Designing Optimal Comb Compatibilizers: AC and BC Combs at an A/B Interface

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ABSTRACT: We used a self-consistent mean field theory to determine the adsorption behavior of AC and BC comb copolymers at the interface between two immiscible homopolymers, A and B. The backbones of the AC combs are composed of A monomers, and the side chains (teeth) are formed from C units. In a similar manner, the BC combs have a B backbone and C teeth. The C segments are themselves immiscible with both the A and B homopolymers. Taking into account the effect of micelle formation, we calculate the reduction in interfacial tension caused by the adsorption of these combs at the A/B interface. At the interface, the combs form a "bilayer": the C teeth associate across the A/B boundary and the backbones remain localized in the respective homopolymers. Our results show that for an optimal choice of comb architecture, the interfacial tension can be reduced to zero. Consequently, these combs constitute effective compatibilizers and emulsifying agents.

Introduction

A fundamental problem in fabricating high-strength polymer composites is that most polymeric mixtures are immiscible and thus, the components phase separate into distinct, macroscopic domains. To enhance the structural integrity and mechanical properties of the resulting material, copolymer "compatibilizers" are commonly added to the mixture. These chains localize at the interface between the immiscible polymers, lower the interfacial tension, and disperse the incompatible polymers into smaller domains. A significant challenge lies in finding polymer additives that act as effective compatibilizers. Previously, diblock copolymers were shown to be useful in reducing interfacial tension;[1–6] however, there is considerable interest in utilizing more cost-effective copolymer additives.[7–9] In a recent study,[10] Monte Carlo computer simulations and experimental studies were combined to determine the compatibilizing activity of comb copolymers. The particular system involved a mixture of two phase-separated homopolymers, A and B, and two types of comb copolymers, AC and BC. The backbones of the AC copolymers are formed entirely from A monomers, whereas the side chains, or teeth, are formed from C units. In a similar manner, the backbone of the BC chains are formed from B segments, and the C segments comprise the teeth. Furthermore, the C segments are incompatible with both the A and B homopolymers.

In this system, the interfacial tension between the immiscible homopolymers drives the combs to the A/B boundary. The A–B repulsion keeps the backbones localized in their respective phases, while A–C and B–C repulsion drives the teeth to associate across the interface (see Figure 1). In this way, the chains form a "molecular velcro":[11] the intertwining teeth effectively bind the two phase-separated regions. The experimental findings on a comparable system[10,12] showed that this behavior dramatically improves the mechanical properties of the composite material.[13] Since the teeth are chemically distinct from the phase-separated homopolymers and can be incompatible with the homopolymers, this technique significantly increases the variety of materials that can be used as compatibilizers for multiphase and multicomponent materials. The results also demonstrate that three immiscible polymers can be combined to yield a macroscopically homogeneous blend.

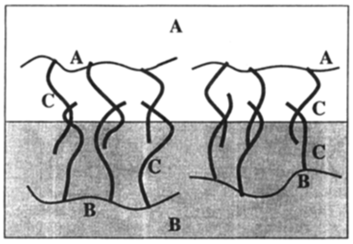

Figure 1. Schematic drawing of the combs localized at the interface. The teeth associate across the A/B boundary, while the backbones remain localized in the respective bulk phases.

In the previous Monte Carlo simulations,[10] each comb contained three teeth. In the experimental system,[10] the combs contained an average of one tooth per backbone. (There was, however, a dispersity in the number of teeth per comb; this dispersity is best described by Gaussian statistics.[14]) In this paper, we use the self-consistent field theory (SCF) of Scheutjens and Fleer[15,16] to determine the effect of the number, length, and arrangement of teeth on the interfacial activity of the AC and BC combs. Our goal is to isolate the architecture that is most effective at reducing the interfacial tension at the A/B boundary. These results can provide further guidelines for synthesizing optimal copolymer compatibilizers.

In the following section, we briefly outline the theoretical model we used in our investigations and describe the calculations that are necessary for determining the properties of our system. As with block copolymers, these combs can form micelles or membranes in the bulk phase. The formation of these structures limits the amount of copolymer that will adsorb at the A/B interface.[4–6,16] In particular, once the concentration of combs reaches the critical micelle or membrane concentration (CMC), the combs will aggregate into the associated complexes rather than localize at the polymer/polymer boundary. Therefore, before we calculate the adsorption isotherm, we must in fact calculate the CMC

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for each of the various comb architectures that we examine. Having determined the isotherm, we then calculate the interfacial tension as a function of the adsorbed amount. The details for these calculations are given below.

The Model

The principles of the SCF theory developed by Scheutjens and Fleer have been described extensively in previous publications and are now detailed in a thorough textbook.[15] Here, we only provide a brief description of this theory in order to give the reader a general acquaintance with the formalism. To simplify the discussion, we limit our comments to the behavior of linear copolymers. The extension of the above formulas to comb copolymers is straightforward and involves modifying the expressions for the distribution functions, or the G's, in eq 4 below. Now the G's must take into account the presence of branch points and the connectivity of these branch points to the other parts of the chain. A detailed discussion of this point can be found in ref 15, along with the appropriate equations for the distribution functions.

Consider a planar lattice that is divided into $z = 1$ to M layers. The probability that a monomer of type i is in layer z with respect to the bulk is given by the factor

$$G_i(z) = \exp(-u_i(z)/kT) \tag{1}$$

where the potential $u_i(z)$ for a segment of type i in layer z is given by

$$u_i(z) = u'(z) + kT \sum_{j(\neq i)} \chi_{ij}(\langle\phi_j(z)\rangle - \phi_j^{\mathrm{b}}) \tag{2}$$

The parameter $u'(z)$ is a "hard-core potential", which ensures that every lattice layer is filled. In the second term, χ_{ij} is the Flory–Huggins interaction energy between units i and j, and ϕ_j^{b} is the polymer concentration in the bulk. The expression $\langle\phi_j(z)\rangle$ is the fraction of contacts an i segment in the z layer makes with j-type segments in the adjacent layers and is given by the following equation:

$$\langle\phi_j(z)\rangle = \lambda_{-1}\phi_j(z-1) + \lambda_0\phi_j(z) + \lambda_1\phi_j(z+1) \tag{3}$$

Here, the λ's are the fraction of neighbors in the adjacent layers: λ_{-1} is for the previous layer, λ_0 is for the same layer, and λ_1 is for the next layer.

Since polymers contain more than one segment, we must take into account that the segments of the chain are connected. We define $G_i(z,s|1)$ as the (conditional) probability (up to a normalization constant) that a segment s is located in layer z, while being connected to the first segment of chain i. This Green's function can be calculated from the following recurrence relation:

$$G_i(z,s|1) = G_i(z)\{\lambda_{-1}G_i(z-1,s-1|1) + \lambda_0 G_i(z,s-1|1) + \lambda_1 G_i(z+1,s-1|1)\} \tag{4}$$

Clearly, $G_i(z,1|1) = G_i(z)$ and the terms for $s > 1$ can be calculated from this relationship and eq 4. In the same way, we can obtain a recurrence formula for $G_i(z,s|r)$, the probability that a segment s is in layer z, given it is connected to the last (rth) segment of the chain.

To obtain the volume fraction of i in the z layer due to segment s, in a chain of r segments, the product of two probability functions is needed: the probability of a chain starting at segment 1 and ending with segment s in layer z and that of a chain starting at segment r and also ending with segment s in layer z. This product must be divided by $G_i(z)$ to compensate for the double counting of the sth segment. Hence, the volume fraction is given by

$$\phi_i(z,s) = C_i G_i(z,s|1) G_i(z,s|r)/G_i(z) \tag{5}$$

Here, C_i is the normalization constant and is equal to

$$C_i = \theta_i/r_i \sum_z G_i(z,r|1) \tag{6}$$

where $\theta_i = \sum_z\phi_i(z)$ is the total amount of polymer segments in the system and $\sum_z G_i(z,r|1)/M$ is the average of the end segment distribution function for a chain of r_i segments. We can also express C_i in terms of ϕ_i^{b}, the volume fraction in the bulk solution, as

$$C_i = \phi_i^{\mathrm{b}}/r_i \tag{7}$$

The total volume fraction of $\phi_i(z)$ of molecules i in layer z can be obtained by summing over s:

$$\phi_i(z) = \sum_s \phi_i(z,s) \tag{8}$$

Expressions 1 and 5 and the condition that $\sum_i\phi_i(z) = 1$ for each layer form a set of coupled equations that are solved numerically and self-consistently. Given that the amount of polymer, θ_i, the length r_i, and χ_{ij} are specified, we can calculate the self-consistent adsorption profile and the equilibrium bulk concentration. (For a given θ_i, ϕ_i^{b} is obtained by equating eqs 6 and 7.)

Our aim is to determine the amount of comb copolymer adsorbed at the A/B interface and, subsequently, the reduction in the interfacial tension due to the presence of these additives. As we noted in the Introduction, the amount of adsorbed copolymer will be limited by the value of the critical micelle (membrane) concentration, or CMC. Adding copolymer beyond the CMC introduces micelles (or membranes) into the bulk phase but does not enhance the concentration at the boundary between the immiscible homopolymers. Consequently, our discussions concerning the adsorbed amount and the reduction in interfacial tension will only be valid up to the CMC. Thus, our first goal is to establish the CMC for each of the cases under consideration. In carrying out this calculation, we adopt the procedure developed by van Lent and Scheutjens.[16] We note that in each case that we examine, we must calculate the chemical potential for both micelle and membrane formation in order to determine which structure is preferred. To distinguish between these two structures, we will now use CMC to refer to micelles and CMeC to refer to the critical concentration for membrane formation. We briefly summarize the procedure for calculating the CMC and then discuss CMeC's.

To facilitate the discussion, let us arbitrarily choose one of the bulk phases, namely the A homopolymer region. (The arguments will apply equally well to the B phase.) Recall that in the AC combs, the backbones are formed entirely from A monomers and the C teeth are incompatible with A. Thus within the A phase, the lyophobic teeth will form the core of the micelles, while the compatible A backbones will form the outer corona. To accurately model such micelles, we must adopt a spherical lattice. In this geometry, the total number of lattice sites in layer z will be referred to as $L(z)$. To calculate the CMC for this system, we start by specifying a certain number of molecules n_i, and a value for $\theta_i = n_i r_i$. From the calculations outlined above, we can obtain the self-consistent values for $\phi_i(z)$ and ϕ_i^{b}. The number of chains within the micelle, or the aggregation number, is calculated as

$$n_i^{\mathrm{ex}} = (\sum_z L(z)\{\phi_i(z) - \phi_i^{\mathrm{b}}\})/r_i \tag{9}$$

These values are then substituted into the equation for A_m^σ, the excess free energy to create a micelle with a fixed center of mass:

$$A_{\mathrm{m}}^{\sigma}/kT = -\sum_i n_i^{\mathrm{ex}} - \sum_z L(z)\{u'(z)/kT - (1/2)\sum_m\sum_n \chi_{mn}(\phi_m(z)\langle\phi_n(z)\rangle - \phi_m^{\mathrm{b}}\phi_n^{\mathrm{b}})\} \tag{10}$$

Note that in the last term, the double summation over types of molecules (i,j) is replaced by that over monomer types (m,n), which makes the equation applicable to copolymers. Next the amount of polymer within the lattice is increased and the whole procedure is repeated.

The values of A_m^σ initially increase as a function of the aggregation number: it is unfavorable for the molecules to aggregate into such small clusters. As the aggregation number increases, A_m^σ reaches a maximum and then decreases, indicating that it takes less and less energy to form a micelle. The value of ϕ_i^{b} corresponding to the maximum in A_m^σ is the CMC:[16] this constitutes the minimum copolymer concentration in the bulk phase for micelle formation to occur.

To visualize the formation of membranes, we again focus on one of the phases, namely A. To create a membrane within this bulk phase, the lyophobic C teeth associate into a bilayer or lamellar layer and the compatible A backbones border both sides of the C region. (Here, we adopt the convention of referring to these bilayers as "membranes".[16]) The CMeC is calculated in a similar manner as the CMC;[16] however, it is calculated on a planar lattice. (Since the lattice is assumed to extend to infinity in the lateral direction, the membrane is assumed to be infinitely long.)

To determine which of the associated structures (micelle or membrane) is the preferred morphology for the copolymer under consideration, we must calculate and compare the chemical potentials for both these structures. The structure having the lower chemical potential is the preferred geometry. The chemical potential is calculated according to the following formula:

$$(\mu_i - \mu_i^*)/kT = \ln(\phi_i^{\mathrm{b}}) + 1 - r_i\sum_j \phi_j^{\mathrm{b}}/r_j + (1/2)r_i\sum_m\sum_n \chi_{mn}(\phi_{mi}^* - \phi_m^{\mathrm{b}})(\phi_n^{\mathrm{b}} - \phi_{ni}^*) \tag{11}$$

Here, μ_i^* is the chemical potential and $\phi_{mi}^* = r_{mi}/r_i$ is the volume fraction of segments of type m in amorphous polymer of type i.

Once we obtain the CMC (or CMeC) for the appropriate structure, we calculate the adsorbed amount as a functiion of ϕ_i^{b}. The adsorbed amount is given by

$$\theta_i^{\mathrm{ex}} = \sum_z(\phi_i(z) - \phi_i^{\mathrm{b}}) \tag{12}$$

The significance of determining the CMC is that we can pinpoint the range over which our values of θ_i^{ex} are relevant. Values of θ_i^{ex} corresponding to ϕ_i^{b} > CMC have no physical meaning since the chains now form micelles rather than adsorb at the interface.

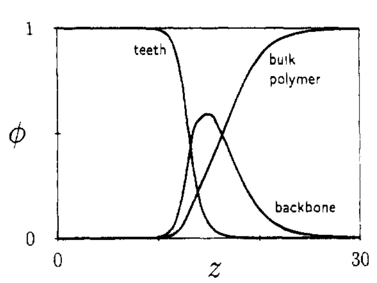

Figure 2. Polymer density profile of an AC micelle within the A homopolymer. The contributions from the C teeth, A backbone, and bulk polymer are labeled on the curve. The length of the backbones is 400 segments. There are 3 teeth on each comb and each tooth is 100 segments long. Here, as in all other calculations, the homopolymers are 100 segments in length. These calculations are performed on a spherical lattice. The C teeth form the core of the micelle, while the A backbones form the outer corona, which extends into the A homopolymer.

Finally, the interfacial tension for the system of the AC and BC combs at the A/B interface is calculated through the following equation:

$$\gamma a/kT = -\sum_i \theta_i^{\mathrm{ex}}/r_i - \sum_z\{u'(z)/kT - (1/2)\sum_m\sum_n \chi_{mn}(\phi_m(z)\langle\phi_n(z)\rangle - \phi_m^{\mathrm{b}}\phi_n^{\mathrm{b}})\} \tag{13}$$

where a is the area per site. (Note this expression is just eq 10 applied to a planar lattice.)

Results and Discussion

Since it is the C teeth associating across the A/B boundary that effectively bind the immiscible phases, it is of particular interest to determine how the number, length, and arrangement of teeth affects the properties of the blend. In the first set of calculations, we investigated the effect of the number of teeth on the interfacial tension. Specifically, we fixed the length of the respective A and B backbones at 400 segments and held the length of each tooth constant at 100 segments. We considered the cases of 1, 2, 3, 7, and 15 teeth per comb. In all these examples, the teeth were evenly spaced along the length of the backbone. Throughout this article, the length of the homopolymers is fixed at 100 segments. Initially, the value of all the relevant χ parameters was fixed at 0.2, i.e., $\chi_{\mathrm{AB}} = \chi_{\mathrm{AC}} = \chi_{\mathrm{BC}} = 0.2$.

In the cases of the 1, 2, and 3 teeth, the calculated CMC's are lower than the corresponding CMeC's and correspondingly, the values of $\mu_{\mathrm{CMC}} < \mu_{\mathrm{CMeC}}$. Therefore, above the CMC, these combs will form micelles in the bulk phase. On the other hand, in the examples of 7 and 15 teeth, the values of CMeC < CMC (and likewise, $\mu_{\mathrm{CMeC}} < \mu_{\mathrm{CMC}}$), which indicates that these combs would rather form membranes than micelles in the bulk phase.

The spatial distribution of the chains in the micelles can be characterized by the radial density profiles; an example is shown in Figure 2. This micelle contains 26 comb copolymers, where each comb contains 3 teeth. As can be seen, the C teeth form a dense core, while the A backbones not only shield the teeth from the homopolymer but also dissolve into the surrounding bulk phase.

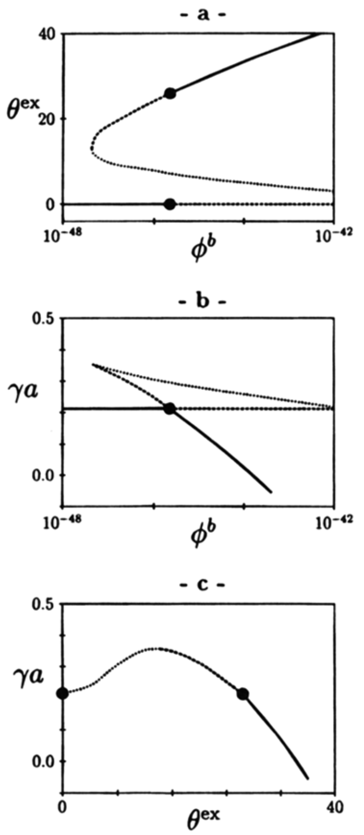

Figure 3. Curves for (a) the adsorbed amount, θ^{ex}, versus ϕ^b, the concentration of polymer in the bulk phase, (b) the interfacial tension, γa, versus ϕ^b, and (c) γa versus θ^{ex}. The solid lines represent the stable solutions of the SCF equations. The dashed lines represent the metastable solutions, and the dotted lines describe the unstable solutions. The dark dot locates the first-order transition from nonadsorbed to adsorbed combs. In these calculations, the combs contain 2 teeth, each 100 segments in length, and the backbones are 400 segments long.

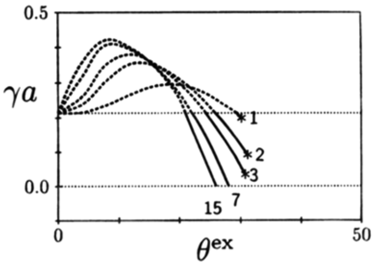

Figure 4. Interfacial tension, γa, versus the adsorbed amount, θ^{ex}. The solid lines represent the stable solutions of the SCF equations. The combs have 1, 2, 3, 7, and 15 teeth, respectively. The length of each tooth is fixed at 100 segments; the backbone is 400 segments in length. The stars indicate the values at the CMC; this indicates the maximum extent to which the interfacial tension can be reduced. The interfacial tension goes to 0 in the cases of 7 and 15 teeth.

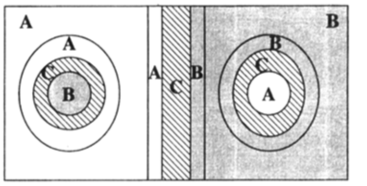

Figure 5. Schematic drawing of the system when the interfacial tension is 0. Here, the combs form additional interfaces by emulsifying the homopolymers into vesicles. In homopolymer A, the A backbones form the outer corona of the vesicle, the C teeth form the central bilayer, and the B backbones form the inner layer, which borders the solubilized B hompolymer. Comparable structures form in the B phase.

To characterize the adsorption of the combs at the A/B interface, we plot the types of curves shown in Figure 3a–c.[17] The plot in Figure 3a displays the adsorbed amount, θ^{ex}, versus ϕ^b. The curve is sigmoidal in shape, showing a hysteresis characteristic of a first-order transition.[18] We used Maxwell's construction to determine the location of the transition (marked by a large dot). The solid, dark lines in the Figures represent the stable solutions of the SCF equations. Below the transition point, the combs are dispersed in the respective bulk phases and are not significantly present at the A/B interface. The solid line above the transition indicates the regime where the combs are localized at the interface and θ^{ex} increases until the CMC is reached. The dashed lines in the curves correspond to the metastable solutions of our equations (local minima in the free energy), and the dotted lines correspond to unstable solutions (maximum in the free energy). In Figures 3b and 3c, we plot the interfacial tension as a function of ϕ^b and θ^{ex}, respectively. Note that in Figure 3b, the transition occurs at the crossing of the interfacial tension lines for the two solutions. In Figure 3c, we see that the meta- and unstable parts of the curves show a higher interfacial tension than the bare A/B interface (dark dot at $\theta^{ex} = 0$); thus these parts of the curve correspond to regimes that are physically unrealistic for a fully equilibrated system.

While Figure 3 shows the general shapes of the relevant curves, Figure 4 reveals the plots of the interfacial tension as a function of θ^{ex} for the various combs described above. (Note that the parameter θ^{ex} represents the amount of both AC and BC combs adsorbed at the interface. Since the system is completely symmetric, we take θ^{ex} for both combs to be twice the value of θ^{ex} for the AC combs.) All the curves extrapolate to the same value at $\theta^{ex} = 0$; as noted above, this point represents the interfacial tension between the immiscible homopolymers in the absence of the copolymers.

For each of the various architectures, the value of θ^{ex} at the CMC (or CMeC) is marked on the curves. (The plots in Figure 3 allows us to determine the appropriate value of θ^{ex} at ϕ^b = CMC.) These points represent the maximum extent to which the interfacial tension can be reduced. It is clear that all the combs are effective at reducing the interfacial tension below the initial $\theta^{ex} = 0$ value. However, increasing the number of teeth results in a more pronounced reduction.

Whenever membrane formation is observed in the bulk, the interfacial tension goes to zero before the CMeC is reached (see Figure 4); the system could form AC:CA membranes in A (or likewise, BC:CB membranes in B); however, the free energy of the system is significantly lowered if these membranes localize at the interface. Consequently, such membranes will never form in the bulk phase. Further addition of these multitoothed combs results in the formation of new interfaces, as explained below. This scenario is not necessarily true when $\chi_{AC} \neq \chi_{BC}$.

The fact that the interfacial tension goes to zero indicates that upon further addition of copolymer the system will form additional interfaces.[4–6,16] One way this can be accomplished is for the AC and BC combs to form vesicles that contain solubilized homopolymer (see Figure 5). Within the A phase, the A backbones form the outer layer, which borders the bilayer of hydrophobic C teeth. The B backbones form the inner

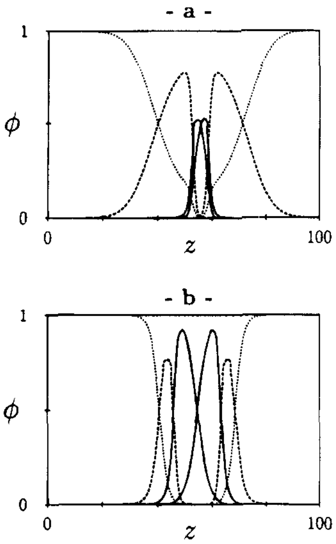

Figure 6. Density profiles of the AC and BC combs at the A/B interface. The profiles are for values of θ^{ex} at the CMC. The solid lines indicate the C teeth, the dashed lines mark the backbones, and the dotted lines reveal the homopolymers. The lengths of the backbones and teeth are the same as in Figure 4. Each comb has 1 tooth in (a) and 7 teeth in (b). Both figures reveal that the teeth from the AC and BC combs overlap at the interface. In addition, the A backbones are localized in the A phase (left side of the figure), while the B backbones remain in the B domain (right side).

boundary of the vesicles, which contains emulsified B homopolymer. Analogous structures can form in the B phase, where it is the A homopolymer that is now solubilized within the vesicles.

In Figure 6, we plot the polymer density profiles (for values of θ^{ex} at the CMC). These figures allow us to visualize the arrangement of the AC and BC combs at the A/B boundary. Figure 6a shows the density distributions in the case where the combs have 1 tooth per chain, while Figure 6b shows the plot for the 7-toothed comb. In the 1-tooth case, the density distributions for the teeth on the AC and BC combs show considerable overlap at the interface, indicating that the C segments are strongly associated. The profiles for the A and B backbones are relatively broad, showing sizable overlap with the respective hompolymers. Pinned to the interface at only one point, the majority of the backbone is free to extend into the surrounding, compatible phase. In the case of the 7-toothed combs, the width of the C layer (Figure 6b) is enlarged due to the relative stetching of the densely grafted teeth. The close grafting also provides less space for interpenetration of the teeth; thus, the degree of tooth–tooth overlap is diminished. We note that the broad C layer pushes the A and B homopolymers further apart. As a consequence, the number of A–B contacts is diminished, which contributes to reducing the interfacial tension. Also note that near the interface, the profiles for the bulk homopolymers become sharper and more steplike as the number of teeth is increased. Finally, the profiles of the A and B backbones are narrower than in Figure 6a: here, the length of the backbone is pinned to interface through the multiple teeth.

To explain the pronounced effect of increasing the number of teeth, we have to consider the mechanism underlying the decrease in the interfacial tension. Note that we replace one unfavorable A/B interface by two unfavorable interfaces, A/C and C/B. The reason that the total free energy nevertheless decreases can be understood by recalling the behavior of AB diblock copolymers,[4] where A and B are incompatible. Whether these copolymers are in the bulk or at the interface, they "are condemned to suffer from such contacts"[4] since the A and B blocks (in our case A and C, as well as B and C) are chemically linked. When we increase the number of teeth on a comb, we increase the number of those inescapable contacts and thereby lower the interfacial free energy when these contacts localize at the interface and replace escapable ones.

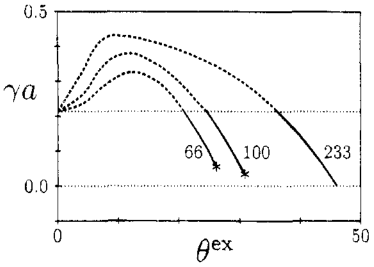

Figure 7. Interfacial tension, γa, versus the adsorbed amount, θ^{ex}. Each comb has 3 teeth; the length of each tooth is marked on the appropriate curve. The length of the backbones is held fixed at 400 segments. The stars indicate the values at the CMC. The interfacial tension goes to 0 in the case of tooth length = 233.

Having examined the effect of tooth number, we next focused our attention on the effect of tooth length. For this study, we fixed the number of teeth at 3 and examined tooth lengths around 33, 66, 100, and 233 segments, such that the combs contain a total of 100, 200, 300, and 700 C sites, respectively. The combs with a tooth length of 33 preferred to remain solubilized within the respective bulk homopolymer, highlighting the fact that a critical tooth length is needed for the chains to localize at the interface. Figure 7 clearly shows that the longer tooth lengths produce a greater reduction in the surface tension, which goes to zero in the case where the teeth are 233 segments in length. We note that increasing the tooth length decreases the solubility of the combs in the respective bulk phases. Consequently, more combs adsorb at the interface before reaching the CMC in the case of the longer teeth. (In the example involving teeth of 233 segments, the tooth length is greater than the spacing between the teeth. One can infer that the teeth would be highly crowded within the micelle, and hence, this structure is not formed.)

The density profiles help clarify the conformation of the chains at the interface (see Figure 8). In the case of the relatively short teeth, or low concentration of C sites, the interface is relatively diffuse, with a degree of overlap between A and C segments, B and C segments, and A and B fragments. As the tooth length is increased, the concentration of C segments in the system is increased; consequently, the separation between the immiscible components is enhanced. Now, the AC combs are less miscible in the bulk A homopolymer and the same is true for the BC combs within the B phase. Thus, the combs become more localized at the interface and the extent of A–C and B–C contacts is diminished. Furthermore, as the width of the C layer is increased, this region once again pushes the energetically unfavorable A and B homopolymers further apart. Note the homopolymer density profiles become sharper and show no overlap when the tooth length equals 233. The decrease in the number of energetically unfavorable contacts at the interface gives rise to the decrease in the interfacial tension.

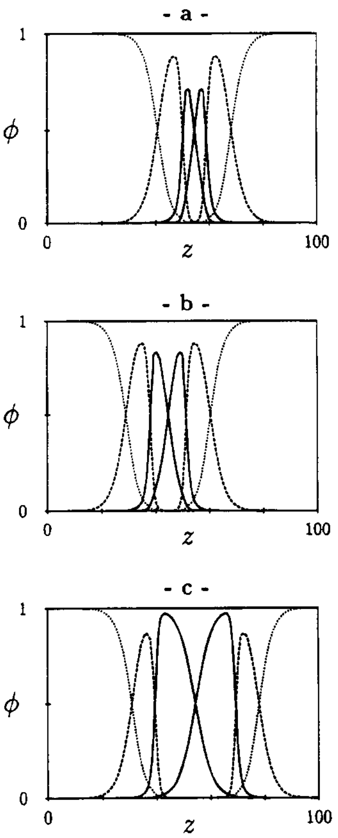

Figure 8. Density profiles of the AC and BC combs at the A/B interface. The profiles are for values of θ^{ex} at the CMC. The solid lines indicate the C teeth, the dashed lines mark the backbones, and the dotted lines reveal the homopolymers. The length of the backbones and number of teeth are the same as in Figure 7. In (a), each tooth is 66 segments in length, in (b), the tooth length is 100, and finally in (c), the length of each tooth is 233 segments.

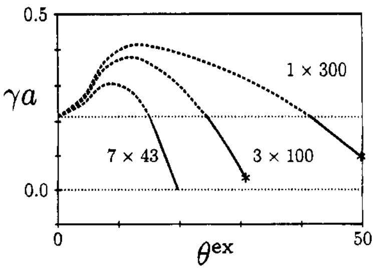

Figure 9. Interfacial tension, γa, versus the adsorbed amount, θ^{ex}. The numbers indicate the structure of the combs: the first value indicates the number of teeth and the second number gives the length of each tooth. The stars indicate the values at the CMC. The interfacial tension goes to 0 in the case of 7 teeth, where each tooth is 43 segments in length.

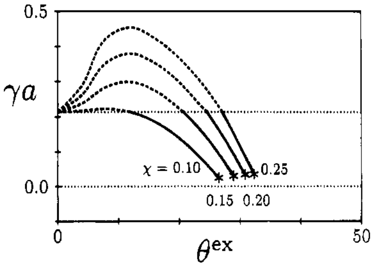

Figure 10. Interfacial tension, γa, versus the adsorbed amount, θ^{ex}. The numbers represent the values of $\chi_{AC} = \chi_{BC}$. The combs have 3 teeth of length 100, and the backbones are 400 segments in length. The stars indicate the values at the CMC.

To assess the relative importance of the number of teeth versus the tooth length in reducing the interfacial tension, we now hold the total number of C monomers fixed at 300 and vary the distribution of C sites among the teeth. In particular, we contrast the reduction in surface tension when the following types of combs are at the interface: 1 tooth of length 300 (1 × 300), 3 teeth, each of length 100 (3 × 100), and 7 teeth of length 43 (7 × 43). The calculations are aimed at determining the optimal way to arrange a fixed number of C monomers: a few, long teeth versus multiple short teeth. By examining Figure 9, which displays γa versus θ^{ex} for each of these cases, we observe that multiple short teeth provide a higher reduction in the interfacial tension than fewer, longer teeth. Furthermore, the interfacial tension goes to 0 in the 7 × 43 case.

The combs with the multiple short teeth are also more "efficient" in lowering the interfacial tension: it takes fewer combs at the interface to produce the observed reductions. The effectiveness of the multiple teeth arises from the fact the ferquent branch points secure the backbone to the interface, thereby localizing the entire comb at the A/B boundary (see Figure 6b). We note that the above studies on the effect of tooth length indicated that a critical tooth length is needed for the combs to adsorb at the interface; thus increasing the number of teeth at the expense of decreasing the tooth length below 43 would not necessarily improve the utility of these combs.

In a final set of calculations, we varied χ_{AC} ($=\chi_{BC}$) relative to χ_{AB} ($=0.2$). The results of these calculations are shown in Figure 10, where we plot γa versus θ^{ex} for χ_{AC} ($=\chi_{BC}$) = 0.1, 0.15, 0.2, and 0.25. Here, the combs have 3 teeth of length 100 and the backbones are fixed at 400 segments. Varying these χ values does not affect the ultimate reduction in interfacial tension, but it does affect to some extent the efficiency of the combs. In particular, its takes a greater number of combs at the interface to lower γa when χ is increased.

A minimum value of χ is needed for the combs to localize at the interface. If χ_{AC} and χ_{BC} are both set equal to zero, we found that the combs remain solubilized in the respective homopolymer phases and do not localize at the interface.

Conclusions

In conclusion, we demonstrated that in a blend of immiscible A and B homopolymers, AC and BC combs will localize at the interface to form an AC:CB "bilayer", with the teeth C intertwined across the boundary between the phase-separated homopolymers. These findings agree with our earlier predictions from Monte Carlo simulations concerning the conformation of the AC and BC combs at the A/B interface.[10] The bilayer lowers the interfacial tension between the immiscible homopolymers and thereby improves the properties of the blend. We found that increasing the number of teeth has the most pronounced effect on lowering this surface tension. In the case where the surface tension is driven to zero, these combs act as emulsifying agents, which solubilize and disperse the immiscible homopolymers. Dispersing the domains of immiscible polymers contributes to improving the mechanical properties of the blends; consequently, the combs constitute useful compatibilizers for enhancing the strength of polymeric composites.

Since these SCF calculations provide information about the state of the system at thermodynamic equilibrium, our conclusions apply to this fully equilibrated state. This region may, however, be difficult to attain experimentally. The plots of the interfacial tension versus adsorbed amount provide insight into the experimental accessibility of this state. Here, the dotted lines (representing the metastable or unstable region of higher surface tension) represent an activation barrier to reaching the equilibrium states: the higher the value of γ in this region, the higher the activation barrier. These meta- or unstable states are nonetheless experimentally accessible and the system may be trapped in this region. Large fluctuations may be required to drive the experimental system through the first-order transition and into the thermodynamically stable regime. Experimental efforts in this direction are currently underway.[19]

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(18) A first-order transition in the adsorption isotherm was also observed by K. Shull (*Macromolecules* **1993**, *26*, 2346) in his self-consistent field calculations for the adsorption of AC diblocks at the A/B interface.
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