" are added to the mixture. The copolymers localize at the interface between the two phases, lower the interfacial tension, and facilitate the dispersion of the incompatible homopolymers into smaller domains. Previously, diblock copolymers [1] were shown to be useful in reducing the interfacial tension. However, these copolymers are expensive to synthesize; consequently, their use in large-scale industrial processes is limited.

Random copolymers, on the other hand, are inexpensive to synthesize [2]. If these copolymers were shown to behave as effective compatibilizers, the findings would have a significant technological impact. A clue to the properties of these chains can be found in theoretical studies on the behavior of a single random copolymer chain at a fluid-fluid interface [3]. The studies revealed that the random copolymer weaves back and forth across the interface, forming large loops [3]. These loops could entangle with both the homopolymer phases and thereby enhance the strength of the interface. Experimental evidence seems to support this contention as recent experiments on reinforcing polymer-polymer interfaces with random copolymers showed a significant improvement in the strength of the interface [2].

To obtain further insight into the behavior of random copolymers, one must go beyond the single chain model and examine the properties of a finite volume fraction of copolymers at a homopolymer-homopolymer interface. Such studies would be difficult to carry out by either analytical calculations or computer simulations. With both these techniques, one models the interface between the two homopolymers as a sharp, flat region. This assumption limits the applicability of the predictions. Furthermore, interfacial tensions cannot readily be calculated from computer simulations. Here we introduce a self-consistent field lattice model that explicitly includes the effect of a random arrangement of monomers along the length of the chains. Using this model, we can now determine the efficiency of random copolymers as compatibilizing agents. In particular, we calculate the reduction in interfacial tension resulting from the presence of these random copolymers. We also examine the effects of chain length and composition on the efficiency of these chains. Finally, we compare the behavior of random copolymers with that of other architectures, such as diblocks and alternating copolymers.

Our self-consistent field (SCF) method is derived from the theory of Scheutjens and Fleer [4,5], where the phase behavior of polymer systems is modeled by combining Markov chain statistics with a mean field approximation. The free energy per site in the mean field approximation can be written as

$$f(r) = -\sum_{i,c} n_{i,c}(r)\ln n_{i,c}(r) + \frac{1}{2}\sum_{j,k}\chi_{jk}\int \eta(r-r')\phi_j(r)\phi_k(r')dr' . \tag{1}$$

The first term represents the entropy of mixing, where $n_{i,c}(r)$ is the number density at r of molecules type i in conformation c. The second term is a result of the energetic contributions. The indices j and k run over all the types of segments present and $\phi_j(r)$ represents the average density of monomers j at r. The term χ_{jk} is the Flory-Huggins interaction parameter and $\eta(r-r')$ is an interaction function that will be replaced by a summation

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over nearest neighbors.

In order to calculate the density distribution of the different segment types that minimizes Eq. (1), we exploit the analogy between the trajectory of a diffusing particle and the conformation of a chain [6]. We define Green's functions of the type $G(r_1,N'|r_2,N'')$ as the combined statistical weight of all conformations of a subchain starting with segment N' at r_1 and ending with segment N'' at r_2. For a copolymer there are two sets of Green's functions: one for $N'<N''$ and another for $N'>N''$. Green's functions in the first set obey the recursion relationship

$$G(r,N'|r_1,1)=\exp[-U_i(r)] \times \int G(r',N'-1|r_1,1)\eta(r-r')dr_1 \tag{2}$$

and the boundary condition

$$G(r,1|r',1)=\exp[-U_i(r)]\delta(r-r') . \tag{3}$$

Here $U_i(r)$ is the potential of mean force felt by segment i and is given by

$$U_i(r)=\alpha(r)+\sum_k \chi_{jk}\int \phi_k(r')\eta(r-r')dr' . \tag{4}$$

$\alpha(r)$ is a hard core potential that ensures incompressibility. Similar relationships can be derived for the second set of Green's functions. The segment density at a site r can then be calculated from the Green's functions as

$$\phi_j(r)=\sum_i C_i\exp[-U_j(r)] \times \sum_{N'\in j}\int G(r,N'|r_1,1)G(r,N'|r_2,N_i)dr_1dr_2 , \tag{5}$$

where N_i is the length of molecule i and C_i is a normalization constant, which can be obtained from the total number of molecules n_i:

$$C_i=n_i\Bigg/\left[\sum_{N'}\int G(r_1,N'|r_2,1)dr_1dr_2\right] . \tag{6}$$

From Eqs. (2)–(6), the self-consistent density distributions for the different segment types can be calculated by discretizing the equations and solving them through standard numerical techniques [5].

An effect of randomness on the properties of polymer chains had been incorporated into the SCF model by van Lent and Scheutjens [7]. They defined a transition probability T_{xyi} as the probability that in molecule i a monomer x is immediately followed by a monomer y. The recursion relationship [Eq. (2)] was then rewritten by incorporating these transition probabilities [7]. As a result of the change in the recursion relationship, the model assumes an annealed randomness where the sequence distribution of the chain constantly adjusts to its environment. This effect can lead to fundamentally anomalous phase behavior, as particular sequences can dominate the properties of the system.

In our calculation, we adopt a different approach to specify the randomness of the chains. We consider each random copolymer as a separate molecule and fix its sequence distribution at the start of the calculation. This models a quenched or frozen randomness, as each chain retains its sequence distribution throughout the calculation. For all the SCF results presented in this paper each system involves specifying 500 different sequences [9]. (Note that this procedure involves calculating the Green's functions [Eq. (2)] for each of the 500 sequences.)

We define an order parameter f for the random copolymer as the fraction of A monomers on the chain ($f\leq 1$). Then we construct our random sequences by designating monomers either A or B with probability f and $1-f$, respectively. Note that the construction of random sequences in this manner results in $f_i\neq f$ for a particular sequence i. This is always true for finite length chains as fluctuations in the sequence distribution decay as $\sqrt{N}$, N being the length of the chain [8].

We fixed the lengths of the immiscible homopolymers A and B at $N_h=100$ and the Flory-Huggins parameter $\chi_{AB}=0.1$. The calculations were performed in one dimension (the direction perpendicular to the interface, referred to as the z direction) with translational invariance assumed in the xy plane.

Since the amount of random copolymer added to the system to achieve a desired reduction in the interfacial tension is dependent on the size of the system, we use two other measures to determine the efficiency of random copolymers. The first quantity is the equilibrium bulk concentration ϕ^b of the random copolymers and the second is the excess number density of copolymer at the interface n^{ex}, which is given by

$$n_i^{\text{ex}}=\frac{1}{N_i}\sum_z[\phi_i(z)-\phi_i^b] , \tag{7}$$

where N_i is the length of molecule i and the sum is over all lattice layers. The first quantity ϕ^b is independent of system size and thus is a true measure of the volume fraction of the compatibilizer. On the other hand, n^{ex} is inversely proportional to the area occupied by a copolymer molecule at the interface.

For the first set of calculations, we fixed $f=0.5$ and studied the effects of varying the length of the random copolymer. In Fig. 1 we plot the interfacial tension γ as a function of the bulk concentration when compatibiliz-

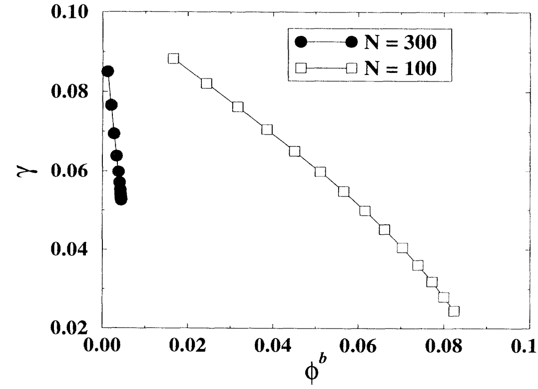

FIG. 1. Plot of the interfacial tension γ as a function of the bulk concentration ϕ^b for random copolymers of length 100 and 300.

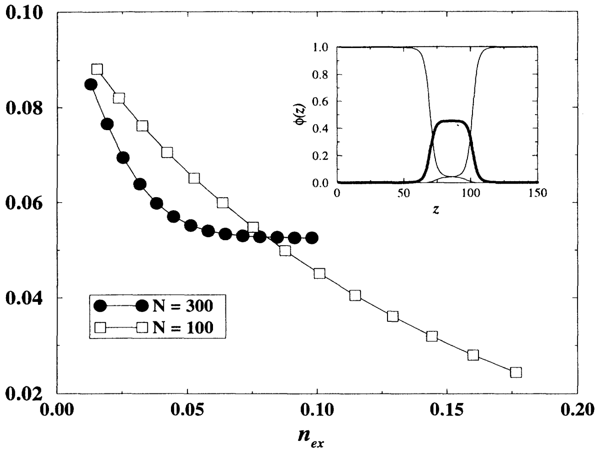

FIG. 2. Plot of the interfacial tension as a function of $n^{\rm ex}$. The inset shows the density profile clearly indicating the formation of the random copolymer phase.

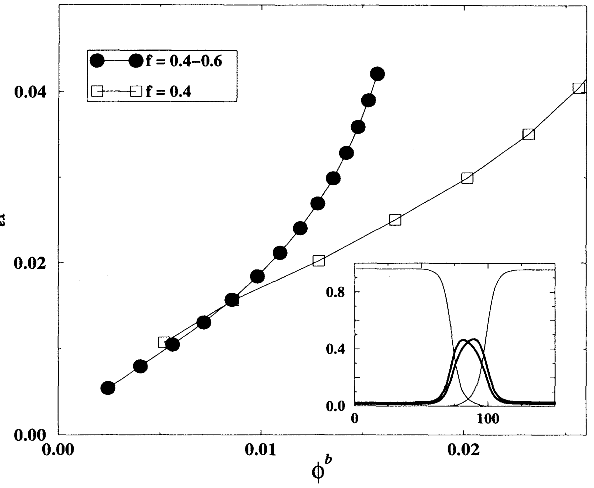

FIG. 4. Plot of the excess number density of chains at the interface as a function of ϕ^b. The $f=0.4$ random copolymer localizes more strongly to the interface when mixed with an equal amount of $f=0.6$ copolymer. The inset shows the density profiles from the mixture of random copolymers.

ers of different lengths are used. The plot clearly shows that a smaller amount of the longer random copolymer is needed to achieve a desired reduction in the interfacial tension. However, there is a limit to the reduction in interfacial tension that can be reached by using the longer random copolymer. This is shown in Fig. 2, where the interfacial tension is plotted as a function of $n^{\rm ex}$. For the longer chain, the interfacial tension saturates at a certain density of copolymers at the interface. We believe that this is a result of the random copolymer forming its own phase between the two homopolymers (see the inset). Once the interfacial tension decreases to the point at which the system can generate two interfaces, the random copolymer phase separates. As a result, the saturation interfacial tension is given by the interfacial tension between the random copolymer and one of the homopolymer components.

As the relevant parameter controlling phase separation in polymer systems is χN, the shorter random copolymer does not phase separate at the value of χ_{AB} used in these calculations. Consequently, a shorter random copolymer is better suited for the purpose of reducing the interfacial tension, as the value at which the interfacial tension will saturate will decrease with decreasing copolymer length.

In the next set of calculations, we fixed the length of the random copolymer at 300 lattice units and studied the effect of composition on the effectiveness of the random copolymer. The symmetry of the problem dictates that the $f=0.5$ random copolymer be the most efficient (Fig. 3). However, it should be noted that the symmetric random copolymer will form its own phase, thus limiting the reduction in interfacial tension. As this restricts the use of random copolymers as compatibilizing agents, it is necessary to suppress the phase separation in order to drive the interfacial tension to a lower value.

One way of accomplishing this goal is to introduce a degree of chemical dispersity in the composition of the

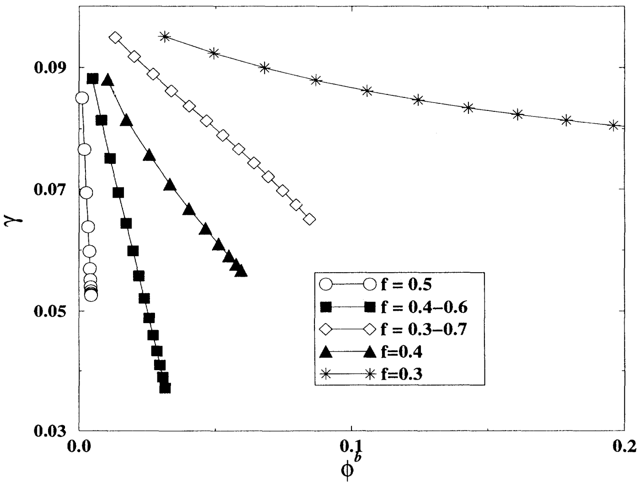

FIG. 3. Plot of the interfacial tension versus the bulk concentration for random copolymers with different values of f.

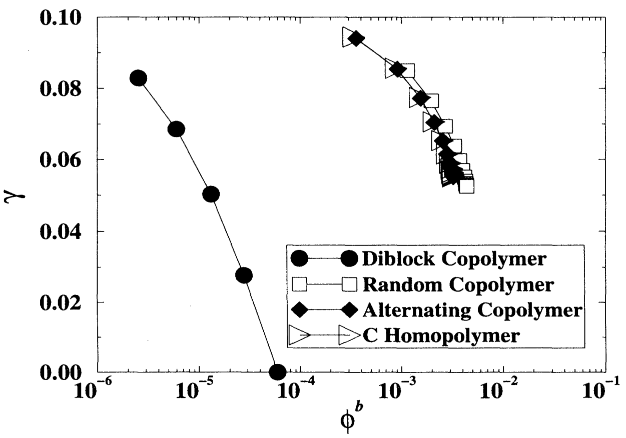

FIG. 5. Plots of the interfacial tension vs ϕ^b for different chain architectures. In all cases the chain length was fixed at $N=300$.

random copolymers. Specifically, we used a mixture of two kinds of random copolymers, i.e., our compatibilizers consisted of 50% $f=0.4$ random copolymers and 50% $f=0.6$ random copolymers. From Fig. 3, it is seen that the blend of random copolymers reduces the interfacial tension to a much lower value than the symmetric random copolymer. By introducing chemical dispersity in the random copolymers, we have created an additional driving force for localizing the copolymers at the interface (see Fig. 4). Since the two types of copolymers are more miscible with each other than with both the homopolymers, there is a net attraction between the copolymers. This attraction effectively drives copolymers from the bulk, increases the number of chains at the interface (relative to the pure $f=0.4$ case), and results in a lower interfacial tension. It should be noted, however, that the mixture of random copolymers cannot have a broad distribution of compositions. If we repeat our calculations with a mixture of $f=0.3$ and 0.7 random copolymers, the interfacial tension reduction becomes less efficient (Fig. 3). Therefore, for optimum results, the mixture of compatibilizers should be closely centered around $f=0.5$.

For the final set of calculations we fixed $f=0.5$ for the random copolymer and compared the random copolymer to diblock copolymers and alternating copolymers. In all cases, the diblock copolymer was the most efficient of the three, with the alternating and the random copolymer showing almost identical behavior (Fig. 5). An interesting result from this calculation is that the same compatibilizing effect can be obtained by replacing a random copolymer by its equivalent homopolymer. In particular, by replacing the symmetric random copolymer ($f=0.5$) with a homopolymer C, which has a reduced interaction given by

$$\chi_{AC}=\chi_{BC}=(1-f)^2\chi_{AB}\ , \tag{8}$$

we see very similar behavior (see Fig. 5).

In conclusion, we extended mean field calculations to random copolymers by accounting for the sequence distribution of the copolymers explicitly. Our results indicate that random copolymers localize at the interface between two incompatible homopolymers and reduce the interfacial tension. However, the reduction in interfacial tension is limited by the random copolymers forming their own phase. The optimum compatibilizing effect is produced with the mixture of random copolymers closely centered around $f=0.5$.

We have also demonstrated that the random copolymer can be replaced by an equivalent homopolymer C, with the appropriate scaling of the χ parameter between the C homopolymer and the A and B components. It is important to note, however, that the interactions between the homopolymer C and the components of the blend have to be symmetric ($\chi_{AC}=\chi_{BC}$) for optimum results. This restriction severely limits the choice of an appropriate homopolymer compatibilizer.

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[9] The total amount of copolymer is partitioned among these 500 sequences with each sequence contributing equally to the total amount of copolymer. The concentration profile of the random copolymer shown is the sum of the profiles of the individual sequences.