Notes

Effect of Composition on the Compatibilizing Activity of Comb Copolymers

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Introduction

The blending of polymers can provide a highly economic means of creating materials that combine the characteristics of the constituents or exhibit new, desirable properties.[1] A drawback to fabricating blends, however, is that most polymer pairs are immiscible. Consequently, the resulting material phase-separates into macroscopic domains, yielding relatively poor mechanical properties. A key to producing polymer blends with enhanced structural integrity involves adding copolymer chains, or "compatibilizers", that lower the interfacial tension and disperse the incompatible homopolymers into smaller, microscopic domains. Previous experimental studies demonstrated that branched or comb copolymers can act as effective compatibilizers.[2] Since these copolymers are relatively inexpensive to synthesize,[3] they constitute a cost-effective alternative to the more traditional, but expensive diblock copolymers. To enhance the utility of these combs, it is important to isolate the conditions under which the combs will display the optimal interfacial activity.

In a previous study,[4] we used analytical arguments and numerical self-consistent field (SCF) calculations to determine the interfacial behavior of AB comb copolymers localized at the interface between two immiscible homopolymers, A and B. In particular, we assumed that the volume fraction of A homopolymers in the mixture was equal to the volume fraction of B homopolymers, or $\phi_A = \phi_B$. We also fixed the molecular weight of the entire comb (N) and set the number of A sites within the comb equal to the number of B sites. We then increased the number of the teeth to probe the effect of copolymer architecture on the reduction in interfacial tension at the A/B boundary. (Since N was held fixed, increasing the number of teeth meant simultaneously decreasing the length of each tooth.) We were thus able to determine the optimal comb architecture and, furthermore, pinpointed conditions under which the comb copolymers are more efficient than diblocks in reducing the interfacial tension.[4]

In this paper, we compare the interfacial activity of comb copolymers in which the length of the backbone and the teeth are fixed; however, the number of teeth, and thus, the total molecular weight of the comb, is allowed to vary. (This construction is comparable to the common experimental situation where combs are "assembled" or fabricated from fragments of fixed molecular weight.[5]) In varying the number of teeth, we also vary the ratio of A to B sites within the chain. Consequently, these studies will allow us to determine how the relative composition of the comb affects the ability of the chains to reduce the interfacial tension.

In the prior study,[4] we adapted the formalism derived by Leibler for the interfacial activity of diblocks[6] and applied the theory to comb copolymers. The results from these analytical calculations showed excellent agreement with numerical self-consistent field calculations on similar chains.[4] We again apply this formalism to probe the behavior of AB combs at an A/B interface. Below, we first summarize the relevant equations from our previous model and then apply the model to isolate the effect of copolymer composition.

Model

We consider a blend that contains a volume fraction ϕ_A of homopolymer A and ϕ_B of homopolymer B. The molecular weights 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 sufficiently sharp that it can be approximated by a flat plane.[6] To this mixture, we add a low volume fraction, ϕ_{bulk}, of AB comb copolymers. The backbones are 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. The composition of these copolymers is specified by $f = N_A/(N_A + N_B)$, where N_A and N_B are the degrees of polymerization for the different components.

The volume fraction of combs in the A-rich and B-rich phases will depend on the molecular weights of the blocks and the volume fraction of homopolymers in the mixture. For low values of ϕ_{bulk}, the volume fraction of combs in the B-rich phase can be approximated as[6]

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

and in the A-rich phase

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

The amount of copolymer at the interface is determined by equating the chemical potentials of the combs in the bulk and at the interface, or

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

where the chemical potential in the bulk is given by

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

and the chemical potential at the interface is given by

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

Here and below, S is the area of the interface and Q is the number of copolymers at the interface. All charac-

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teristic lengths are expressed in the units of the monomer size *a*, which is assumed to be the same for both the A and B monomers, and all energetic values are expressed in units of kT.

We now assume that the combs form a "dry brush" on both sides of the interface. That is, the homopolymers do not penetrate into the copolymer 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 chains:[6]

$$F_{\mathrm{film}} = \gamma_0 S + Q F_{\mathrm{str}} \tag{6}$$

where $\gamma_0 = (\chi/6)^{1/2}$ is the interfacial tension of the pure A−B homopolymer interface.[7] For combs localized at the interface, we further 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. With these assumptions, the stretching energy of a comb at the interface is equal to[4]

$$F_{\mathrm{str}} = n(F_{N_A/n} + 2F_{N_B/2n}) = (\pi^2 N/8\sigma^2)(4 - 3f) \tag{7}$$

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

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

Now, at equilibrium σ is given by

$$\sigma = [(3\pi^2 N/8\mu_{\mathrm{bulk}})(4 - 3f)]^{1/2} \tag{9}$$

We previously showed that the interfacial tension is equal to[4]

$$\gamma = \gamma_0 - 2F_{\mathrm{str}}/(\sigma n) \tag{10}$$

which yields

$$\gamma = \gamma_0 - (2/\pi)(2/3)^{3/2} n^{-1} N^{-1/2} (\mu_{\mathrm{bulk}})^{3/2} (4 - 3f)^{-1/2} \tag{11}$$

Equation 11 reveals that when N, f, and ϕ_{bulk} are held fixed, the interfacial tension increases with n, the number of teeth. Under these conditions, increasing the number of teeth in the comb decreases the effectiveness of these copolymers. As we show below, this is not the case when N and f are allowed to vary.

Results

We fix the degree of polymerization of the B backbone at N_B and degree of polymerization of each A tooth at N_t and vary the number of teeth to determine an optimal tooth number. Under these conditions, a change in the number of teeth, n, means a change in the total degree of polymerization, $N = N_B + N_A$, where $N_A = nN_t$. A change in n also implies a change in the copolymer composition, characterized by $f = N_A/N$.

An important characteristic of the system is ϕ_{sat}, the value of ϕ_{bulk} when $\gamma = 0$. The lower the value of ϕ_{sat}, the smaller the amount of compatibilizer that must be added to the blend and consequently, the more efficient the compatibilizer. Figure 1 shows the dependence of ϕ_{sat} on f for combs with different backbone lengths. This figure clearly shows that the smallest ϕ_{sat} can be reached with a symmetric comb, i.e., that the symmetric ($f = 0.5$) combs are the most efficient. To gain insight into the physical meaning of this result, we analyze the limiting cases of very low ($f \ll 1$) and very high ($f \approx 1$) numbers of teeth.

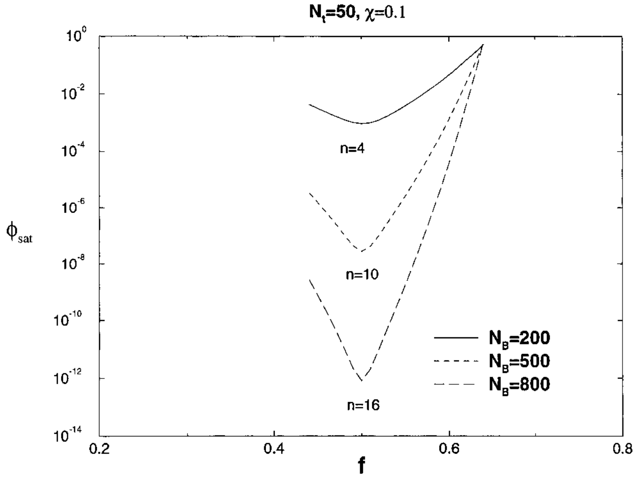

Figure 1. Plot of ϕ_{sat} versus f. Here, N_t, the tooth length, is held fixed at 50 units and χ is set equal to 0.1. Curves for three different molecular weight combs are shown. Once N_t is fixed and N_B, the molecular weight of the backbone $(=(1 - f)N)$, is chosen, f is varied by varying n, the number of teeth. The number of teeth corresponding to $f = 0.5$ is marked for each curve. The plots clearly show that these symmetric combs are the most efficient. Furthermore, at fixed f, the combs with the highest N are the most effective.

In varying the number of teeth, we traverse the range of combs from the B-rich, which mainly localize in B homopolymer, to the A-rich, which mainly localize in the A phase. According to eq 1, the volume fraction of combs in the B-rich phase in the limit of low and high numbers of teeth are

$$\phi_+ = \begin{cases} (\phi_{\mathrm{bulk}}/\phi_B), & \text{for } N_A \ll N_B \\ (\phi_{\mathrm{bulk}}/\phi_A)\exp(\chi(N_B - N_A)), & \text{for } N_A \gg N_B \end{cases} \tag{12}$$

The parameter ϕ_+ is a rapidly decreasing function of n at high N_A (since $N_A = nN_t$) and attains a constant value at low N_A. The decrease in ϕ_+ leads to a decrease in the entropic contribution, $\ln \phi_+$, to the chemical potential, μ_{bulk} (see eq 4). However, the enthalpic contribution to μ_{bulk} (arising from the unfavorable A−B interactions between the A teeth and B homopolymers) increases with an increase in n. In the limit of a low and high number of teeth, μ_{bulk} can be determined from a balance of these entropic and enthalpic contributions. In particular, through eqs 4 and 12, we obtain

$$\mu_{\mathrm{bulk}} = \begin{cases} \ln(\phi_{\mathrm{bulk}}/\phi_B) + \chi N_A = \mathrm{const} + \chi n N_t, & \text{for } N_A \ll N_B \\ \ln(\phi_{\mathrm{bulk}}/\phi_A) + \chi N_B = \mathrm{const}, & \text{for } N_A \gg N_B \end{cases} \tag{13}$$

The chemical potential of the chains in the bulk phase is an increasing function of n at low N_A and is a constant at high N_A. Here, the enthalpic term dominates over the entropic contribution at small n, while at large n, both terms are approximately of the same size, and the chemical potential remains constant.

Once the value of μ_{bulk} is known, we can obtain an equation for the equilibrium area per tooth, σ, through eq 9:

$$\sigma = (3\pi^2/8)^{1/2} \times \begin{cases} [(N_A + 4N_B)/(\ln(\phi_{\mathrm{bulk}}/\phi_B) + \chi N_A)]^{1/2} \sim n^{-1/2}, & \text{for } N_A \ll N_B \\ [(N_A + 4N_B)/(\ln(\phi_{\mathrm{bulk}}/\phi_A) + \chi N_B)]^{1/2} \sim n^{1/2}, & \text{for } N_A \gg N_B \end{cases} \tag{14}$$

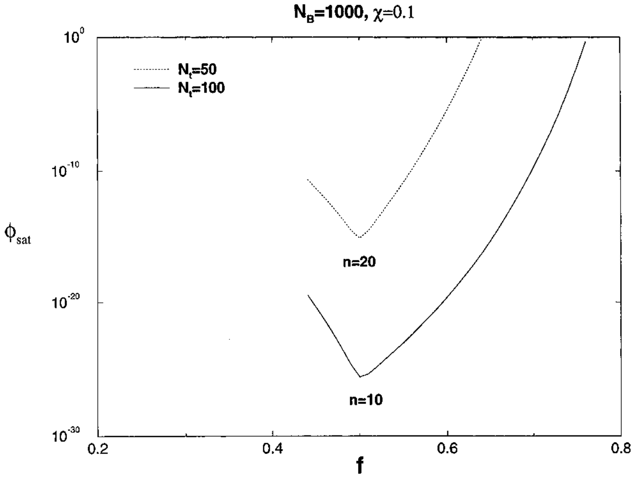

Figure 2. Plot of $\phi_{\rm sat}$ versus f. The length of the backbone is held fixed at $N_{\rm B} = 1000$ and χ is set equal to 0.1. At each value of f, the molecular weights of the combs in the dotted ($N_{\rm t} = 50$) and solid curves ($N_{\rm t} = 100$) are the same. Thus, increasing tooth length, $N_{\rm t}$, means decreasing n, the number of teeth. The number of teeth are marked for the $f = 0.5$ case. The plots reveal that at fixed N, combs with fewer, longer teeth are more effective than combs with multiple, short teeth.

This variable is nonmonotonic in its behavior. The nonmonotonic character arises from a balance between two competing trends: the contributions to the chemical potential that force chains to sit at the interface, and a stretching energy that drives chains back into the bulk.

As we previously showed and as can be seen from eq 10, the chains that yield the highest value of $F_{\rm str}/(\sigma n)$ are the most efficient at reducing the interfacial tension.[4] Recalling that $F_{\rm str} \approx N/\sigma^2$ and utilizing eq 14, we obtain the following asymptotic behavior for the stretching energy:

$$F_{\rm str}/(n\sigma) = {\rm const} \times \begin{cases} (\ln(\phi_{\rm bulk}/\phi_{\rm B}) + \chi N_{\rm A})^{3/2}/n(N_{\rm A} + 4N_{\rm B})^{1/2} \sim n^{1/2}, & \text{for } N_{\rm A} \ll N_{\rm B} \\ (\ln(\phi_{\rm bulk}/\phi_{\rm A}) + \chi N_{\rm B})^{3/2}/n(N_{\rm A} + 4N_{\rm B})^{1/2} \sim n^{-3/2}, & \text{for } N_{\rm A} \gg N_{\rm B} \end{cases} \tag{15}$$

This energy will have a maximum since $F_{\rm str}/(n\sigma)$ is an increasing function at $N_{\rm A} \ll N_{\rm B}$ and a decreasing one at $N_{\rm A} \gg N_{\rm B}$. By equating the asymptotes for low and high n, we find that the maximum occurs at

$$\chi(N_{\rm B} - N_{\rm A}) = \ln(\phi_{\rm B}/\phi_{\rm A}) \tag{16}$$

For $\phi_{\rm A} = \phi_{\rm B}$, this is equivalent to $N_{\rm A} = N_{\rm B}$ or $f = 0.5$. The optimal behavior at $f = 0.5$ can be understood by realizing that a symmetric comb yields the greatest surface density, $1/\sigma$, of copolymer at the interface (see eq 14). This, in turn, produces the greatest reduction in the interfacial tension (see eq 10) and thus the most efficient comb copolymers. (As indicated by eq 16, when $\phi_{\rm A} \neq \phi_{\rm B}$, the optimal behavior is shifted from $f = 0.5$. Thus, the optimal copolymer composition depends on the relative volume fraction of homopolymers in the blend.)

Recalling eq 10, we obtain the following asymptotic behavior for the interfacial tension:

$$\gamma = \gamma_0 - (2/3)^{1/2}(4/3\pi) \times \begin{cases} (\ln(\phi_{\rm bulk}/\phi_{\rm B}) + \chi N_{\rm A})^{3/2}/n(N_{\rm A} + 4N_{\rm B})^{1/2}, & \text{for } N_{\rm A} \ll N_{\rm B} \\ (\ln(\phi_{\rm bulk}/\phi_{\rm A}) + \chi N_{\rm B})^{3/2}/n(N_{\rm A} + 4N_{\rm B})^{1/2}, & \text{for } N_{\rm A} \gg N_{\rm B} \end{cases} \tag{17}$$

Through these asymptotes, we can determine the behavior of $\phi_{\rm sat}$, the value of $\phi_{\rm bulk}$ where $\gamma = 0$:

$$\phi_{\rm sat} = \begin{cases} \phi_{\rm B} \exp[(3\pi/8)^{2/3} n^{2/3} (\chi(N_{\rm A} + 4N_{\rm B}))^{1/3} - \chi N_{\rm A}], & \text{for } N_{\rm A} \ll N_{\rm B} \\ \phi_{\rm A} \exp[(3\pi/8)^{2/3} n^{2/3} (\chi(N_{\rm A} + 4N_{\rm B}))^{1/3} - \chi N_{\rm B}], & \text{for } N_{\rm A} \gg N_{\rm B} \end{cases} \tag{18}$$

It follows from eq 17 that $\phi_{\rm sat}$ decreases at low n and increases at high n, with the optimal number of teeth corresponding to $N_{\rm A} = N_{\rm B}$. We have already observed this behavior in Figure 1.

Once the tooth length ($N_{\rm t}$) and f are fixed, Figure 1 also reveals that the most efficient comb is the one with the highest molecular weight. This follows directly from eq 17, where $\phi_{\rm sat} \sim {\rm e}^{-\chi N}$ for all values of f.

Figure 2 demonstrates the result of fixing N and varying $N_{\rm t}$. Here, increasing the length of the teeth means decreasing n, the number of teeth. Under these conditions, the figure reveals that fewer, long teeth are more effective than multiple, short teeth in enhancing the efficiency of the combs.

The curves in the Figures 1 and 2 are only valid for some region around $f = 0.5$, where micellization does not occur. We used eq 22 from ref 4 to calculate the boundaries of these regions on Figures 1 and 2. This region is symmetric for diblock copolymers and spreads from $f = 0.3$ to $f = 0.7$.[6] For comb copolymers, however, this region is not symmetric since micelles with teeth inside the core and backbones in the corona ($f < 0.5$) can form more easily than reverse micelles with the backbone in the core and teeth in the corona ($f > 0.5$).[4]

Conclusions

Our findings show that efficiency of the combs in reducing the interfacial tension is highly dependent on composition. Symmetric combs prove to be the most effective at reducing γ (when the volume fractions of immiscible homopolymer are the same, i.e., $\phi_{\rm A} = \phi_{\rm B}$). This condition provides a prescription for determining the optimal number of teeth. The findings also show that at fixed N and f, long teeth are highly effective at increasing the efficiency of the combs. These findings provide guidelines for synthesizing ideal copolymer compatibilizers.

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References and Notes

(1) Utracki, L. A. *Polymer Alloys and Blends: Thermodynamics and Rheology*; Hanser Publishers: New York, 1989.
(2) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, p 35.
(3) Peiffer, D. G.; Rabeony, M. *J. Appl. Polym. Sci.* **1994**, *51*, 1283.
(4) Lyatskaya, Y.; Gersappe, D.; Balazs, A. C. *Macromolecules* **1995**, *28*, 6278.
(5) Dennis Peiffer, private communication.
(6) Leibler, L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 1.
(7) Helfand, E.; Tagami, Y. *J. Polym. Sci., Part B* **1971**, *9*, 741.

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