Polymer—polymer adhesion with mobile promoters: Connector length dependence

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ABSTRACT

The adhesion between two immiscible polymers stitched together via mobile chains is studied with large scale molecular simulations employing a coarse-grained bead-spring model. An adhesion model is presented that incorporates both connector molecular slipping out viscously and bulk dissipation in two dissimilar glassy polymers, in which one is dense melt and another is loose. The contributions to the separation work from thermodynamics and chain suction are studied in dependence of the connector length, at constant temperature, and at fixed basic molecular parameters. It is shown that connector length relative to its entanglement length can enhance the adhesion toughness and interfacial strength. Bulk dissipation is not considerable with low connector areal density in mushroom regime, while becomes more evident in the loose melt with increasing connector length when the coverage density is increased up to overlapping brush regime. The results provide insight into the structure evolution of adhesion interface with mobile promoter molecular, which are useful for future developments of continuum cohesive models for fracture of polymer—polymer interfaces.

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1. Introduction

Immiscible polymers can be jointed together by adhesive promoters dissolved into either bulk, while miscible polymers can be adhered by self-adhesion through weak van der Waals interactions. Above glass transition temperature T_g, promoter molecules can adhere or penetrate into either polymer as bridges, while molecules from miscible polymers interact with each other directly, and chains will be entangled or cross-linked with each other, thus the macroscopic interface becomes interdiffused. Adhesion toughness is then largely determined by the rearrangement or restructuring of surface molecules to enhance the contacting bonds (e.g., interdigitating chain segments) across the interface. Under mechanical loading, the surface chains could be sucked out and/or undergo scission, which is known as adhesive fracture. Adhesion between any pair of polymers can be well enhanced if the interface can sustain sufficient stress to induce dissipation, such as flow, yield or crazing, in the bulks. To evaluate adhesion strength of weak interface, chemical bonding, chain entanglement, areal density of connectors, mismatch of bi-materials, mechanical roughness, and loading rates etc. should be considered to bridge the gap between polymer science and fracture mechanics [1—4]. However, the microscopic mechanism of fracture or debonding of polymer adhesion is still open due to the complexity of the real situation of molecular level coupling at the interface with/without connectors and the energy dissipation process in the bulks adjacent to the interface, despite of existed excellent two-dimensional models [5—9].

For studying polymer systems, one of the main unresolved problems is the time-scale and length-scale gaps between computational and experimental methods. Coarse-grained molecular dynamics simulations (CG-MD) representing a system by a reduced number of degrees of freedom and elimination of fine interaction details become a powerful tool, and goes faster than that for the same system in all-atom representation [10—21]. As a result, an increase of orders of magnitude in the simulation time and length scales can be achieved.

Previous CG-MD simulations mainly focused on the adhesion between a glassy polymer and a rigid substrate chemically attached with end-grafted chains. However, real adhesion junctions often contain two polymer blocks and promoters that are free at both ends and can wander into the polymer matrix, which is extremely sensitive to the polydispersity of mobile connectors [5], Fig. 1 describes the situation. The pullout/scission of connector chains from bulk melts and dissipation taking place on either melt cannot be ignored. It was also shown that the areal density and molecular weight of the copolymer chains played important roles on the
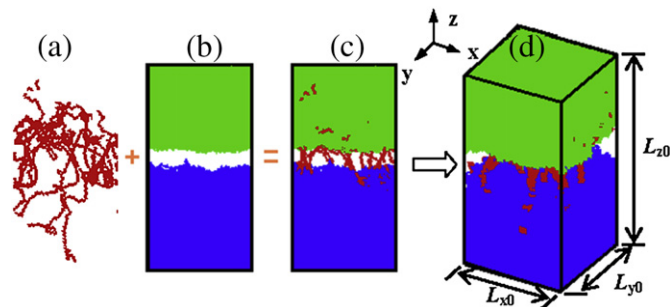
Fig. 1. Adhesion models of two immiscible glassy polymers with connector promoters. (a) Mobile connector molecules (red) with a areal density of $0.008\sigma^{-2}$ (or $0.024\sigma^{-2}$) enter freely into (b) one dense melt (green) and another loose melt (blue) to form a (c) 2D (y view)/(d) 3D model in an MD cell (black) with initial dimensions of $L_{x0} \approx 32\sigma$, $L_{x0} \approx 32\sigma$ and $L_{x0} \approx 65\sigma$ before equilibration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fracture mechanism at PS/PVP interfaces reinforced with PS—PVP block copolymers in experiments [22] and simulations [23].

The mechanism of interface failure has been found to depend on the molecular weights/lengths of the coupling chains. Short chains can be pulled out of bulk materials at a force that increases with the length of the pulled-out section. As the lengths of the chains increase to somewhere between one and four times the length required to form an entanglement in the melt, the force required for pullout becomes greater than the force to break chains, so they fail by scission. However scission failure is not expected for a tough interface, elastic and capillary forces during pull-out of connectors are desired to strengthen the adhesion.

We here conduct large amounts of CG-MD simulations on adhesion of two glassy polymers (one dense melt and another loose) jointed together by mobile connector chains, considering the deformations and dissipations of both bulks and connectors. The complicated viscous process involving chain pulling out, crazing and scission is strongly dependent on the separation strain rate $d\gamma_{zz}/dt$, the areal density of connector Σ, and the length of connector chain n. This parameter space is more abundant than one can investigate at the same time, however we only focus attention to the effects of $n = 100, 150, 200$ at a fixed temperature $T = 0.1\varepsilon/k_B$, with $\Sigma = 0.008\sigma^{-2}$ (mushroom regime) or $0.024\sigma^{-2}$ (overlapping brush regime), while another possibility of chemical scission for the connectors is not incorporated presently for our loose system at relative slow strain rate $d\gamma_{zz}/dt = 0.5 \times 10^{-5}\tau^{-1}$ (the LJ units will be noted below). In fact, for most loose systems, the force on the connectors is far below the chemical rupture forces [5]. Thus, in the low-velocity regime, scission is indeed negligible for loose systems of unbranched connectors.

2. Coarse-grained bead-spring models of polymers

Our simulations follow the methodology described in previous literature. A generic bead-spring model that describes the coarse-grained behavior of polymers is used. The polymer chains (either belonging to the bulks or a connector) are treated as sequences of beads interconnected by springs, using a representation based on the Kremer-Grest model [21], but extended to account for stiffness along the chain backbone and attractive interaction as well. The connectors penetrate sequentially into both bulks: each successive connector is immersed in a different polymer bulk while only one-stitch is made at the interface, and uniformly distributed at the interface between the two melts at a specific areal density Σ. Each chain of polymer melt contains $N = 500$ spherical beads with a bead density of $\rho = 0.85\sigma^{-3}$ that interact through a truncated and shifted Lennard-Jones (LJ) potential

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right], r \leq r_c, \quad (1)$$

where r is the distance between any two beads, and $U_{LJ}(r) = 0$ for $r > r_c$. The binding energy ε and molecular diameter σ are used to define our units in dimensionless values relative to the LJ units. The unit of time $\tau = (m\sigma^2/\varepsilon)^{1/2}$, where m is the bead mass. LJ units can be conversed with SI units for a particular material in which the bead is a possible group of polymer units, e.g. $\sigma \approx 0.5$ nm, $\tau \approx 1.9$ ps for PMMA ($m = 1.660 \times 10^{-25}$ kg). Inside individual polymer bulk, the interaction between any two bulk beads is with the same σ and ε. Two beads from dissimilar bulks repel each other directly, the LJ interaction is repulsive. However, to realize the adhesion, the attractive part of the LJ potential is incorporated for connector-bead and bulk-bead interaction by setting $r_c > 2^{1/6}\sigma$. Adjacent beads along the chain are coupled with the finitely extensible nonlinear elastic (FENE) potential

$$U_{FENE}(r) = -kR_0^2\ln\left[1 - \left(\frac{r}{R_0}\right)^2\right], r < R_0. \quad (2)$$

The standard values $k = 30u_0/\sigma^2$ and $R_0 = 1.5\sigma$ are employed. The $U_{LJ} + U_{FENE}$ combination is asymmetric with respect to the equilibrium bond length $\sim 0.96\sigma$ [21]. 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. Consequently, extension of bonds is more favorable than their compression. Overall, the bonds are slightly stretched and a non-zero average tension exists in the bonds.

The entanglement density is varied by the stiffness along the polymer chain that is enhanced by using a bending potential and a torsion potential acting respectively on three or four consecutive connected beads. The bending potential maintains the angle between adjacent pairs of bonds close to the equilibrium value 109.5°. The torsion potential constrains the dihedral angle to three possible equilibrium values 180°, 60° and 300°. For all simulations presented here our semiflexible chains have bending and torsion stiffness: $k_\theta = 25\varepsilon$, $k_\varphi = 1\varepsilon$ (Rotational Isomeric State chains, RIS) [24,25].

In addition, each bead from the polymer bulks interacts with the virtual upper and lower rigid walls of MD simulation box via an integrated Lennard-Jones (LJ) potential

$$U_{LJ}^{wall}(z) = \frac{2\pi\varepsilon_{wall}}{3}\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^{9} - \left(\frac{\sigma}{z}\right)^{3}\right], z < z_c^{wall}, \quad (3)$$

with $z_c^{wall} = 2.2\sigma$, the binding energy $\varepsilon_{wall} = 2.0\varepsilon$. Possibly strong attractive walls are employed to prevent adhesive failure between bulk melts and walls during stretching [26].

3. MD sample and its equilibration

The MD-samples are prepared carefully prior to the debonding simulations. The polymer chains from the bulks are generated as random walks with constraints for the bond lengths, bending and torsion angles around their equilibrium values needed for the specific potentials. The connector chains are generated such that they have a predefined conformation at the interface with a certain number of stitches and a certain number of beads between the stitches. The two polymer bulks are placed on top of each other and the preformed connectors are uniformly distributed at the interface according the desired areal density of the connectors. The resulted intertwining between connector chains and bulk chains, which cannot cross each other, consequently establishes the adhesive