Adhesion promotion at a homopolymer–solid interface using random heteropolymers

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We investigate the potential uses for random heteropolymers (RHPs) as adhesion promoters between a homopolymer melt and a solid surface. We consider homopolymers of monomer (segment) type A which are naturally repelled from a solid surface. To this system we add RHPs with both A and B (attractive to the surface) type monomers to promote adhesion between the two incompatible substrates. We employ Monte Carlo simulations to investigate the effects of variations in the sequence statistics of the RHPs, amount of promoter added, and strength of the segment–segment and segment–surface interaction parameters. Clearly, the parameter space in such a system is quite large, but we are able to describe, in a qualitative manner, the optimal parameters for adhesion promotion. The optimal set of parameters yield interfacial conformational statistics for the RHPs which have a relatively high adsorbed fraction and also long loops extending away from the surface that promote entanglements with the bulk homopolymer melt. In addition, we present qualitative evidence that the concentration of RHP segments per surface site plays an important role in determining the mechanism of failure (cohesive versus adhesive) at such an interface. Our results also provide the necessary input for future simulations in which the system may be strained to the limit of fracture. © 1998 American Institute of Physics.

I. INTRODUCTION

The adhesion of polymers to solid substrates is important in a wide array of applications ranging from semiconductors to food packaging, but what happens if a homopolymer with certain desirable properties and the desired substrate are incompatible? In this article, we explore the possibility for “compatibilizing” such a homopolymer–solid interface using random heteropolymers (RHPs). These are multicomponent polymers with disordered sequence distributions. In the present context, we consider using RHPs composed of two types of segments with one type favoring interactions with the homopolymer chains and the other type favoring interactions with the surface. The issue we wish to explore in detail is: under what conditions can RHP promoters “stitch” the homopolymer and substrate together? That is, what are the optimal parameters such that the RHP organizes itself into long loops that can entangle with the bulk homopolymer melt while having sufficiently long trains capable of anchoring strongly to the solid surface?

The rationale for selecting RHPs rather than other more finely tailored heteropolymers (e.g., diblock, triblock, etc.) or end-grafted chains is that RHPs are easier to synthesize and therefore, less expensive. Thus, they may have more potential in real applications. RHPs have, in fact, been used in practice to promote adhesion, but the methodology has been empirical. There is not a systematic understanding of the physics underlying the observed increase or decrease in adhesion strength upon variation of parameters such as amount of promoter and RHP sequence statistics.

In contrast, the behavior of RHPs and block copolymers at polymer blend interfaces has been investigated in detail. More generally, the behavior of RHPs has been of considerable interest in recent years because RHPs constitute an interesting class of quenched disordered materials and because they exhibit a transition akin to protein folding. Further, the adsorption of RHPs from solution and their behavior in random media have been considered extensively. Fredrickson and Donley have also studied random multiblock copolymer melts near surfaces. Experimental characterization of the strengthening and failure mechanisms of homopolymer–solid interfaces with block copolymer additives has been investigated by Kramer and co-workers.

The efficacy with which a certain type of polymeric additive promotes adhesion is clearly dependent upon the way that the chains arrange themselves at the interface. The interfacial chain conformational statistics, and hence the strength of adhesion, should depend upon the RHP sequence distribution statistics, the number of RHP segments per unit of adsorbing area, and the strength of the various intersegment and segment–surface interaction strengths.

In this article, we employ the Monte Carlo method to simulate a homopolymer-RHP-surface system and attempt to explore this parameter space with an eye towards finding the optimal parameters for adhesion promotion. At low RHP sur-
face coverage, the properties of individual RHP chains are unperturbed by the other RHP chains in the system. For these conditions, we find that there are regions of parameter space in which each RHP chain contains a large fraction of adsorbed segments while also extending long loops into the homopolymer phase, two necessary conditions for adhesion promotion. At higher RHP coverage, a separate RHP phase may develop (depending upon segment–surface and segment–segment interaction strengths) and the homopolymer–RHP–surface system has the potential to fail at either the solid–polymer interface or the new polymer–polymer interface (i.e., adhesive or cohesive failure). Our simulations allow us to make some qualitative predictions about the best set of parameters ($f_A$—the fraction of $A$-type segments in a given RHP chain, $C_{RHP}$—the amount of promoter added to the system, $\{V_{XX}\}$—the various intersegment interactions, $\{V_{XS}\}$—the various segment–surface interactions) for adhesion promotion. In the near future, we hope to perform fracture calculations using the equilibrated Monte Carlo results using methods similar to those employed by Termonia and Smith$^{39–43}$ in order to make these ideas quantitative.

The article is organized as follows: in Sec. II, we provide a precise definition of the system we have studied and describe the simulation methodology. In Sec. III, we discuss the results of the simulations for the range of parameters studied, and in Sec. IV we present our conclusions and suggest a course for future study.

II. MODEL AND METHODS

We consider a homopolymer melt composed of $A$-type segments bounded by two homogeneous solid surfaces. The segment–surface interaction $V_{AS}$ is repulsive, and the segment–segment interaction $V_{AA}$ is attractive. We make this choice for convenience; the key physics is contained in the intersegment interactions being more favorable than the segment–surface interactions. To this system, we add random heteropolymer chains composed of $A$- and $B$-type segments, and we investigate the subsequent equilibrium organization of the system. The segment–surface interaction $V_{BS}$ is attractive, the segment–segment interaction $V_{BB}$ is attractive, and the segment–segment interaction $V_{AB}$ is repulsive. Thus, the surface has a tendency to segregate the two differing types of RHP segments. Also, $\chi_f = \frac{1}{2}(V_{AA} + V_{BB} - 2V_{AB}) < 0$ which means that the $A$- and $B$-type segments will also tend to segregate in the bulk.

The sequence statistics of these RHP chains are fully specified by two variables: $f_A$ and $\lambda$. The parameter $f_A$, as mentioned above, is the fraction of $A$-type segments in the RHP chain and is the parameter of immediate interest to us here. The parameter $\lambda$ ranges between $-1$ and 1 and describes the range of chemical correlations along the chain.$^{15,44}$ For $\lambda < 0$, the sequence distributions tend to be statistically alternating in character, and for $\lambda > 0$, the sequence distributions tend to be statistically blocky. We will explore the effects of variations in $\lambda$ in a forthcoming article. For the work presented here, we consider RHPs with $\lambda = 0$; thus, the composition, $f_A$, is the only measure of the sequence statistics.

Our simulations are carried out on a cubic lattice (coodination $Z = 6$). Impenetrable surfaces are located at $z = 0$ and $z = L$, and periodic boundary conditions are imposed in the $x$ and $y$ directions. In our simulations, typical system size parameters are lattice side $L = 72$, chain length $N = 400$, and number of chains $M = 680$. These values imply lattice occupancy of 70%.

An important question to ask at this point is: is this occupancy high enough to reproduce melt conditions? Obviously, incompressibility will not be enforced. Algorithms which are useful at full occupancies such as chain-breaking algorithms$^{45–49}$ cannot be used to investigate our system because they would destroy the quenched sequence distribution of the RHP chains, and the system would be allowed to anneal to the most favorable equilibrium sequences and conformations. This would be unphysical as chain connectivity precludes such sequence annealing in a real system. We believe that for the occupancies examined, our system modeled with the reptation algorithm described below behaves like a melt. This belief is based on the fact that we observe scaling characteristic of the molten state; $^{50}$ the radius of gyration $R_g$ scales with chain length as $R_g \sim N^{0.52}$ and the center of mass velocity $V_{cm}$ of the polymer chains scales with chain length as $V_{cm} \sim N^{-3}$. These results are presented in Fig. 1. In Fig. 1(a) the logarithm of the average radius of gyration is plotted against the logarithm of chain length for a bulk homopolymer melt with periodic boundary conditions in all directions (no surfaces). The scaling exponent $\nu$ is 0.52, indicative of random walk scaling rather than self-avoiding walk scaling for which the exponent $\nu$ would be 0.59. In Fig. 1(b), the logarithm of $V_{cm}$ is plotted against the logarithm of chain length, and we observe a crossover from Rouse type scaling ($N^{-2}$) to melt-like scaling ($N^{-3}$) as the chain length increases. For the system of interest, we simulate chains with $N$ large enough to be in the melt regime. We turn next to how these results and data for the full homopolymer-RHP-surface system are actually generated.

A straightforward reptation algorithm is employed to effect the simulations.$^{51–54}$ First, a polymer chain is selected at random. One end of this chain is selected at random, and an attempt is made to remove this segment and replace it at the other end of the chain such that a new bond vector of random orientation is created. This move is carried out according to a standard Metropolis Monte Carlo criterion$^{55}$ in which the energy change associated with the move is computed and the move accepted if:

$$\min[1,\exp(-\beta \Delta E)] > P,$$

where $\beta = 1/k_B T$, and $P$ is a random number between 0 and 1. In this way, the chain slithers or reptates along its contour in a tube. We now turn to the initial configuration of the system on which the move described above is repeatedly attempted.

Initially, homopolymer chains are placed on the lattice in an ordered nonequilibrium state (the high occupancies used in the simulation preclude placing random coils on the lattice in conformations close to those at equilibrium) and allowed to relax into a typical equilibrium state. Relaxation to equilibrium is monitored by examining the average radius of gyration of the chains. Equilibrium is considered to be attained
when this quantity reaches a steady value. For the chain lengths and lattice occupancies typical of the simulations presented here, the system equilibrates in approximately 10 million attempted moves per chain. At 70% lattice occupancy, the acceptance rate of moves is approximately 25% for the system parameters studied. This means that in the course of equilibration, each chain undergoes approximately 2.5 million reptation moves, or put another way, each chain reptates along its own length approximately 6750 times. Initial relaxation is carried out with 20 million attempted moves per chain to ensure equilibrium is attained. The relaxation of the radius of gyration is shown in Fig. 2. As the chain length increases, the time for relaxation to equilibrium also increases and does so in a nonlinear fashion such that the time for equilibration for the chain length of interest \(N=400\) is very long.

After the homopolymer-solid system has equilibrated, the random heteropolymer chains are introduced. In the equilibrated system, RHP chains are substituted for homopolymer chains randomly until the desired concentration of RHP chains has been attained. The system is then allowed to relax to a new equilibrium state (approximately 40 million attempted moves per chain). Averages of the desired equilibrium properties (e.g., density profiles, adsorbed fraction, average loop lengths, average train lengths, etc.) are subsequently taken over approximately 100 data points each separated by 100,000 attempted moves per chain (75 chain lengths).

This algorithm allows for simulations and equilibrium averages to be carried out in a reasonable amount of computer time (2 to 3 days on a 533 MHz DEC Alpha Processor for a given set of parameters). Normally, reptation algorithms are exceedingly slow for heteropolymers with a quenched sequence distribution because a single move will destroy many favorable segment-segment contacts and create many unfavorable segment-segment contacts resulting in a large energy change and low acceptance probability. In the system we are investigating, however, each RHP chain is mostly surrounded by homopolymer. This means that most contacts are A-B and A-A interchain contacts, and there are very few B-B intrachain contacts. New configurations will have similar numbers of contacts and the energy change for an RHP slithering through a homopolymer melt will not be prohibitively large.

We are able make a further simplification which allows an enormous saving in computation time. Because we are not interested in dynamics but rather equilibrium properties and because the homopolymer melt mitigates the heteropolymeric effects as described above, we are able to save computation time in our simulations by not shifting the RHP sequence and recalculating the entire chain energy for each move. As mentioned above, the energy changes are small,
but the important point to note is that while the sequence changes as monomers are removed from one end and placed at the other, the effect on the overall RHP sequence statistics is negligible if the chains are long enough. This does not mean that we anneal the sequence. For a chain of length 400, with $f_A=0.5$, there are $10^{120}$ possible sequences, and this methodology explores only 400 of these which all have roughly the same value of $\lambda$. Recall that $\lambda$ is the parameter that describes the range of chemical correlations along the polymer chain as it is synthesized. The change or error in $\lambda$ introduced by this simplification is proportional to $1/N$. That is, at any given step of the procedure, the number of bonds $N_{XY}$ of each type (A-A, A-B, B-B) in the new chain sequence differs by at most 1 from the original chain sequence:

$$|N_{XY} - N_{XY}^0| \leq 1.$$  

For $N=400$, this amounts to a maximum standard deviation in $\lambda$ of 0.01 and maximum deviation of 0.03 for $|\lambda|$ close to 1. For $\lambda=0$ and $f_A=0.5$, the error introduced is even smaller ($\sim 0.003$). In generating a given sequence with fixed $N, f$, and $\lambda$, we allow deviations in the computed $\lambda$ of at most $\pm 0.01$. So each new sequence generated as we cycle through the segments has a $\lambda$ which deviates from the desired value of $\lambda$ well within the acceptable error range. Because we do not have to shift the sequence, the energy calculation for each attempted move becomes independent of the chain length, and we achieve an enormous reduction in computation time.

If we wish to reduce the error further, we may increase $N$. Of course, we can eliminate this error entirely by shifting the sequence as the reptation proceeds but at much larger computational expense. We note also that if we were interested in the dynamics of the interfacial system, we could not employ this simplification as the chain moves would be unphysical.

III. RESULTS AND DISCUSSION

We have systematically studied the influence of a range of parameters on the equilibrium conformational statistics of RHP adhesion promoters. The results aid in understanding why certain ranges of parameter space may be most useful for adhesion promotion and provide the necessary data for computing interfacial strength via future fracture simulations. The scenarios we have investigated are most logically differentiated by the amount of RHP introduced into the system. We have studied three different RHP coverages: 0.075 RHP segments per surface site, 1.275 RHP segments per surface site, and 5.1 segments per surface site. In our system, this corresponds to 0.5%, 5% and 20% of the chains being RHPs, respectively. For each coverage, we have further investigated the effects of varying the sequence distribution statistics. In addition to the parameters mentioned above, we also vary the various segment—segment and segment—surface interaction strengths. Most of the simulations have been carried out with $V_{AA} = V_{BB} = -V_{AB} = -0.1 k_B T$ and $V_{AS} = V_{BS} = 1.0 k_B T$. We also present simulation results for other values of these parameters in order to demonstrate the effect of the interaction strengths on various properties. As we shall see, no major qualitative differences are observed as a consequence of changing these parameters.

![Fig. 3. The homopolymer segment density profile (---) as a function of Z in a system without random heteropolymer (RHP) additives. The density is depleted at the at the surfaces ($Z=0.72$) due to a repulsive interaction between the polymer and surface ($V_{AS} = +1.0 k_B T$).](image)

A. $C_{RHP}=0.075$ segments per site

At these coverages, only a very small fraction of the chains in the system are heteropolymer chains. Therefore, each RHP behaves essentially independently of the other RHPs, and its equilibrium properties are determined solely by interactions with the surface, the homopolymer, and itself. As the coverage of RHP chains is increased, RHP–RHP interactions will become important and will give rise to some new behavior. These effects will be discussed in the following sections.

Because the number of RHP chains is small, the equilibrium homopolymer density profile (shown in Fig. 3) is unperturbed, and we focus our discussion on the organization of the RHP chains alone. These density profiles are shown in Figs. 4(a)–4(c). In these figures, the RHP segment density is plotted as a function of distance from the $Z=0$ surface. The other surface could just as easily have been chosen as the results are the same due to the symmetry of the system. The different curves in Fig. 4(a) represent RHPs of different compositions (differing $f_A$’s), and the results are as one would expect. RHP chains with a small value of $f_A$ adsorb strongly in flat conformations while chains with larger $f_A$ adsorb weakly and have loops extending further into the homopolymer melt. In Figs. 4(b) and 4(c), we focus further on the distribution of the different types of segments within the RHP chains, and see evidence of microscopic ordering. For chains with a large fraction of A-type segments, the A-type segment density profile peaks at $Z=1$ [Fig. 4(c), $f_A=0.8$]. This is because chain connectivity forces the few B-type segments that do adsorb to bring A-type segments to the surface with them.

The density profiles shown in Fig. 4 give some immediate insight into the design parameters that will promote adhesion. If the goal is to stitch the homopolymer and the surface together with the RHP chains, then to achieve this, we
entangle with the homopolymer. RHP chains with small
in the RHP chains.

In Fig. 5 are the adsorbed fraction of RHP chains at
which these two competing effects are best balanced. Plotted
f A
need (1) a large adsorbed fraction and (2) long loops which
can entangle with the homopolymer. RHP chains with small
f A have the highest adsorbed fraction, but RHP chains with
large f A give rise to the longest loops as they are the most
similar to the homopolymer. So, we will have to find values
of f A which lead to the best compromise—a significant con-
tribution from the two effects mentioned above.

The results presented in Fig. 5 clearly show the region in
which these two competing effects are best balanced. Plotted
in Fig. 5 are the adsorbed fraction of RHP chains at Z = 0
and the average loop size as a function of f A . In the region
of the intersection of the two curves (f A ~ 0.75), the ad-
sorbed fraction is approximately 20% and the average loop
length is of the order of 80 segments. Therefore, an RHP
chain with 20% of its segments adsorbed (mostly B-type
segments) is firmly anchored. Also, the average loop length
of 80 segments is long enough so that the loops will be
entangled with the homopolymer chains. So, there are re-

gen regions, located near the intersection of the two curves in Fig.
5, wherein the RHP chains can be expected to strengthen the
homopolymer–solid interface and promote adhesion. A point
to note is that it is pure coincidence that the region of interest
occurs at the intersection of these two curves; both curves
just happen to have inflection points and rise to desirable
values in the vicinity f A = 0.75.

B. C_{RHP} = 1.275 segments per site

For these simulations, 5% of the chains in the system are
RHP chains, and these chains distribute themselves fairly
evenly between the two bounding surfaces. In Figs. 6(a)–
6(d) we present the equilibrium segment density profiles near
the Z = 0 surface. The presence of heteropolymer now per-
turbs the homopolymer distribution, and we must examine
the interplay between the two types of chains to understand
the nature of adhesion promotion.

In Fig. 6(a), the overall density profiles for a range of
values of f A are presented. As f A ranges from 0 to 0.8, the
nature of these curves changes dramatically. At small values
of f A , the Z = 0 surface is mostly covered with heteropoly-
mer. However, the overall density immediately begins to
drop off as Z increases and actually dips below the bulk value (ρ_{bulk} = 0.7) before achieving the bulk value at ap-
proximately Z = 4. This dip in the overall density arises be-
cause of the strong tendency of RHP chains with a large
fraction of B-type units to segregate from the homopolymer.
This dip may be seen clearly in Fig. 6(c). Chains with small
values of f A will tend to segregate from the bulk homopoly-
mer chains, and as we shall see in Sec. IV, if we add enough
RHP, a separate RHP phase with its own bulk properties will
actually form. As f A increases, the surface concentration
drops, and the dip in the overall density disappears as the
heteropolymer chains become more and more like the ho-
mopolymer. A typical density profile in this regime is shown in Fig. 6.

In the previous section, the competition between the two effects (number of surface contacts versus loop length) was described, and the conclusion was that there is an optimal composition yielding an appreciable adsorbed fraction and while retaining long loops. In Fig. 6, we plot the case for $f_A = 0.8$. At this composition, both the contacts and the long loops help to promote adhesion. For $f_A$ approaching 0, the density at the surface is enriched, but away from the surface, the density dips below the bulk value before reaching the bulk value at $Z = 5$. (b) Overall RHP segment density profiles for various $f_A$: $f_A = 0.2$, $f_A = 0.6$, $f_A = 0.8$. For $f_A$ approaching 1, the RHP chains extend away from the surface in long loops. For $f_A$ approaching 0, the RHP chains localize entirely within the first 2 to 3 layers near the surface in flat conformations and are unable to entangle with the homopolymer chains. (c) Segment density profiles for $f_A = 0.2$. The dip in the overall density profile is apparent as is the fact that the RHP and homopolymer chains are relatively unentangled. (d) Segment density profiles for $f_A = 0.8$. The RHP and homopolymer chains are more entangled but the adsorbed fraction at the surface is small and the overall density profile is still depleted near the surface.

As we saw in the previous section, chains with small $f_A$ localize near the surface in flat conformations while the chains with larger $f_A$ extend farther away from the surface. Since the RHP chains with small values of $f_A$ localize near the surface in flat adsorbed conformations, the overall polymer segment density exhibits a dip [see Fig. 6(a)] indicative of weak cohesion between the heteropolymer and homopolymer chains. In assessing the interfacial strength, then, we have to account for the fact that failure may occur at the new RHP–homopolymer interface that appears. Therefore, we need some method with which we may quantify the magnitude of this effect. Before examining this in more detail though, we present results for the final coverage regime studied, as it is in this regime that the heteropolymer–homopolymer interface is most clearly defined.
Beyond a certain surface coverage of RHP chains, the RHP chains and the homopolymer chains phase separate with the RHP phase located closest to the surface. Similar physics have been noted in the context of studying reinforcement of polymer–polymer interfaces using RHPs.\textsuperscript{1–13} The tendency to phase separate is reduced as the RHPs become more like the homopolymers as $f_A \rightarrow 1$. At these coverages, then, we can easily examine all of the interfaces and possible failure planes which may arise in our system. At these coverages, there is a well defined RHP bulk phase and a well defined interface between the two polymer phases. For small $f_A$ and high $C_{\text{RHP}}$ the possibility exists for formation of a third possible plane of failure in the system. For RHP compositions for which $f_A$ is close to 0, some RHP chains will adsorb in flat conformations and the bulk RHP chains may be unable to entangle with the strongly adsorbed RHP chains.\textsuperscript{56} It is necessary to investigate all of these regimes in order to determine the optimal RHP compositions, coverages, and interaction strengths and the plane of failure.

The density distributions obtained from our simulations for $C_{\text{RHP}} = 5.1$ are shown in Figs. 7(a)–7(d). The overall density profiles differ very little from the overall density distributions at the previous coverage. However, the RHP densities [Fig. 7(b)] are markedly different than those for the previous coverage, especially for small $f_A$. At small values of $f_A$, the RHP chains segregate from the homopolymer chains, and two distinct bulk phases are formed as can be seen from the plateaus at the bulk occupancy in Fig. 7(b). The tendency to separate is still strong at $f_A \sim 0.7$, the region in which the best compromise between adsorbed fraction and loop size was found for lower RHP coverages (\textit{vide supra}). Therefore, the adhesion promotion we predict in the 5.1 segments per site, $f_A \sim 0.7$ case is
expected to be lower than in the 1.275 segments per site, $f_A=0.7$ case due to the cohesive weakness of the polymer–polymer interface present at these coverages. However, only future fracture calculations on the system will bear out this point.

If we examine regions of the parameter space with smaller segment–segment interactions, the chains will segregate to a lesser extent, and we may be able to mitigate this effect. However, in a real system, if the segment–segment interactions are small, it is likely that the segment–surface interactions will be similarly reduced. In the following we examine the situation for interaction strengths which are up to an order of magnitude smaller than those discussed above $V_{AA}=V_{BB}=0.01k_BT$; $V_{AB}=-0.1k_BT$. The results are presented in Figs. 8(a)–8(d). As can be seen from the plots, the effect of the reduced interactions on the system is to lessen the tendency to segregate. In Fig. 8(c), we see that as the interaction strength decreases, the RHP chains extend further into the bulk homopolymer phase and the drop off in RHP concentration becomes less sharp. From Fig. 8(a), it is clear that the dip in the density profile present in the results presented in Fig. 7(c) disappears as the interaction strength is reduced, indicating a less well-defined and more entangled interface. However, the density at the surface also decreases and adhesion to the surface is now also much weaker.

**D. Examining the polymer–polymer interface**

In order to determine the location of interfacial failure in this system, we need to be able to compare in a quantitative manner the interaction strengths of all of the interfaces present in the system. Will the system fail at the surface or at some distance away from the surface due to a lack of cohesion between the RHP and the homopolymer? To know this, we must perform simulations in which the system is strained.
until fracture occurs. While such simulations are still to be done, we suggest a methodology for examining the available Monte Carlo data in a qualitative way to locate possible failure points in our system. To do this, we employ the qualitative concept of an entanglement.\textsuperscript{50,57}

An entanglement is a topological constraint. However, an entanglement is an abstract concept and its precise physical definition is still a subject of debate in the polymer physics community. We choose here to seize upon ideas set forth by Kavassalis and Noolandi\textsuperscript{58} and consider a point entangled if it meets a specific criterion that loosely measures topological constraints. If we look at a snapshot of the equilibrated system and focus on an individual segment, we say that a chain segment is entangled if there are at least a critical number of segments from other chains within a given volume centered on the segment of interest. For our simulation data we can carry out such calculations easily. First, we examine every 5th internal chain segment in the system and compute the total number of segments from other chains $S_{\text{diff}}$ in a $5 \times 5 \times 5$ cube centered on that segment. An internal segment is a segment located a specific distance $d$ from either of the chains ends ($d = 10$ for the calculations presented here). We then compute the average and standard deviation of $S_{\text{diff}}$. We consider a segment to be entangled if $S_{\text{diff}}$ is more than one standard deviation above the average of $S_{\text{diff}}$. This criterion should be adjusted so that the number of entanglements per chain matches experimental results. We have only used one standard deviation here to illustrate how microstructure obtained from simulations can be mapped onto a set of topological constraints; the distribution of such constraints can shed light on the strength of the interface and possible failure locations. For example, in Fig. 9, we show a graph of the number of entanglements per layer $N_{c, \text{layer}}$ together with a plot of the overall density for a system with 5.1 RHP segments per surface site and $f_A = 0.1$. The variation of the number of entanglements with distance (Fig. 9) clearly shows that the interface is much weaker than one would infer if one looked solely at the overall density in the system. The dip in the density profile is much less pronounced than the dip in the entanglement curve and indicates a weak RHP/homopolymer interface. As $Z$ increases, $N_{c, \text{layer}}$ gradually reaches its average value characteristic of the bulk melt.

**IV. CONCLUSIONS**

We have simulated a homopolymer–solid interface with added RHP promoters with the ultimate goal of understanding how such an interface may be strengthened by the addition of random heteropolymers. As a first step, we have carried out Monte Carlo simulations on this system to investigate the dependence of interfacial chain conformational statistics on various parameters. Adhesion promotion will best be achieved if the RHPs arrange themselves near the surface in a fashion such that there are a sufficient number of directly adsorbed segments to anchor the RHP chains strongly to the surface, while also maintaining long loops that can entangle with the bulk homopolymer chains. To find the optimal set of parameters for adhesion promotion, we must strike a compromise between these two competing effects. For the interaction strengths investigated, we infer that for compositions in the range $0.6 < f_A < 0.8$, the RHP promoters arrange themselves in such a manner as to have the two desirable equilibrium properties necessary to stitch the homopolymer–solid interface together. Further, we have examined the effect of varying the coverage of RHP in the system from 0.075 segments per surface site to 5.1 segments per surface site; we find that coverages of the order of 1.275 segments per surface site allow for high surface coverage and also entanglement with the homopolymer chains; at lower RHP coverages there are not enough promoters in the system to affect the overall interfacial properties; at higher RHP coverages, a separate RHP phase forms adjacent to the solid surface. This introduces a greater possibility for cohesive failure at a new weak interface between the RHP and homopolymer phases. This suggests that the optimal coverage occurs when the number of RHP segments and the number of surface sites are of the same magnitude, but further calculations need to be carried out to determine the optimal
coverage with any precision. Also, the precise mechanism of failure for a given set of parameters is not yet understood and can only be determined by fracture simulations and experiments. However, the results presented here will help guide future efforts and help narrow the focus to regions of the large parameter space which appear to be the most promising.

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