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Forced reptation revealed by chain pull-out simulations

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We report computation results obtained from extensive molecular dynamics simulations of tensile disentanglement of connector chains placed at the interface between two polymer bulks. Each polymer chain (either belonging to the bulks or being a connector) is treated as a sequence of beads interconnected by springs, using a coarse-grained representation based on the Kremer–Grest model, extended to account for stiffness along the chain backbone. Forced reptation of the connectors was observed during their disentanglement from the bulk chains. The extracted chains are clearly seen following an imaginary “tube” inside the bulks as they are pulled out. The entropic and energetic responses to the external deformation are investigated by monitoring the connector conformation tensor and the modifications of the internal parameters (bonds, bending, and torsion angles along the connectors). The work needed to separate the two bulks is computed from the tensile force induced during debonding in the connector chains. The value of the work reached at total separation is considered as the debonding energy G . The most important parameters controlling G are the length (n) of the chains placed at the interface and their areal density. Our *in silico* experiments are performed at relatively low areal density and are disregarded if chain scission occurs during disentanglement. As predicted by the reptation theory, for this pure pull-out regime, the power exponent from the scaling $G \propto n^a$ is $a \approx 2$, irrespective of chain stiffness. Small variations are found when the connectors form different number of stitches at the interface, or when their length is randomly distributed in between the two bulks. Our results show that the effects of the number of stitches and of the randomness of the block lengths have to be considered together, especially when comparing with experiments where they cannot be controlled rigorously. These results may be significant for industrial applications, such reinforcement of polymer-polymer adhesion by connector chains, when incorporated as constitutive laws at higher time/length scales in finite element calculations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3193725]

I. INTRODUCTION

The dynamics of one polymer chain in solution is by itself a very complex problem: the random motion of each monomer is restricted by the chain connectivity and by the interaction with other monomers. In dense ensembles of polymer chains (e.g., melts and glasses), the chain dynamics is even more complicated by the supplementary restrictions arisen due to the fact that the chains are entangled and cannot pass through each other during their motion. The dynamic behavior of the chains inside polymeric systems is ultimately revealed in the macroscopic properties of the material with tremendous influence on a large number of industrial applications. So, in condensed matter physics, there is a continuous, great interest in understanding the chain dynamics in dense polymer ensembles.

The most widely used theory for polymer melt dynamics is the reptation model of de Gennes¹ and Doi and Edwards.² This model reduces the problem to a single chain motion in an effective medium. The chain motion is constrained by the entanglements with other polymers in such a way that the chain moves only along an immaterial “tube” in a snakelike

manner (see Fig. 1). The chain “reptates” through a tube that follows its contour. The tube is simultaneously rebuilt when a chain extremity escapes the original one.

Thus, the overall motion of one chain is the result of a one-dimensional (1D) diffusion of the chain center of mass along the three-dimensional (3D) random walk path (the tube). Consequently, the chain self-diffusion D is drastically slowed down and scales as N^{-2} , where N is the chain mass, in contrast with N^{-1} dependence specific for normal diffusion.

To prove the reptation theory, different approaches have been used during time. A power exponent $\nu \approx 2$ for the $D \propto N^{-\nu}$ dependence has been found experimentally^{3–7} and in computer simulations.^{8–11} This diffusional reptation is a long time process influenced by the chain length and ensemble density. It is directly reflected in the bulk macroscopic properties and experimental measurements of viscosity, birefringence,² and light or neutron scattering¹² have also been reported to support the theory. Nevertheless, these experiments were not sufficient to validate the tubelike motion of the chains, since different microscopic behaviors could lead to identical macroscopic properties.

For demonstrating the reality of the tube, the help came from biology. The snakelike motion through an entangled mesh of surrounding molecules was observed for diffusive

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FIG. 1. Schematic representation of the restrictive motion of a polymer chain (in gray) inside a dense ensemble of chains (in black). The tube formed due to the constraints imposed by chain entanglement is plotted with dashed lines.

semiflexible actin filaments¹³ and for DNA molecules dragged by one of their end with optical tweezers.¹⁴ In the first case, the tube is formed during diffusional reptation, while in the second, the chains are being forced out of their tubes by an applied force. This kind of reptation, named *forced* reptation, is also specific in case of polymer fracture when chains are extracted from the bulk during deformation.

In this paper we want to reveal the snakelike motion of linear polymers when they are pulled out from a dense ensemble of identical chains. For this we have chosen to study a system that mimics closely a situation met in polymer industry: two immiscible polymer bulks bonded together via connector chains placed at their interface and entangled with both of them.¹⁵ The connectors effectively “sew” the two bulks together and thus strengthen the interface adhesion by sometimes more than a hundred times. The reinforcement produced in this way depends on the areal density, molecular weight, and chain stiffness of the connectors, as well as on their spatial configuration—the way in which they weave back and forth across the interface to create one or multiple stitches.

By studying such systems by molecular dynamics (MD), we inquire not only the nature of the chain motion during pull-out, but we also qualitatively evaluate the debonding energy, namely, the adhesion strength.

II. MODEL AND SIMULATION METHOD

We perform continuous-space MD simulations of a system formed by two polymer bulks placed on top of each other and bonded together by connector chains. Each bulk consists of M linear polymer chains with N beads per chain, while m connector chains with n beads per chain are placed at their interface. The connectors penetrate sequentially into both bulks: each successive connector block (of length n_i) is immersed in a different polymer bulk while s stitches are made at the interface, as shown in Fig. 2.

The two polymer bulks are modeled as half-infinite slabs. They are placed in separated simulation boxes with periodic boundary conditions in the X and Y -directions and with repulsive walls normal to the Z -direction.

FIG. 2. Schematic representation of the architecture of connectors at the interface between two glassy polymer bulks A and B. The number of stitches in the figure varies from $s=1$ up to $s=4$. The stitches are drawn as thick bonds and the connector length n is the sum of connector block length n_i .

The connectors are uniformly distributed at the interface between the two bulks at a specific areal density Σ , in such a way that they form one or more stitches. Successive blocks (tails or loops depending on s) of each individual connector chain are immersed alternately in the two polymer bulks. In most simulations the generated connectors have equal blocks between stitches: $n_b = n/(s+1)$. For special cases the connector blocks are not equal and the connector configuration is explicitly described (e.g., $n_1:n_2:n_3:n_4$ for a three stitch connector), or the blocks have completely random lengths. In this way the junction between bulks is created as the result of the intertwining between connector chains and bulk chains.

The polymer chains (either belonging to the bulks or being a connector) are treated as sequences of beads interconnected by springs using a coarse-grained representation based on the Kremer–Grest model,⁹ but extended to account for stiffness along the chain backbone.¹¹

All unconnected beads interact via the Lennard–Jones (LJ) potential

$$V_{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right], \quad r_{ij} < r_{\text{cutoff}}. \quad (1)$$

Inside polymer bulks, the interaction between any two bulk beads is purely repulsive with σ and ϵ setting the length and energy units and $r_{\text{cutoff}} = \sqrt[6]{2}\sigma$. Two beads from dissimilar bulks do not feel each other directly. The connector–connector bead LJ interaction is also repulsive. However, to realize the adhesion between connectors and bulks, the attractive part of the LJ potential is incorporated for connector

FIG. 3. Potentials used for the interaction between the bulk chains and the walls (LJ integrated wall) and between two connected beads (FENE+LJ for the chains in the bulks and CB for the connectors).

bead-bulk bead interaction; this is done by setting $r_{\text{cutoff}} = 2\sqrt[6]{2}\sigma$.

Each two connected beads from the bulk chains interact through the combination of two potentials: the repulsive LJ potential [Eq. (1) with $r_{\text{cutoff}} = \sqrt[6]{2}\sigma$] combined with the finite extensible nonlinear elastic (FENE) potential

$$V_{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}kR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], & r_{ij} \leq R_0 \\ \infty, & r_{ij} > R_0 \end{cases} \quad (2)$$

with $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$. This bond interaction ensures the chain connectivity and, coupled with the excluded volume interaction between unconnected beads, prevents the chains from crossing each other, thus yielding an entangled polymer ensemble.⁹ It is important to observe that the FENE+LJ combination (the blue dashed line in Fig. 3) is asymmetric with respect to the equilibrium bond length $b_0 = 0.96\sigma$. Consequently, the extension of bonds is more favorable than their compression. Overall, the bonds are slightly stretched¹¹ and a nonzero average tension exists in the bonds.

This will compete with the tension induced in the connectors during bulk separation. To separate these effects and to have a clear measurement of the debonding work, we replace the bond potential with a new “symmetrized” potential to act on the connector bonds (CB)

$$V_{\text{CB}}(r_{ij}) = \begin{cases} -\frac{1}{2}k_r R_r^2 \ln \left\{ \left[1 - \left(\frac{r_{ij}}{R_r} \right)^2 \right] \times \left[1 - \left(\frac{2\sigma - r_{ij}}{R_r} \right)^2 \right] \right\}, & r_{ij} \leq R_r \\ \infty, & r_{ij} > R_r. \end{cases} \quad (3)$$

This potential controls in a symmetric manner both the elongation as well as the compression of the polymer bonds

around the equilibrium bond length 1.0σ (see red line in Fig. 3).

By setting the maximum elongation $R_r = 1.3\sigma$ and the elastic constant $k_r = 50\epsilon/\sigma^2$, the CB potential overlaps as much as possible with the FENE+LJ potential over the active range of bead distances in the neighborhood of the equilibrium bond length (see Fig. 3). When a connector bond exceeds the value $R_r = 1.3\sigma$, the bond is considered broken and the simulation is disregarded.

The stiffness along the polymer chain is enhanced by using a bending potential V_B and a torsion potential V_T acting on three, respectively, four consecutive connected beads. The bending potential maintains the angle θ_i between adjacent pairs of bonds close to the equilibrium value $\theta_0 = 109.5^\circ$,

$$V_B(\theta_i) = \frac{1}{2}k_\theta(\cos \theta_i - \cos \theta_0)^2. \quad (4)$$

The torsion potential constrains the dihedral angle ϕ_i to three possible equilibrium values $\phi = 180^\circ$ (*trans*), $\phi = 60^\circ$ (*gauche*⁺), and $\phi = 300^\circ$ (*gauche*⁻). We use a form of the torsion potential that depends also on bending angles, such that the force cancels when the dihedral angle ϕ becomes undefined as two consecutive bonds align,

$$V_T(\theta_{i-1}, \theta_i, \phi_i) = k_\phi \sin^3 \theta_{i-1} \sin^3 \theta_i \sum_{n=0}^3 a_n \cos^n \phi_i, \quad (5)$$

with $a_0 = 3.0$, $a_1 = -5.9$, $a_2 = 2.1$, and $a_3 = 10.9$. For all simulations presented here the bulk chains have bending and torsion stiffness $k_\theta = 25\epsilon$, $k_\phi = 1\epsilon$ [referred to, hereafter, as rotational isomeric state (RIS) chains], while the connector stiffness is modified to investigate its effects on the adhesion strength.

Supplementarily, each bead from the polymer bulk interacts with the upper and lower walls of its simulation box via an integrated LJ potential

$$V_{\text{LJ}}^{\text{wall}}(z) = \frac{2\pi\epsilon^{\text{wall}}}{3} \left[\frac{2}{15} \left(\frac{\sigma^{\text{wall}}}{z} \right)^9 - \left(\frac{\sigma^{\text{wall}}}{z} \right)^3 \right], \quad z < z_{\text{cutoff}}^{\text{wall}}, \quad (6)$$

where $\sigma^{\text{wall}} = 1\sigma$, $\epsilon^{\text{wall}} = 0.85\epsilon$, and $z_{\text{cutoff}}^{\text{wall}} = 0.85\sigma$. As a result, the chain beads are strictly kept inside the simulation box on Z-direction. This LJ-wall potential (Fig. 3) mimics the interaction of a particle from the bulk with an infinite half-space uniformly filled with standard 6-12 LJ [Eq. (1)] particles.^{16,17} By contrast, the connector beads do not feel this interaction since they are either too far from the external wall or free to penetrate the internal walls during disentanglement. This chain-wall interaction is essential in ensuring that the system is confined to a finite range along the Z axis. It also prevents the bulk particles from being pulled out of the simulation box in Z-direction as they are engaged by the connector chains. In this way the bulk is prevented from undergoing supplementary global plastic deformation (e.g., crazing).

Prior to the debonding simulations, careful preparation and equilibration of the samples are required. The polymer chains are generated as random walks with constraints for the bond lengths, bending, and torsion angles around their equilibrium values.¹¹ This method is also appropriate for

FIG. 4. An example of a connector crossing the two melts. Only the thick bonds are considered for computing the transmitted force.

connectors since the working areal densities are low and, consequently, the connectors do not interact with each other.^{16,18} Supplementary constraints are imposed during generation to keep bulk polymers inside the simulation box in the Z -direction and to create certain stitch architectures of the connectors at the interface.

Tensile debonding is achieved by moving up the top bulk as a whole (together with its walls) at a constant velocity v_{pull} . The fracture is complete when there is no connector with beads located inside both simulation boxes and thus no force is transmitted across the interface. While performing debonding simulations under different conditions, we are interested in determining the adhesion strength and in understanding the mechanism of connector disentanglement.

The work W necessary to separate the two bulks (A and B) is computed from the tensile force F induced in the connector chains by the pulling action. Following an idea from Refs. 19 and 20, for computing the tension force in the vertical Z -direction, we consider the sum of the bond forces $\mathbf{f}_j$ in all the connector bonds that cross the lower boundary of melt A and, subsequently, the upper boundary of melt B, or vice versa (see Fig. 4),

$$F(t) = \frac{1}{2} \sum_{\text{conn}} \sum_j \mathbf{f}_j(t) \cdot \mathbf{e}_z, \quad (7)$$

where $\mathbf{e}_z$ is the unit vector in Z -direction. The first sum goes over all connectors and the second over all bonds from individual connectors that cross the two simulation boxes in sequence. The factor $1/2$ in Eq. (7) arises from the fact that the Z -component of the tension is considered for the bonds crossing the interface both with A and B. Within statistical limits, these two forces are equal and, by averaging, a more accurate measure of the total debonding force is obtained.

As an example, for the connector represented in Fig. 4, there are four such bonds and

$$\sum_j \mathbf{f}_j = \mathbf{f}_{2-3} + \mathbf{f}_{5-6} + \mathbf{f}_{9-10} + \mathbf{f}_{11-12} \quad (8)$$

with $\mathbf{f}_{n-m} = -\nabla V_{\text{CB}}(r_{nm})$. The bond contributions from r_{14-15} and r_{17-18} are disregarded since they do not transfer the tension between the bulks.

FIG. 5. Time dependences of the force F transmitted between the two polymer bulks (gray) and the work W spent during debonding (black) for a system with $m=30$ one-stitch connectors with $n=150$ beads per connector at an areal density $\Sigma=0.008\sigma^{-2}$. The debonding energy G is defined as the plateau value of W that appears at the total debonding time t_D . A, B, and C mark the moments 1τ , 600τ , and 1200τ .

With the time-dependent force computed from Eq. (7) the work needed to separate the two simulation boxes up to time t is

$$W(t) = \frac{1}{A} \int_0^t F(t') v_{\text{pull}} dt', \quad (9)$$

where $A=l_{\text{box}}^2$ is the interfacial area with l_{box} as the box width.

We emphasize that the tensile force, and henceforth the work of debonding, results only from the CB potential acting on the connector bonds; all other interactions (bending or torsion) will ultimately have an indirect effect on the tension. The connectors will be disentangled from inside the two bulks under the action of this tension force and, as we will see further, the results fully reflect the nature of this reptation process.

Figure 5 shows an example of the time evolution of the force F and the work of debonding W . The total debonding energy G is defined as the plateau value of $W(t)$ reached after the total debonding time t_D .

The simulations are performed at constant temperature T and volume V (for each simulation box). The constant volume concept is consistent with the way in which we impose straining, as discussed above. In addition, it avoids the supplementary tensions that would arise from a constant pressure simulation when the volume is adjusted and which would pollute monitoring of the work of debonding.

The temperature is kept constant by coupling the system to a heat bath: the friction coefficient is $\Gamma=0.5\tau^{-1}$ and the strength of the Gaussian white-noise force is $6k_B T \Gamma$. The experiments are performed at $T=0.3\epsilon/k_B$. This value was chosen as it is below the glass transition temperature of polymer bulks with RIS chains, estimated as $T_g^{\text{RIS}}=0.7\epsilon/k_B$ by Bulacu and Van der Giessen.²¹ The equations of motion are

integrated using the “velocity-Verlet” algorithm²² with a time step $\Delta t = 0.01\tau$. A boxing scheme is used for the efficient implementation of the LJ interactions.

Results will be presented from simulations with different connector chain lengths $n \leq 500$ and areal densities Σ , while the connector chain stiffness will be varied. The simulation box size was chosen such that the connectors do not come close to the walls opposite the interface. In each case, the length of the bulk chains was $N=500$, while the number of chains M was computed to obtain the desired bead density ($\rho = 0.85\sigma^{-3}$) inside the simulation boxes. The final results are averaged over ~ 20 independent experiments to account for the variation caused by the random distribution of the connectors at the interface.

III. RESULTS AND DISCUSSION

In this section we will show that the debonding energy G depends on the connector length as n^2 as a consequence of the nature of the polymer chain motion inside a dense entangled ensemble of other polymer chains. We also investigate how the connector stiffness and the number of stitches formed by the connectors at the interface influence this law.

A. Forced reptation as chain pull-out mechanism

During the debonding, as the interface widens, the connectors are first extended, and then parts of them are gradually pulled out from the bulks into the empty region between the two simulation boxes. In Fig. 6 it can be seen how a polymer block of a one-stitch connector is pulled out from a bulk. In black is represented the part of the connector that is still located in the bulk at the times specified in the figure. It can be seen that all these configurations are restricted to a limited space inside the bulk left available by the connector's neighboring chains (not included in the picture). This imaginary tube through that the connector is creeping along is depicted in gray by the superposition of the 100 snapshots of the connector. These are taken during the whole debonding at equal time intervals and include all the ones in black. The connector has to avoid certain obstacles since the force field used made chain crossing practically impossible. Subsequently, it gets more freedom and the connector trajectory is not the contour length itself but a larger tube around the chain. The shape of the tube is also modified during pulling since the surrounding constraints vanish and reform dynamically when the surrounding chains move as well (see the arrows). Next we attempt a simple theoretical description of this phenomenon along the lines of Ref. 23. If we consider a part of a chain of length l (with n_1 beads and bond length b) immersed in a polymer bulk, the force required to extract it must overcome Stokes's drag force

$$f = \gamma v, \quad (10)$$

where γ is the drag coefficient and v is the pulling velocity. The coefficient γ may be considered the inverse of the mobility and, according to Einstein's relation, $\gamma = k_B T / D$. If we assume the reptation theory, i.e., the polymer chain diffuses along a tube determined by the neighboring chains in a 1D, particlelike manner, then the diffusion coefficient D may be

replaced with $D = D_0 / n_1$,²⁴ D_0 being the bead diffusion coefficient. In this way, Eq. (10) becomes

$$f = \mu_0 l v, \quad (11)$$

where $k_B T / D_0 b$ has been replaced with μ_0 that can be regarded as a bead friction coefficient. Consequently, the total work required to completely pull out an entire connector chain of length L (n beads) is given by

$$w = \int_{l=0}^{l=L} \mu_0 l v dl = \frac{\mu_0}{2} L^2 v = \frac{\mu_0 b^2}{2} v n^2. \quad (12)$$

This dependence $w \propto n^2$ for the pull-out regime relying on reptation theory has been deduced using several other approaches for glassy polymer fracture or reinforced interfaces with diblock copolymers.^{23,25–27} Washiyama *et al.*²⁸ demonstrated this scaling to be a good fit to the data obtained experimentally for a polystyrene-polyvinylpyridine interface reinforced with diblock copolymers of polystyrene and polyvinylpyridine acting as connectors in a pure pull-out regime.

However, in real polymeric systems, alternative mechanisms to chain pull-out appear usually during debonding, changing this dependence. Chain *scission* occurs for sufficiently long or stiff connectors or at high debonding velocity when the force needed to pull the connectors exceeds the force needed to break a covalent bond in the chains. *Crazing* appears at high connector areal density if the connectors interact with each other and form fibrils during debonding. Ultimately, the fibrils elongate and break by chain pull-out or scission. Both these mechanisms are more complex and rely on the understanding of the chain pull-out. That way, the numerical experiments presented here are restricted to relatively low areal densities $\Sigma < 0.008\sigma^{-2}$ in a so-called “mushroom” regime.²⁹ When long chains are placed at the interface, scission events appear during their disentanglement due to the extreme elongation of some bonds. These simulations are disregarded. In this way we tried to separate the pull-out mechanism from the others and to investigate it independently. Finding a clear $G \propto n^2$ law would be a proof of the forced reptation mechanism during pull-out.

We start out by investigating the time evolution during debonding of a system with diblock connectors placed in between two polymer bulks (one stitch at the interface). Figure 7 shows three snapshots (at moments marked as A, B, and C in Fig. 5) from the simulation of a system with $m = 30$ connectors with $n = 150$ beads each ($n_1 = n_2 = 75$).

To obtain a complete separation, all connectors must be removed out of at least one polymer bulk. Since the interaction between the connectors and either of the two bulks is identical, and the connectors are symmetric (in this case), the slippage of the chains has no preferred direction. Indeed, as shown in Figs. 7, in the final stage 15 chains have been pulled out from the top bulk and 15 from the bottom bulk. Figure 8 shows the expected behavior for the debonding energy G versus the chain length n for diblock connectors that make one stitch at the interface (full square dots).

More quantitative information on how the connectors act during debonding can be obtained by investigating their deformation and orientation. The internal deformation along

FIG. 6. Representation of one connector motion during its disentanglement from a polymer bulk during the MD simulation. The gray curves are 100 snapshots of the polymer connector taken at equal time intervals and superimposed in all subfigures to visualize the reptation tube. To see how the chain reptates through this available space, the part of the chain located in the bulk is highlighted in black at the times indicated in the figures. The arrows show the release of the tube when the surrounding constraints disappear. The chain part represented here has 75 beads.

the connectors is revealed in the histograms of bonds, bending angles, and torsion angles from Fig. 7. The histograms are collected by computing all the bond lengths (b), bending (θ), and torsion (ϕ) angles along the entire connector chain, irrespective of their location (whether inside or outside the bulks). From the histograms of the bond lengths we can see that as debonding progresses, the bonds are more and more stretched from the equilibrium value of 1.0σ up to a maximum of about 20% elongation. This effect is the basis for computing the work of separation by integrating the tensions in the connector bonds. The bending angles evolve toward

values closer to 180° , while in the distribution of torsion angles, the initial $gauche^+(\phi_0=60^\circ)$ and $gauche^-(\phi_0=300^\circ)$ states disappear leaving a dominant $trans$ state ($\phi_0=180^\circ$). As the connectors are completely pulled out from one bulk and do not transfer the tension anymore, the bond lengths and bending angles return to their equilibrium values. On the contrary, the torsion angles remain in the $trans$ state because the energy barrier to the $gauche$ states cannot be surpassed due to the very low temperature.

More complex behavior is observed for longer connectors ($n=500$) in Fig. 9. Not all the bonds along the chain

FIG. 7. Three snapshots from the tensile debonding simulation of a system with $m=30$ one-stitch connectors with $n=150$ beads per connector at an areal density $\Sigma=0.008\sigma^{-2}$. The elapsed time is indicated below each figure. For clarity, the polymer chains from the two bulks are not shown. Below each snapshot, we represented the corresponding histograms for the bond length b , bending angle θ , and torsion angle ϕ of the connector chains.

deform uniformly: some are significantly elongated, while others remain unstressed, thus giving rise to the two separate peaks in the bond length distribution. By comparing with the previous figure, we observe that the bonds that are stretched are, in fact, subjected to a larger tension and deviate more

from the equilibrium value. This leads to a larger integrated work of debonding. The tension acts on the portion of the connector chains situated between the two bulks. For this region, the bending angles open to 180° , giving rise to the sharp peak in the θ histogram in Fig. 9. When the bending

FIG. 8. The debonding energy vs the number of beads per connector for different number of stitches at connector areal density $\Sigma=0.008\sigma^{-2}$. The curves are power-law fits to the data.

angles are close to 180° , the torsion potential vanishes and, as a result, the histogram of dihedral angles flattens. This behavior is observed also for shorter chains when the pull velocity is increased (not shown).

Irrespective of the chain length, the modifications in the histograms of the bonds, bending, and torsion angles start simultaneously and evolve with comparable speeds during the debonding. During their disentanglement from the polymer bulks, the connectors suffer also an overall reorientation. To characterize this reorientation we have computed the uniaxial order parameter S_α for all the connector bonds,

$$S_\alpha = \frac{1}{2} \langle 3 \cos^2 \theta_\alpha - 1 \rangle, \quad (13)$$

where α denotes the reference direction (e.g., X, Y, and Z) and θ_α is the angle between this direction and each individual bond along the connector. The averaging is done for all the connector bonds. Perfect parallel alignment with the chosen axis is indicated by $S_\alpha=1$, perfect perpendicular alignment by $S_\alpha=-0.5$, and random orientation by $S_\alpha=0$. Figure 10 shows the evolution during debonding of the order parameters with respect to the pulling direction (S_Z) and to a direction included in the plane perpendicular to pulling (S_X).

As the debonding evolves, the connectors align progressively to the pulling direction. Then, when some of them are completely pulled out, this overall orientation is again lost since in between the bulks the connector bonds are free.

The connector deformation and orientation can be described together by the conformation tensor $\tilde{\mathbf{c}}$ with the components $c_{\alpha\beta}$ (α and β being X, Y, or Z directions) defined as

$$c_{\alpha\beta} = \frac{3 \langle R_\alpha R_\beta \rangle}{\langle R^2 \rangle_0}. \quad (14)$$

R_α and R_β denote the projections on a specific direction of the connector end-to-end distance $\mathbf{R}$ and the subscript 0 refers to the equilibrium conditions. The brackets denote the average over all connectors in the system.

FIG. 9. Histograms of the bond length b , bending angle θ , and torsion angle ϕ for a system with long one-stitch connectors with $n=500$ beads at the moment of maximum tension in the connectors.

As defined in Eq. (14), the conformation tensor $\tilde{\mathbf{c}}$ is the unit tensor for an undeformed melt. But, as soon as the polymeric system is subjected to deformation, it deviates from the unity and its components will relate with the free energy change induced by deformation.^{30,31} In Fig. 11 the diagonal components c_{ZZ} and c_{XX} are plotted during the debonding. The component on the pulling direction increases as the two bulks are separated, slightly exceeding the separation distance. The components on the perpendicular plane to pulling are practically unmodified.

In a crude approximation, we have estimated the free energy change by $(k_B T/2) \text{tr}(\tilde{\mathbf{c}})$ (based on the entropic spring model in the case of Gaussian chains). In this way, we have tried to separate the energetic effects resulting through the chain reorientation and change in chain conformation induced during the debonding. While the time evolution of the free energy change shows similar behavior with the one of the work spent to separate the two bulks (included in Fig. 5), its instantaneous values are smaller than the total work exerted in the connectors. The ratio between the debonding work and the free energy change strongly depends on the connector length: ≈ 3 for connectors with $n=150$ beads and ≈ 7 for $n=400$. This is understandable since the computed work includes also the disentanglement effects that are naturally chain length dependent. However, this is a very generic

FIG. 10. Time evolution during debonding of the uniaxial order parameters S_z (delta symbols) and S_x (circle symbols) for two systems with one-stitch connectors of length $n=150$ (solid symbols) and $n=500$ (open symbols).

estimation used to highlight the chain entanglement effects. A more in depth study remains to be done to get more insight into the energetic responses of polymers to deformation in general.

B. Influence of connector chain architecture on debonding energy

The relationship $G \propto n^2$ is less obvious for cases in which the connectors make different number of stitches at the interface or have variable chain rigidity. These will be investigated subsequently in this subsection.

In Fig. 12, we compare the dependence of G on n for different connector stiffness. The default stiffness settings for our experiments were $k_\theta=25\epsilon$ and $k_\phi=1\epsilon$ —RIS conformations both for the bulks as well as for the connector chains. In addition, three modified chain rigidities are considered

FIG. 11. Diagonal components c_{zz} and c_{xx} of the conformation tensor $\tilde{c}$ as a function of the debonding time.

FIG. 12. Debonding energy G vs connector length n ($s=1$ one-stitch) for different connector stiffness. The open symbols denote the case with the default stiffness for this study.

now only for the connectors. Two of them result by disregarding the torsion potential while keeping the bending one in the case of freely rotating chains (FRCs): FRCa with $k_\theta=100\epsilon$, $k_\phi=0$ and FRCb with $k_\theta=25\epsilon$, $k_\phi=0$. By disregarding both the bending and the torsion interactions ($k_\theta=0$, $k_\phi=0$), the freely jointed chain (FJC) case is obtained. This accounts only for the intrinsic stiffness induced only by the excluded volume interactions.

The connectors are generated as RIS chains for all types of stiffness to avoid differences in the initial spatial conformation and to retain only the effect due to the interaction potentials. For the specific fracture mechanism treated in this paper (pull-out only), the debonding energy is higher for stiffer chains, see Fig. 12. The difference is noticeable between intrinsic stiffness and bending stiffness, while the extra contribution due to torsion stiffness seems negligible, requiring further investigation. The overall sensibility of the measured G to the variation in connector's stiffness indicates that, indeed, the total tension induced during debonding ultimately appears in the elongation of the connector bonds/chains.

The strengthening effect of the connector chain rigidity in the pull-out regime cannot be immediately translated into improved adhesion, since other fracture mechanisms may have a different sensitivity to chain rigidity. In particular, stiff long chains tend to break easier than flexible ones. This explains why opposite effects of the chain rigidity on debonding energy (including multiple fracture mechanisms) are reported both in experimental studies^{32,33} and in simulations.¹⁶

A better reinforcement of the polymer interface is expected by increasing the number of stitches (the way in which the connectors weave back and forth across the interface, interweaving with both polymer bulks), but exactly how to control the adhesion strength by changing connectors architecture is still an open research question with potential benefit in practical applications. Several experimental

FIG. 13. The last snapshot from tensile debonding simulations for systems with (a) $s=2$, (b) $s=3$, and (c) $s=4$ stitches at the interface. All the systems have the same number of connectors $m=30$ with equal blocks between stitches $n_b=50$. The connector areal density was constant at $\Sigma=0.008\sigma^{-2}$.

studies^{34,35} have been done by replacing the diblock connectors that form a single stitch at the interface with multiblock connectors that form multiple stitches. Due to the fact that the connectors make multiple excursions across the interface, the areal density of stitches differs from the areal density of connectors. In experiments, the connector density can be controlled but the stitch density remains uncertain, despite the preformed chemical structure (e.g., triblock). In computer simulation, however, it is possible to completely control the initial configuration of the connectors at the interface—both the number of stitches and the number of beads in each block between the stitches. Our procedure for generating the connectors allows for an extensive study of the influence of the number of stitches on the adhesion strength at constant connector areal density as well as at constant stitch areal density.

Figure 13 shows the last snapshot at complete tensile separation of systems with different numbers of s stitches (as defined in Fig. 2). In the two-stitch situation, Fig. 13(a), most of the connectors remain attached to the upper bulk after fracture since the main polymer disentanglement occurs for the tails from the bottom bulk. For the three-stitch case, the partition of connectors is more balanced between the two bulks due to the symmetry of the initial conformation [see Fig. 13(b)]. In the case of $s=4$ shown in Fig. 13(c) most chains stick to the bulk in which they have the central loop and the tails at the beginning of the simulation (please refer to the last panel in Fig. 2).

When the total length of the connector chain is kept constant, only a moderate increase in G with the number of stitches is observed (see Figs. 14 and 8). As the number of

FIG. 14. Adhesion strength G vs number of s stitches. Two cases are considered: (1) constant connector length ($n=240$ beads with equal blocks between stitches—open symbols) and (2) constant block length ($n_b=50$ beads—solid symbols). The total length of the connector is $n=n_b(s+1)$.

stitches increases, each connector block becomes shorter. Due to this, a peculiar situation occurs for $s=2$, where we observe that adhesion is weaker than for the one-stitch case. The tails of the two-stitch connectors are shorter (1/3 from the entire length) and consequently easier to extract than the tails of the one-stitch connectors (1/2 of the length). The increase in G due to the stitches is more pronounced for longer chains, as can be seen in Fig. 8, which contains the G versus n dependences for several systems in which the number of stitches made on the interface was varied. For all cases the power exponent from $G \propto n^a$ dependence was calculated and included in Table I.

The power exponent increases with the number of stitches (except for $s=2$) since, for a certain connector length, more loops have to be disentangled when more stitches are formed. In real samples, however, there is an uncontrolled distribution of the number of stitches or the lengths of the blocks in between stitches. To mimic such situation, the lower curve (open square symbols) in Fig. 8 shows the n dependence for one-stitch connectors with random block lengths (named $1r$ in Table I). An evident decrease in debonding strength is noticed due to the fact that the chain blocks effectively extracted from the bulks are shorter than half of the connector length (as in one-stitch connector with equal blocks). Consequently, the power ex-

TABLE I. The power exponent from $G=n^a$ obtained for systems with different connector stiffness and variable number of s stitches. The considered stiffnesses are RIS ($k_\theta=25\epsilon, k_\phi=1\epsilon$), FRCa ($k_\theta=100\epsilon, k_\phi=0$), FRCb ($k_\theta=25\epsilon, k_\phi=0$), and FJC ($k_\theta=0, k_\phi=0$). r denotes a random distribution of the block lengths n_i between stitches while “cr” represents the complete random case for which the number of stitches as well as the number of blocks are randomly designated.

$s=1$				RIS					
RIS	FRCa	FRCb	FJC	$s=2$	$s=3$	$s=4$	$s=1r$	$s=2r$	$s=cr$
2.14	2.16	2.04	2.03	2.00	2.25	2.38	1.69	1.67	2.02

ponent a decreases below 2.0. For a completely random generation of the connectors, each connector placed at the interface having a random number of s stitches and random n_i block lengths, the effects of stitches and effective block lengths are superimposed and $a \approx 2.0$ is recovered.

The influence of the stitches on adhesion strength was investigated in computer simulation by only one other known study.^{19,20} The authors reported a larger improvement of the adhesion strength with the number of stitches for a constant chain length. The disagreement probably relies on the significant differences between the models: in that study, the bulks are modeled as two-dimensional networks of fixed obstacles, the connectors have rigid bonds, and they are grafted on the surface of one bulk during the pull-out. Our system is much more fluid because all our interactions are continuous and the connectors are free at the interface. Our results, showing a moderate increase in the tensile work with the number of stitches at the same chain length, are in better qualitative agreement with experimental results that indicate random copolymer connectors as “surprisingly effective in reinforcing polymer interfaces,” but not better than diblock (one-stitch) connectors of the same length at the same connector areal density.^{34–39} In the chain pull-out regime, the external work goes mainly into the stretching of the connector molecules, which does not change dramatically from the one-stitch case to the many-stitch cases.⁴⁰

When the length of each block is kept constant and the total length of the connector multiplies with the number of stitches, the adhesion strength G grows significantly mainly due to the increased length of the chains. This case is represented by solid symbols in Fig. 14.

The number of stitches per connector dramatically changes the time evolution of the total force transmitted by the connectors during debonding and, thereby, of the work W . These effects can be distinguished in Fig. 15. The plateaus in the force response curves are due to the sequential extraction of connector blocks from the two bulks. They occur at almost the same simulation time, and hence separation distance, since all the blocks considered have the same length. Evidently, when the block lengths n_i along the connector are randomly distributed these plateaus attenuate.

IV. CONCLUSIONS

In this paper, a detailed MD investigation has been performed to reveal the mechanisms by which polymer chains disentangle from a dense ensemble of identical chains. The results have not only theoretical implications but can be used as a first step in understanding a very common industrial application: reinforced adhesion via connector chains placed at the interface of two immiscible polymer bulks.

The two polymer bulks are represented as realistic, 3D, dense entangled ensembles of polymer chains with connectors weaving back and forth across the interface to reinforce it via one or multiple stitches. The total work G needed to separate the two polymer bulks by completely pulling out the connector chains that connect them was calculated. The re-

FIG. 15. Time dependences of total force F transmitted between the two polymer bulks for connectors with different numbers of stitches and equal number of beads per block.

sulted values were compared for connector with different length and stiffness or making different number of stitches at the interface.

Consistent with the working conditions, small areal density and limited length of the connectors, we have distinguished a clear tube shape in which a polymer chain is constricted during disentanglement. The chain is forced to reptate through the available space left by interacting with the other chains. The tube changes itself since the surrounding constraints vanish and reform dynamically when the surrounding chains move as well. As predicted using reptation concepts,^{23,25–27} the dependence of debonding energy G on the chain length is $G \propto n^2$ when disentangling connectors with equal tails immersed in the two bulks.

The debonding energy is influenced slightly stronger by the total connector length $a > 2$ when three or four stitches are formed at the interface, whereas a randomly distributed length between stitches leads to $a < 2$. A clear $G \propto n^2$ is found instead for a distribution of connectors with random stitches and random block lengths between stitches. These results show that the effects of the number of stitches and of the randomness of the block lengths have to be considered together.

A moderate increase in debonding energy can be produced also by enhancing the connector rigidity. This paper shows that polymer chain entanglement is the basis for bounding two bulks together and helps in understanding the pull-out mechanism during polymer fraction.

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