Molecular weight effects on chain pull-out fracture of reinforced polymeric interfaces

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Using Brownian dynamics, we simulate the fracture of polymer interfaces reinforced by diblock connector chains. We find that for short chains the interface fracture toughness depends linearly on the degree of polymerization $N$ of the connector chains, while for longer chains the dependence becomes $N^{3/2}$. Based on the geometry of initial chain configuration, we propose a scaling argument that accounts for both short and long chain limits and crossover between them.

$G \sim N^a,$ \hspace{1cm} (1)

where estimates give variably $1 \leq a \leq 2$. Both linear and quadratic dependences of $G$ on $N$ have been predicted, utilizing a tube picture \cite{24}. Different constitutive equations have been proposed which relate the local stress in planar cohesive zone near the crack tip to various phenomena, such as, the penetration depth of the cracks, their surface density, and the pulling rate \cite{13,14}. These studies have been focused mainly on the pull-out fracture in tensile mode, when the applied force is normal to the interface. An alternative mode of interface failure is shear fracture, or the resistance of the interface against slip. In fracture mechanics of bulk materials generally only the tensile or opening mode is important, since cracks normally travel in a direction that maximizes the opening mode. However, for the interface between two different materials, the situation can be more complex: The crack is often constrained to follow the interface, giving rise to the possibility of crack propagation involving a combination of tensile and shear modes \cite{3}. Herein we study the dynamics of chain pull-out fracture in both tensile and shear mode separately and examine the dependence of $G$ on $N$.

We use a Brownian dynamics method, due to Picket, Jasnow, and Balazs \cite{18,19}, to simulate the pull-out of a single connector chain of length $N$ from a two-dimensional

Creating advanced materials often means mixing different homo-polymers to produce systems with desired combined properties. However, most polymer blends are immiscible: They form macroscopically phase-separated mixtures with only interfacial van der Waals forces keeping domains of different phases together. The fracture toughness of such blends is limited by one of the intermingling domains of different phases together. The fracture of incompatible homo-polymers to produce systems with desired surface energy of homo-polymer $A \gamma_a$ and homo-polymer $B \gamma_b$ is the interfacial free energy. Reinforcement of these weak polymeric interfaces is often achieved by the addition of $A-B$ diblock copolymers which compatibilize the blend and strengthen the interface \cite{13,14}. The strengthening can be attributed to the miscibility of each block with one of the homopolymers. This causes the block copolymer to expand and entangle with homo-polymer phases on either side of the interface. The interfacial tension (energy) is reduced, the interfacial width is increased, and the adhesion thereby improved. Fracture toughness and failure mechanisms of such reinforced polymeric interfaces have been investigated extensively by, for example, experiments on different incompatible systems of polymer glasses \cite{19,20} and cross-linked networks (elastomers) \cite{13,14} to explain the reinforcing effect of connector chains in both elastomers and glassy polymers. A “failure mechanism map” has been developed \cite{13,14,19,20} which relates the mechanism of interface failure to the polymerization index $N$, surface density $\sigma$ of connector chains, and the time scale on which the deformation occurs. According to the failure map there are three major mechanisms: (i) chain scission, which happens whenever the stress along the connector chain becomes larger than the strength of the covalent bond between segments of the chain, (ii) pull-out of the connector chain as a result of disentanglement from homo-polymer phase, and (iii) failure by craze formation, followed by chain scission or chain pull-out, which take place when a large stress is transferred to the bulk of the homo-polymer phases.

\begin{equation}
\sigma \lesssim N^{3/2} \left( \gamma_a + \frac{\gamma_a - \gamma_b}{N} \right),
\end{equation}

\begin{equation}
G \propto N^{\alpha},
\end{equation}

\begin{equation}
\alpha \approx \frac{1}{2} \left( \frac{\gamma_a - \gamma_b}{N} \right)^2.
\end{equation}
homo-polymer phase. To quantify the interface toughness for different chain length, we calculate the work that is required to pull out the chain with constant velocity $v_0$. The homo-polymer phase is modeled by a two-dimensional semi-infinite square lattice of obstacles. Each obstacle represents an entanglement or cross linked point, depending on the glassy or elastomeric structure of the homo-polymer phase, and provides lateral constraint on the movement of the connector chain. The connector is represented by a freely jointed chain with $N$ links wherein there is no self-interaction. Hence individual monomers can freely pass over each other, provided links have a constant length. The initial configuration is created by putting the first monomer at the boundary and then continuing the chain as a random walk in dimension $d = 2$, with a reflecting boundary at the interface. The random walk is restricted by requiring, as we shall see below, that monomers are repelled by the obstacles. The pull-out dynamics is simulated by pulling the chain by the first monomer at a constant velocity in either tensile mode (perpendicular to the interface) or shear mode (parallel to the interface). This is done conveniently by moving the obstacle matrix at velocity $-v_0$ while keeping the first monomer fixed. That is, if $r_i$ is the position of the $i$th monomer, $dr_i/ dt = 0$.

The movement of the other $i = 2, \ldots, N$ monomers is governed by the following over-damped Langevin equation:

$$\nu \left( \frac{dr_i}{dt} - v_0 \right) = \tau_i (r_{i+1} - r_i) - \tau_{i-1} (r_i - r_{i-1}) + F_i + \eta_i,$$  

for $1 < i < N - 1$. This results in a tridiagonal matrix equation for the $\tau_i$’s [25]:

$$\frac{d(r_{i+1} - r_i)}{2 dt} = \tau_{i+1} (r_{i+2} - r_{i+1}) (r_{i+1} - r_i) - 2\tau_i l^2 + \tau_{i-1} (r_i - r_{i-1}) (r_{i+1} - r_i) + (F_{i+1} + \eta_{i+1} - F_i - \eta_i) (r_{i+1} - r_i).$$

Ideally, by applying the constant segmental length constraint, the left-hand side of Eq. (4) should be zero. However, after several updates of the simulation, as a result of accumulation of roundoff errors, the distances between some of the adjacent monomers differ slightly from $l$. To improve the stability of the algorithm, a correction, restoring the original segment length, is introduced:

$$\frac{d(r_{i+1} - r_i)}{2 dt} = -|r_{i+1} - r_i| \cdot \frac{(r_{i+1} - r_i) - l}{l dt}.$$  

Eq. (2) is solved using a fourth-order Runge-Kutta algorithm.

We consider reduced units in which $\nu, \nu_0, \sigma, k_B T,$ and $D$, the distance between obstacles, are set equal to unity. The distance between two adjacent monomer in connector chain $l$ is chosen to be 0.4. The time step of the simulation, typically $10^{-4}$ to $10^{-5}$, is adjusted so that the average difference in segment length from $l$ in each run is less than 0.1 percent. The results were averaged over $20 - 100$ independent realizations of the initial conditions.

\begin{align}
|r_{i+1} - r_i|^2 &= l^2, \\
\frac{d(r_{i+1} - r_i)}{2 dt} &= \tau_{i+1} (r_{i+2} - r_{i+1}) (r_{i+1} - r_i) - 2\tau_i l^2 + \tau_{i-1} (r_i - r_{i-1}) (r_{i+1} - r_i) + (F_{i+1} + \eta_{i+1} - F_i - \eta_i) (r_{i+1} - r_i). \\
\frac{d(r_{i+1} - r_i)}{2 dt} &= -|r_{i+1} - r_i| \cdot \frac{(r_{i+1} - r_i) - l}{l dt}.
\end{align}
FIG. 1. Snapshot of a simulation of fracture for a chain of $N = 700$ monomers: (a) tensile and (b) shear mode.

Fig. 1 shows a snapshot of the simulation for both tensile and shear pull out. We quantify the fracture toughness of the interface by determining the work $G$ required to remove the connector chain completely from the obstacle lattice. The work is $G = \int P \, dt$, where the power $P$ is obtained via $P = v_0 \tau$, $v_0$ is the constant pulling velocity, and $\tau$ is the instantaneous tension in the segment crossing the boundary of the obstacle lattice in the pulling direction at each time step.

Fig. 2 shows the fracture toughness $G$ as a function of the polymerization index $N$ of the connector chain for tensile and shear modes. Naturally, the fracture toughness grows as the degree of polymerization of the connector chain increases. This growth is more significant for larger $N$ due to the fact that longer connectors can penetrate well beyond the neighborhood of the interface. They entangle efficiently with the bulk polymers of the compatible phase. It also shows that the effect of reinforcement on the interface is higher in tensile mode, by a factor of about five for the present model [26]. One can notice the existence of two scaling regimes for $G$ vs. $N$, corresponding to short connectors, $N < N_c$, and long connectors, $N > N_c$ where $N_c$ is the crossover length.

Figure 3 shows the power-law dependence of $G$ on $N$. For short connectors $G$ scales linearly with $N$, $G \sim N$, while for long connectors it scales as $G \sim N^{3/2}$.

These regimes can be understood as follows. For small $N$, the chain is entangled with one or two layers of obstacles, even if the free radius of gyration $R_g \approx l\sqrt{N}$ is of order or smaller than the obstacle lattice spacing $D$. Since the initial configuration is repelled by the obstacles, the available phase space for a chain is quite restricted. For the first few chain segments, the reflecting boundary condition and the area taken up by the obstacles, results in the chains going straight into the lattice. After passing the first row or two of obstacles, the chain, if it is long enough, usually bends, with tight loops around obstacle cores being highly improbable. When the chain is pulled out, the dominant deterministic part of the tension equals the total viscous drag force. This force is roughly proportional to the number of monomers $N_{\text{move}}$ simultaneously in motion. Since pulling tension cannot propagate through a loop unless it is tightened around an obstacle core, for short chains $N_{\text{move}}$ is of order of the number of monomers stretched in one obstacle lattice spacing $D$, that is $D/l$. Hence for small $N$, the
total work to pull the chain out can be estimated as

$$ G \approx v_0^2 \frac{D}{v} \int_0^{N_1/v_0} dt = v_0 \nu N D, $$

(7)

which is consistent with the linear scaling regime observed in simulations for short connectors.

For large $N$, the penetration depth increases. Indeed, for sufficiently large $N$, the chain center of mass is located at a distance of order of the radius of gyration $R_g$ from interface. Then, the number of monomers that are simultaneously in motion becomes proportional to this distance, $N_{\text{move}} \approx R_g \sim N^{1/2}$, which we have observed directly. Consequently, the pull-out fracture energy becomes

$$ G = v_0 \int_0^{N_1/v_0} F_{\text{drag}} dt \approx v_0 \nu N^{3/2} l. $$

(8)

This is roughly analogous to what happens when one pulls on a wet garden hose of length $N$, left on the ground by a gardener who has performed a random walk among a grove of trees. Upon pulling, only the currently stretched segment starts to move, if friction in the self-intersections of the hose is negligible. If the hose configuration was created as a result of random walk, the length of such a segment scales as a typical size of such a walk, $\sqrt{N}$, where $N$ is the total length of the hose. The hose configuration may include a few loops around the tree trunks, which, upon tightening, also start to move. The total length of these tightened loops has no important contribution: That length scales as a winding angle of a random walk of the length $N$, i.e., as $\ln N$ (see, for example, Ref. [27]). As a result, the drag force is proportional to the length of the hose that is constantly in motion, $\sqrt{N}$.

Although our numerical work is in two dimensions, these physical arguments also follow in three dimensions, and are applicable to experimental systems [28]. The small $N$ regime overlaps with a large $N$ regime when the radius of gyration $R_g$ becomes of order of the obstacle spacing $D$. That gives $N_{\text{cross}} \sim |D/l|^2$, and we expect

$$ G = N f(N/N_{\text{cross}}), $$

(9)

where the crossover scaling function obeys $f(x \to 0) = \text{const}$, and $f(x \to \infty) = x^{1/2}$.

As mentioned earlier, different forms of the power-low dependence of $G$ on $N$ have been proposed in previous theoretical studies: Both $G \sim N$ and $G \sim N^2$ have been predicted. The results from experiments are somewhat ambiguous. The linear dependence of $G$ on $N$ [13] is predicted for very slow crack propagation velocities, and therefore corresponds to $G \to G_0$, where $G_0$ is the fracture toughness threshold or minimal energy required to break the interface when $v_0 \to 0$. On the other hand, $G \sim N^2$ is predicted for pull-out fractures where the crack propagation speed is high or at least larger than a critical velocity. In other words, these two predicted regimes differ by the pull-out velocity. The crossover between the two scaling regimes $G \sim N$ and $G \sim N^{3/2}$ is predicted for pull-out fractures where the pulling velocity $v_0$ exceeds $v_0 = k_B T/(\nu D)$, which in turn results in high crack propagation speeds. Our work is in the same regime, and indeed extends the numerical work and theoretical arguments of Picket, Jasnow, and Balazs [13], wherein this model was introduced. For large $N$, Picket et al. argued $G \sim N^2$ in contrast to our result of $G \sim N^{3/2}$. This was based on an analogy of the polymer to the motion of a rope in “block and tackle” pulleys. In that case, the average drag force to pull the connector chain out of the matrix is $f_{\text{drag}} \sim \nu v_0 N$. Hence, it follows that the number of monomers instantaneously in motion are $N_{\text{move}} \sim N$. In fact, the correct analogy is not to pulleys, but to the motion of a garden hose lying on grass, as described above. Then $f_{\text{drag}} \sim N^{1/2}$, giving rise to the $3/2$ exponent. Our numerical results, which are more extensive than those of the earlier work, support this picture.

To conclude, we studied the chain pull-out fracture of a reinforced polymeric interface in tensile and shear modes using molecular dynamics algorithm. Our results confirm the nonlinear dependence of the fracture toughness of the interface on the length of the connector chain observed in experiments. We found that, depending on the length of connector chain, the fracture toughness of the interface shows different scaling dependences: For short chains, $G$ scales linearly with $N$, while for long connectors, we observed a crossover to a new scaling regime $G \sim N^{3/2}$. Our results can be tested experimentally on elastomeric networks for long connector chains in the low coverage mushroom regime [30].

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