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Effect of Copolymer Architecture on the Efficiency of Compatibilizers

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ABSTRACT: We use analytical arguments and numerical self-consistent field (SCF) calculations to calculate the interfacial tension, γ, for a system of AB copolymers localized at the interface between two immiscible homopolymers, A and B. In particular, we fix the molecular weights of the copolymers but vary their architecture from diblock, star, and various comb copolymers. The results from both methods show that diblock copolymers are the most efficient at reducing γ. We also observe that at fixed molecular weight (N), as the number of teeth (n) is increased, the comb becomes significantly less efficient and the disparity between combs and diblocks grows larger. However, when we compare combs and diblocks with different molecular weights, we observe a trade-off between N and n. In particular, long combs with multiple teeth are more efficient than short diblocks. These studies allow us to predict the reduction in interfacial tension produced by a wide variety of copolymers and thereby permit a rational design of effective compatibilizers.

Introduction

Polymer blends hold significant promise since the properties of the blend can be tailored by varying the type and quantity of polymers that go into the mixture. Most polymers, however, are immiscible and the mixtures separate into distinct domains. Copolymer additives, or "compatibilizers", can enhance the structural integrity of these composites by localizing at the interface between the immiscible polymers, lowering the interfacial tension, and dispersing the incompatible polymers into smaller domains. A significant challenge lies in finding copolymer additives that act as effective compatibilizers. One unresolved issue is the role copolymer architecture plays in the compatibilizing activity. To date, there have been few experimental[1–3] or theoretical[4,5] studies comparing compatibilizers with fixed molecular weights but different architectures. Carrying out such experimental studies poses considerable synthetic challenges,[6] and there are few theories to describe the interfacial activity of copolymers with complex structures.

In this paper, we calculate the reduction in interfacial tension that occurs when different AB copolymers localize at the interface between two immiscible homopolymers, A and B. In particular, we fix the degree of polymerization of the copolymers but vary their architecture. Consequently, the calculations allow us to determine the optimal copolymer architecture for reducing the interfacial tension.

To carry out these calculations, we adapt the formalism derived by Leibler[7] for the interfacial activity of diblocks[8] and apply the theory to comb and star copolymers. To test the validity of our analytical findings, we perform self-consistent field (SCF) calculations on comparable systems and finally compare the results from the two techniques. These studies allow us to predict the reduction in interfacial tension produced by a wide variety of copolymers and thereby permit a rational design of effective compatibilizers.

Methods

We consider a blend that contains a volume fraction ϕ_A of homopolymer A and ϕ_B of homopolymer B. The degrees of polymerization of the respective homopolymers are given by P_A and P_B and the Flory–Huggins χ parameter characterizes the energetic interaction between the A and B monomers. We consider the limit where χ is relatively high, or $\chi P_i \gg 1$. Under these conditions, the interface between the A-rich and B-rich phases will be relatively sharp and can be approximated by a flat plane.[7] To this mixture, we add a relatively low volume fraction, ϕ_{bulk}, of AB copolymers. The composition of these copolymers is specificed by $f = N_A/(N_A + N_B)$, where N_A and N_B are the degrees of polymerization of the respective blocks. We let $N = (N_A + N_B)$. Below, we first describe the theory for diblock copolymers and then apply this formalism to model the behavior of comb copolymers.

Diblocks. For low values of ϕ_{bulk}, the volume fraction of diblocks in the B-rich phase can be approximated as[7]

$$\phi_+ = \phi_{\text{bulk}}/[\phi_B + \phi_A \exp\{\chi(N_A - N_B)\}] \tag{1}$$

and in the A-rich phase

$$\phi_- = \phi_{\text{bulk}}/[\phi_A + \phi_B \exp\{\chi(N_B - N_A)\}] \tag{2}$$

The amount of diblock at the interface (and the related area per chain, σ) can be determined by equating the chemical potentials of the diblocks in the bulk and at the interface, or

$$\mu_{\text{bulk}} = \mu_{\text{film}} \tag{3}$$

where the chemical potential in the bulk is given by

$$\mu_{\text{bulk}} = \ln \phi_+ + \chi N_A = \ln \phi_- + \chi N_B \tag{4}$$

and the chemical potential at the interface is given by

$$\mu_{\text{film}} = \delta F_{\text{film}}/\delta Q|_S \tag{5}$$

Here and below, S is the area of the interface, Q is the number of copolymers at the interface, and $\sigma = S/Q$, is the area per diblock at the interface. All characteristic

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lengths are expressed in the units of the monomer size a (the diameter of a monomer), which is assumed to be the same for both the A and B monomers, and all energetic values are expressed in units of kT. Equations 1–5 were previously derived by Leibler,[7] and we refer the reader to this paper for further details.

We now assume that the diblocks form a "dry brush" on both sides of interface. That is, the homopolymers do not penetrate into the diblock brush. The free energy of this interfacial layer or film can be written as the sum of the interfacial energy and stretching energy of the blocks:

$$F_{\text{film}} = \gamma_0 S + QF_{\text{str}} \tag{6}$$

where $\gamma_0 = (\chi/6)^{1/2}$ is the interfacial tension of the pure A–B homopolymer interface[9] and

$$F_{\text{str}} = F_A + F_B = \pi^2 N/8\sigma^2 \tag{7}$$

is the stretching energy of a diblock copolymer at the interface. Here, we use a self-consistent-field result for the stretching energy (corresponding to a distribution of chain ends throughout the brush)[10] instead of the "Alexander" (step function) approximation that was used by Leibler.[7] Nevertheless, the difference between these two formulas is only a numerical coefficient ($\pi^2/8$ instead of 3/2). Through eqs 5 and 7, we can obtain the chemical potential of the film:

$$\mu_{\text{film}} = 3\pi^2 N/8\sigma^2 \tag{8}$$

It is useful to note that $\mu_{\text{film}} = 3F_{\text{str}}$, a point that will be discussed later.

Now, eqs 3 and 8 yield the equilibrium area per chain in the brush:

$$\sigma = (3\pi^2 N/8\,\mu_{\text{bulk}})^{1/2} \tag{9}$$

and, from eqs (6) and (9), we can calculate the interfacial tension:

$$\gamma = \delta F_{\text{film}}/\delta S|_Q = \gamma_0 - (2/\pi)(2/3)^{3/2} N^{-1/2}(\ln \phi_+ + \chi N f)^{3/2} \tag{10}$$

The volume fraction $\phi_{+\text{sat}}$ at which $\gamma = 0$ is of special interest and can be obtained from eq 10 as

$$\phi_{+\text{sat}} = \exp[(3\pi/8)^{2/3}(\chi \text{N})^{1/3} - \chi N f] \tag{11}$$

Note that here and below, we explicitly specify the formula for $\phi_{+\text{sat}}$, the volume fraction of copolymer in the B-rich phase. The corresponding value of ϕ_{bulk} can easily be derived from ϕ_+ through eq 1.

Combs. In this section, we will use the above arguments to develop a theory for the properties of AB comb copolymers at an A–B interface. In formulating this theory, we make the following list of assumptions: (1) The backbone is composed entirely of B monomers and the teeth are made up of A units. All the A teeth are equally spaced along the length of the B backbone. (2) For combs localized at the interface, we assume that the section of backbone between adjacent teeth is sufficiently long that it can be described by Gaussian statistics. Then, we simply cut this section of backbone into two equal parts. (3) The degree of polymerization of the entire comb, N, is held fixed regardless of the number of teeth. Thus, increasing the number of teeth also means decreasing the length of each tooth. For example, in the case of one tooth, we have a T-structure with one A tooth and two B/2 "arms". We consider a two-toothed comb to be a branched molecule that, when cut into two parts, produces two T-structures, each having one A/2 tooth and two B/4 arms.

With these assumptions, the stretching energy of a comb at the interface is equal to

$$F_{\text{str}} = n(F_{N_A/n} + 2F_{N_B/2n}) = (\pi^2 N/8\sigma^2)(4 - 3f) \tag{12}$$

where n is the number of teeth and σ is the area per tooth, or $(S/(Qn))$. Hence

$$\mu_{\text{film}} = (3\pi^2 N/8\sigma^2)(4 - 3f) = 3F_{\text{str}} \tag{13}$$

Note that μ_{bulk} is still given by eq 4, since at fixed N and ϕ_{bulk}, μ_{bulk} is independent of the architecture of the molecule.

Now, at equilibrium σ is given by

$$\sigma = [(3\pi^2 N/8\mu_{\text{bulk}})(4 - 3f)]^{1/2} \tag{14}$$

Hence, the interfacial tension is

$$\gamma = \gamma_0 - (2/\pi)(2/3)^{3/2} n^{-1} N^{-1/2}(\ln \phi_+ + \chi N f)^{3/2}(4 - 3f)^{-1/2} \tag{15}$$

Equation 15 reveals that the interfacial tension increases with n, the number of teeth. Thus, increasing the number of teeth in the comb decreases the effectiveness of these copolymers (provided that ϕ_{bulk} is held fixed).

A comparison of eqs 10 and 15 yields a simple estimate of the relative efficiency of comb and diblock copolymers in lowering the interfacial tension:

$$\Delta\gamma^{c}/\Delta\gamma^{d} = 1/n(4 - 3f)^{1/2} < 1 \tag{16}$$

where $\Delta\gamma^i = |\gamma^i - \gamma_0|$, and c stands for comb and d represents diblock. The other important characteristic of the system, $\phi_{+\text{sat}}$, corresponding to $\gamma(\phi_{+\text{sat}}) = 0$, can be found from eq 15 and is given as

$$\phi_{+\text{sat}} = \exp[(3\pi/8)^{2/3}(\chi N)^{1/3}(4 - 3f)^{1/3} n^{2/3} - \chi N f] \tag{17}$$

The ratio $\phi^{c}_{+\text{sat}}/\phi^{d}_{+\text{sat}}$ provides another measure of the relative efficiency of combs with respect to diblocks:

$$\phi^{c}_{+\text{sat}}/\phi^{d}_{+\text{sat}} = \exp[(3\pi/8)^{2/3}\,(\chi N)^{1/3}\{(4 - 3f)^{1/3}\, n^{2/3} - 1\}] \tag{18}$$

Thus, as the number of teeth, n is increased (at fixed N and χ), the comb becomes significantly less efficient and the disparity between combs and diblocks grows larger. At higher values of N and χ, the difference between the architectures becomes more pronounced. Since the dependence on n, N, and χ is exponential in character, small changes in either of these variables yield large changes in efficiency.

We have made a number of assumptions in this formulation: (1) The copolymers at the interface are assumed to form a "brush", which implies that the bulk volume fraction must be sufficiently high, or $\phi_{\text{bulk}} > \phi_{\text{min}}$. (2) On the other hand, the volume fraction of copolymer must be sufficiently low to prevent the copolymer from separating into a distinct phase within the blend, i.e., $\phi_{\text{bulk}} \ll 1$. (3) We assume the copolymer is sufficiently symmetric that micelle formation does not occur before γ reaches 0. (4) The brush is "dry": there is no penetration of the homopolymer into the copolymer layer. This leads to a restriction on the chain lengths: $N_{A,B} < P_{A,B}$. (5) The distance between teeth in the comb copolymers is sufficiently large that we only need to consider the stretching of the chains perpendicular to the surface and can neglect the stretching of the chains parallel to the surface.

Although constraints 2, 4, and 5 are straightforward, conditions 1 and 3 need further elaboration. To find the value of $\phi_{+\min}$ noted in (1), we use eq 4, together with eqs 9 and 14 for the respective σ's, to obtain

$$\phi^{d}{}_{+\min} = \exp[3\pi^2/8N - \chi Nf] \qquad (19)$$

and

$$\phi^{c}{}_{+\min} = \exp[\{3\pi^2(4 - 3f)n^2/8Nf^2\} - \chi Nf] \qquad \text{for } f \le 0.5 \quad (20)$$

We note that at reasonable values of χ, N, and $f \approx 0.5$, these volume fractions are very low; thus, condition 1 is easily satisfied.

For the critical micelle concentration (cmc), we use Leibler's result for diblock copolymers:

$$\phi^{d}{}_{+\mathrm{cmc}} = \exp[(3/2)^{4/3}f^{4/9}\,(\alpha f^{-1/3} - 1)^{1/3}(\chi N)^{1/3} - \chi Nf] \qquad (21)$$

where $\alpha \approx 1.74$ is a numerical constant.[7] We then apply this formalism to derive the $\phi^{c}{}_{\mathrm{cmc}}$ for comb copolymers:

$$\begin{aligned}\phi^{c}{}_{+\mathrm{cmc}} &= \exp[n^{2/3}(3/2)^{4/3}f^{4/9}(\alpha_1 f^{-1/3} - 4)^{1/3}(\chi N)^{1/3} - \chi Nf] \qquad \text{for } f \le 0.5\\ &= \exp[n^{2/3}(3/2)^{4/3}(1 - f)^{4/9}(\alpha_2(1 - f)^{-1/3} - 1)^{1/3}(\chi N)^{1/3} - \chi Nf] \qquad \text{for } f \ge 0.5 \quad (22)\end{aligned}$$

Here, $\alpha_1 = (\alpha + 3)$ and $\alpha_2 = 4\alpha - 3$. In all the analytical calculations described below, we checked that both ϕ_{bulk} and $\phi_{+\mathrm{sat}}$ were $< \phi_{\mathrm{cmc}}$, thus ensuring that condition 3 was always satisfied.

The approach outlined above can also be applied to determine the interfacial behavior of star copolymers. For a four-armed star, with two (A/2) and two (B/2) "arms", this analysis yields the following equations for the stretching energy and interfacial tension:

$$F_{\mathrm{str}} = \pi^2 N/2\sigma^2 \qquad (23)$$

$$\gamma = \gamma_0 - (1/\pi)(2/3)^{3/2}N^{-1/2}(\ln \phi_+ + \chi Nf)^{3/2} \qquad (24)$$

These equations allow us to determine the relative efficiency of this star architecture and other diblock copolymers in lowering the interfacial tension as

$$\Delta\gamma^{\mathrm{star}}/\Delta\gamma^{d} = 1/2 \qquad (25)$$

To test these predictions, we used numerical self-consistent field calculations on both diblocks and comb copolymers. Our self-consistent field method is based on that developed by Scheutjens and Fleer,[11] which in turn is based on a Flory–Huggins approach, combining Markov chain statistics with a mean-field approximation. The equations in this model are solved numerically and self-consistently. The self-consistent potential is a function of the polymer segment density distribution and the Flory–Huggins interaction parameters. 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.[11] We refer the reader to this text for a general review of the SCF formalism.

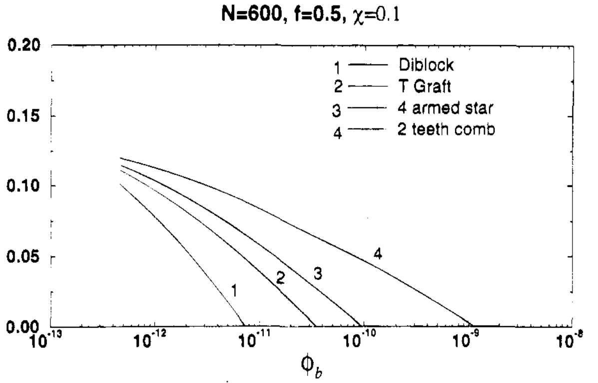

Figure 1. Plot of γ versus ϕ_{bulk} for a diblock copolymer, a four-armed star, and various combs (n = 1 and 2). In all these calculations, we set $\chi = 0.1$, $N = 600$, and $f = 0.5$. The results were obtained from the analytical theory. Here and in all subsequent figures, the symbol ϕ_b is used to designate ϕ_{bulk}.

To contrast the two techniques that were used in our analysis, we note that the numerical SCF theory imposes fewer assumptions than the analytical arguments. The salient differences between the two models can be summarized as follows: (1) Leibler's original treatment was formulated for infinitely long chains, while the SCF calculations take into account finite-length polymers. (2) The interface is not assumed to be a sharp boundary in the SCF model. Rather, the A/B interface has a finite width, which becomes broader with decreasing values of χ. (3) The SCF method does not require us to assume a density profile for the copolymers at the interface; this density profile is, in fact, self-consistently calculated in the model. (4) There is some penetration of the homopolymer into the copolymer layer; thus the film is not a "dry" brush in the SCF model. (5) While we cut the segments of the backbone between neighboring teeth in our analytical theory for comb copolymers, this assumption is not made in the SCF method: the entire comb remains intact in the course of the calculations. These differences in approach can lead to differences in the actual values obtained from the two models.

Results and Discussion

We used eqs 10, 15, and 24 to plot γ versus ϕ_{bulk} for a diblock copolymer, a four-armed star, and various combs (n = 1 and 2). In all these calculations, we set χ = 0.1, the degree of polymerization N = 600, and composition f = 0.5. The results are shown in Figure 1, which clearly reveals that the diblock produces the lowest interfacial tension at all values of ϕ_{bulk}. As a consequence, the diblock is the most efficient compatibilizer: lower values of ϕ_{bulk} are needed to produce a given value of γ (see Figure 1). The next in the sequence is the T (the one-toothed comb), followed by the star and then the comb with n = 2. The plot also illustrates eq 18: the ratio ($\phi^{c}{}_{\mathrm{sat}}/\phi^{d}{}_{\mathrm{sat}}$) grows exponentially with increasing n. (Note that at $f = 0.5$, $\phi_+ = \phi_- = \phi_{\mathrm{bulk}}$. In all the above examples, γ reaches 0 before ϕ_{bulk} reaches the cmc, as calculated from eqs 21 and 22).

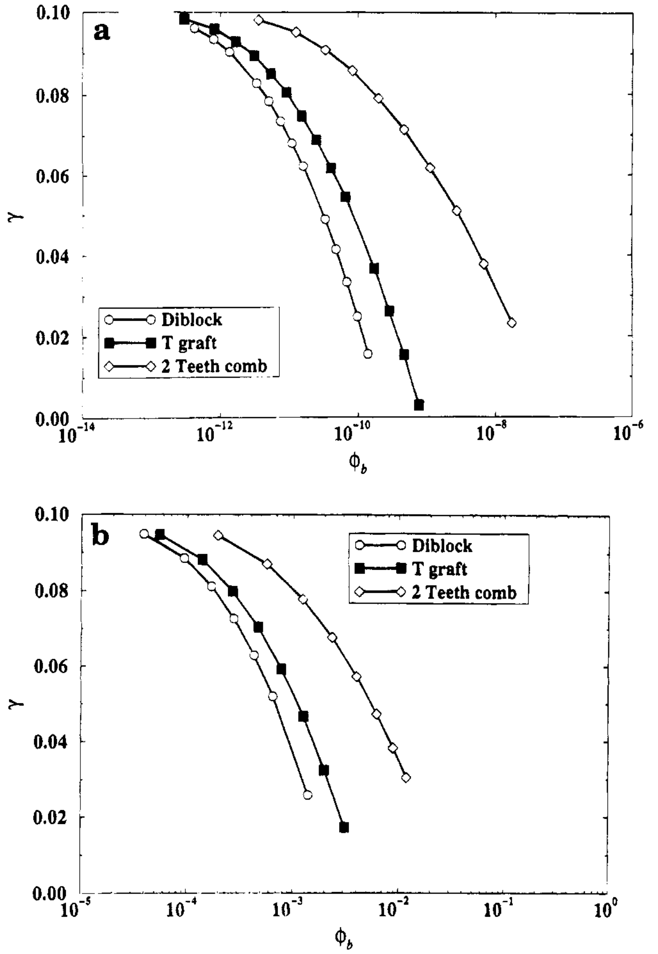

Figure 2. Plot of γ versus ϕ_{bulk} for a diblock copolymer and combs with $n = 1$ (the T) and 2. In all these calculations, we set $\chi = 0.1$ and $f = 0.5$. In (a) $N = 600$ and in (b) $N = 200$. These results were obtained from the numerical SCF theory. Here, we must also specify the length of the homopolymers, N_h, which was set to 100 for both the A and B chains.

In performing the SCF calculations, we also fixed $\chi = 0.1$ and composition $f = 0.5$. Two different copolymer degrees of polymerization were examined, $N = 600$ and $N = 200$. The calculations were carried out on a diblock, a T, and a comb with two teeth. Here, we specify θ, the total amount of copolymer in the system. From the value of θ, the values of ϕ_{bulk}, as well as the amount of copolymer at the interface, θ^{ex}, are calculated self-consistently. The results from the SCF calculations are plotted in Figures 2, which reveals the same trend as the analytical calculations.

As noted above, the density profiles for the polymers at the interface can be calculated self-consistently through the numerical SCF model. Figure 3 shows plots of $\phi(z)$, the volume fraction of polymer in layer z, versus z, the direction perpendicular to the interface. The diblocks show the greatest overlap between the A,B blocks and the respective homopolymers. The mechanical properties of a blend depend not only on the reduction of the interfacial tension but also on the extensive overlap and entanglement of the copolymers with the appropriate homopolymer domains.[12] Our results show that the symmetric diblocks are effective at meeting both of these criteria.

We can gain yet further insight into the interfacial behavior of these chains by plotting the amount of copolymer adsorbed at the interface versus ϕ_{bulk} for the different architectures. The analytical results show that more diblocks are localized at the interface than any of the other copolymers (see Figure 4). Similar results are obtained from the SCF calculations, as can be seen in Figure 5.

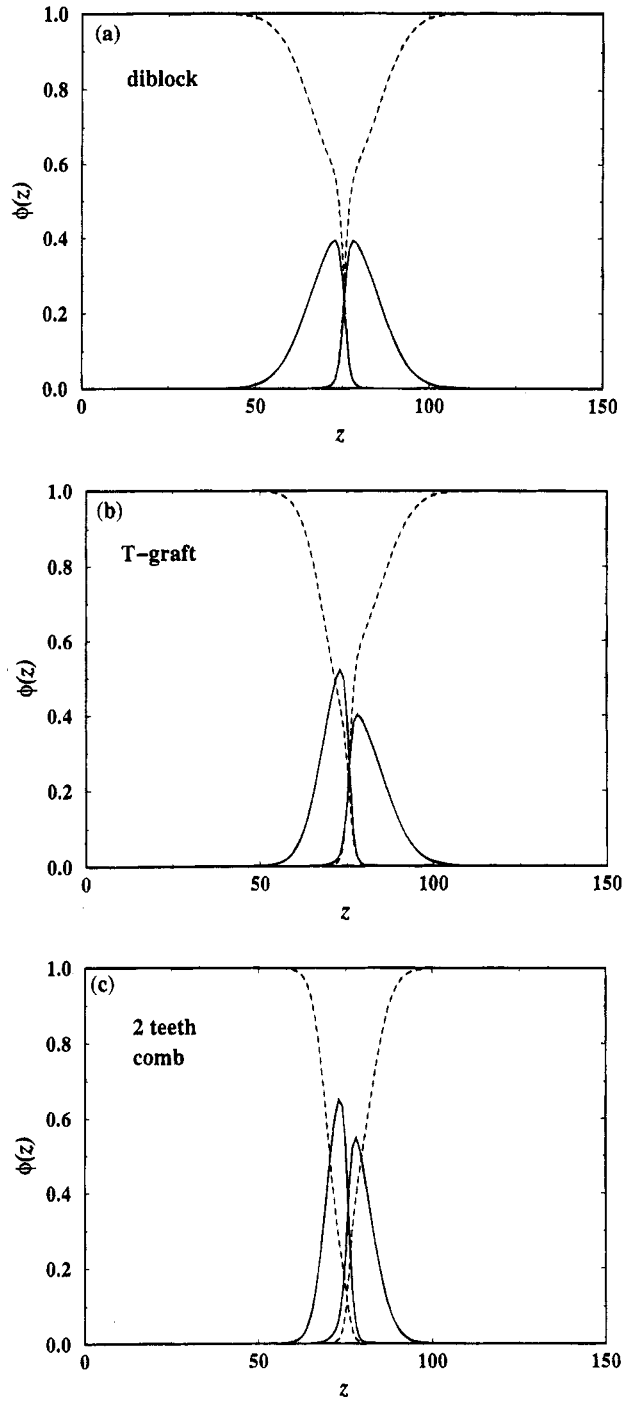

Figure 3. Plots of the polymer density profiles, $\phi(z)$ versus z, for the different copolymer architectures. The results were obtained from the numerical SCF calculations. The parameters are the same as in Figure 2a. The amount of copolymer adsorbed at the interface, θ^{ex}, is the same in all the figures. The solid lines mark the density profiles for the copolymers, while the homopolymer profiles are shown in dashed lines. Part a shows the density profile for the diblock, part b displays the profile for the T, and part c reveals the profile for the two-toothed comb copolymers. The left-hand side of the plots in (b) and (c) shows the density profiles for the "backbones" and the right-hand side shows the "tooth" profiles. The backbone profiles are narrower than the tooth profiles since they are more pinned to the interface. Since $f = 0.5$, the areas under the backbone and tooth density profiles are equal.

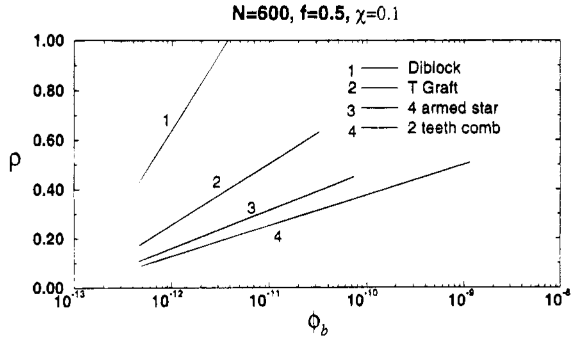

Figure 4. Plots of ϱ, the amount of copolymer adsorbed at the interface per unit area, versus ϕ_{bulk} for the different copolymer architectures. For the diblocks, $\varrho = N/\sigma$ and for the combs, $\varrho = N/\sigma n$. The results were obtained from the analytical theory. Here, $\chi = 0.1$, $N = 600$, and $f = 0.5$.

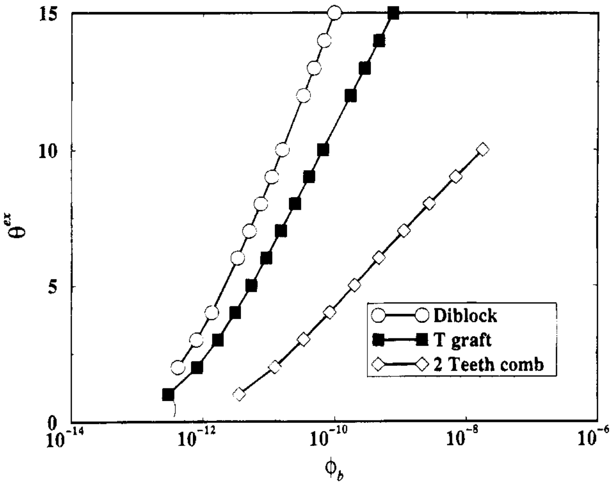

Figure 5. Plot of the amount of copolymer adsorbed at the interface, θ^{ex}, versus ϕ_{bulk} for the different copolymer architectures. The results were obtained from the numerical SCF theory. Here, $N = 600$ and $N_{\mathrm{h}} = 100$. Similar trends are seen in the case where $N = 200$ (and $N_{\mathrm{h}} = 100$). Here, $\chi = 0.1$ and $f = 0.5$.

It is also of interest to explore the relative roles of N and n. In Figure 6a, we use our analytical expressions to plot γ versus ϕ_{bulk} for diblocks of different degrees of polymerization, i.e., $N = 200$, 400, 600, and 800. The figure clearly reveals that the longest diblock is the most efficient at reducing the interfacial tension. The same effect can be seen by comparing parts a and b of Figure 2. In Figure 6b, we again use the analytical formulas to plot γ versus ϕ_{bulk} for combs in which we fixed the degree of polymerization at $N = 800$ but vary the number of teeth so that $n = 2$, 3, 5, and 10.

A comparison of Figures 6a and 6b confirms that at fixed N, the diblock and the combs with fewer teeth are more efficient. But the figures also illustrate the trade-off between n and N. Put succinctly, a long comb with multiple teeth is more efficient than a short diblock. This can be seen by comparing the $N = 800$ and $n = 2,3$ combs with the $N \leq 600$ diblocks. Similar behavior can be seen for the $N = 800$, $n = 5$ comb and the $N \leq 400$ diblocks. Even when $n = 10$, the long comb is more efficient than the shortest diblock. The region where long combs of degree of polymerization N_{c} are more efficient than short diblocks of degree of polymerization N_{d} can be determined by evaluating the inequality $[\phi^{\mathrm{c}}{}_{+\mathrm{sat}}(N_{\mathrm{c}})/\phi^{\mathrm{d}}{}_{+\mathrm{sat}}(N_{\mathrm{d}})] < 1$. For $N_{\mathrm{c}} > N_{\mathrm{d}}$, this yields the condition

$$(3\pi/8\chi N_{\mathrm{d}})^2(4 - 3f)/f^8 \lesssim \{(N_{\mathrm{c}}/N_{\mathrm{d}}) - 1\}^3/n^2(N_{\mathrm{c}}/N_{\mathrm{d}}) \quad (26)$$

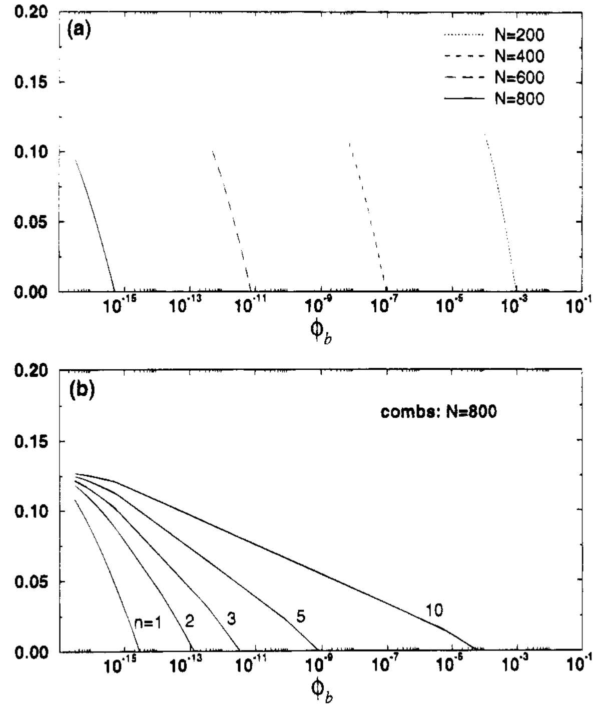

Figure 6. Plot of γ versus ϕ_{bulk} for (a) diblocks with $N = 200$, 400, 600, and 800 and (b) combs with $N = 800$ and $n = 2$, 3, 5, and 10. The results were obtained from the analytical theory. Here, $\chi = 0.1$ and $f = 0.5$.

At fixed N, the reason why diblocks are better than combs can be explained as follows. For the sake of simplicity, we will compare diblocks and T copolymers. Since the chemical potentials of these species are the same in the bulk (see eq 4), at equilibrium their chemical potentials at the interface will also be equal (see eq 3). Recalling that $\mu_{\mathrm{film}} = 3F_{\mathrm{str}}$ for both architectures further implies that the stretching energies per chain will be the same. This is possible if the area per chain for the T's is larger than that for diblocks. That this indeed is the case can be observed from eqs 9 and 14, as well as Figures 4 and 5. In particular, the figures show that for fixed values of ϕ_{bulk}, the concentration of T's at the A/B boundary is smaller than the volume fraction of adsorbed diblocks, implying that each T occupies a larger interfacial area. Now, recalling eq 10 for the interfacial tension, we can rewrite γ as

$$\gamma = \gamma_0 + \delta F_{\mathrm{str}}/\delta\sigma = \gamma_0 - 2F_{\mathrm{str}}/\sigma \quad (27)$$

Thus, at constant stretching energy, higher values of σ yield higher γ's and thus lead to less efficient copolymers. In terms of a physical interpretation, the smaller the area per chain, the more crowded the chains, and consequently, the more pronounced the relaxation will be when σ is increased.

Different arguments apply to the case of long versus short copolymers. Here, the difference in chain lengths leads to different chemical potentials in the bulk, and, consequently, different stretching energies. In particular, the long copolymers will be more stretched than the short chains. Thus, the response of the interface to an increase in the interfacial area is more pronounced in the case of the long copolymers.

Conclusions

In summary, we used both analytical arguments and numerical SCF theory to contrast the compatibilizing activity of AB diblock and comb copolymers at an A/B interface. We fixed the degrees of polymerization of the copolymers and determined which structure is most efficient at reducing the interfacial tension. Both methods point to the fact that the diblocks offer the best compatibilizing activity. Our results show qualitative agreement with the available experimental data: the experimental studies conducted by Riess and Jolivet on the emulsifying effects of diblock and comb copolymers.[1] The researchers considered ternary blends of PS (polystyrene), PI (polyisoprene), and PS–PI copolymers and determined the compatibilizing activity of the copolymers by examining the optical clarity of the blends. Effective compatibilizers can turn a hazy blend into a clear one. Keeping the composition and molecular weights of the copolymers approximately fixed, Riess and Jolivet found that diblocks are more effective at producing clear films.

We also compared the efficiency of long combs with multiple teeth and short diblocks. The analytical results emphasize the important role that a high degree of polymerization plays in enhancing the efficiency of the copolymer compatibilizers. Since comb copolymers are less expensive to synthesize than symmetric diblocks, our results provide a prescription for optimizing the utility of these comb copolymers. In particular, using combs that have a high degree of polymerization for the backbones and significant spacing between the teeth can provide a cost-effective means of compatibilizing blends.

In comparing copolymers of fixed degree of polymerization, increasing the number of teeth also meant deceasing the length of the teeth. However, comb copolymers are frequently synthesized or “assembled” from backbones of fixed length and teeth that are also of fixed length.[13] Thus, in a future paper, we will compare the interfacial activity for comb copolymers in which the length of the backbone and the length of the teeth are fixed but, the number of teeth are varied. Given the experimental constraints of creating combs from fixed-length sections, these studies will be helpful in indicating how the tooth number effectives the compatibilizing activity of the copolymers.

Our findings indicate that these theoretical methods can be used to predict the efficiency of a large class of compatibilizers and therefore can provide guidelines for fabricating not only effective copolymers but also high-strength polymer blends.

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