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MOLECULAR DYNAMICS SIMULATIONS OF FRACTURE OF MODEL EPOXIES

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INTRODUCTION

The failure of thermosetting polymer adhesives is an important problem which particularly lacks understanding from the molecular viewpoint. While linear elastic fracture mechanics works well for such polymers far from the crack tip, the method breaks down near the crack tip where large plastic deformation occurs and the molecular details become important [1]. Results of molecular dynamics simulations of highly crosslinked polymer networks bonded to a solid surface are presented here. Epoxies are used as the guide for modeling. The focus of the simulations is the network connectivity and the interfacial strength.

In a random network, the bond stress is expected to vary, and the most stressed bonds will break first [2]. Crack initiation should occur where a cluster of highly constrained bonds exists. There is no reason to expect crack initiation to occur at the interface. The results to be presented show that the solid surface limits the interfacial bonding resulting in stressed interfacial bonds and interfacial fracture. The bonds in highly-crosslinked random networks do not become stressed as expected.

The sequence of molecular structural deformations that lead to failure has been determined and found to be strongly dependent upon the network connectivity. The structure of these networks and its influence on the stress-strain behavior will be discussed in general. A set of ideal, ordered networks have been constructed to manipulate the deformation sequence to achieve different fracture modes (i.e. cohesive vs. adhesive).

SIMULATION METHOD

Model. Following a large body of work on polymeric systems [3], MD simulations are performed on a coarse-grained, bead-spring polymer model. Because of the long relaxation times typical of polymer dynamics, atomistic simulations are not viable. By coarse-graining, a sufficient increase in computational speed is achieved to treat the relaxation times while still treating the fundamental aspects of polymers. Also, the coarse-grained models are closer to the continuum models with which we ultimately want to connect. A modification of the successful Kremer-Grest bead-spring model is used [4]. Polymer chains are composed of beads which interact via a Lennard-Jones (LJ) interaction with a cutoff at 2.5.

$$U_{LJ}(r) = 4U_0[(d/r)^{12} - (d/r)^6] \qquad (1)$$

where U_0 is the LJ energy unit and d is the length unit and particle diameter. The bond potential is composed of two parts. The first part is the purely repulsive LJ potential with a cutoff at $r = 2^{1/6}$. In order to break bonds and preserve the continuity of the bond force a quartic potential is used to create a potential with two minima. With a cutof at r_2,

$$U_4(r) = k_4(r - r_1)(r - r_2)(r - r_s)^2 + U_s \qquad (2)$$

The parameter set 1 is: $k_4 = 1200$, $r_1 = 0.75$, $r_2 = 1.55$, $r_s = 1.3$ and $U_s = 34.69$. The parameter set 2 is: $k_4 = 1434.3$, $r_1 = 0.74$, $r_2 = r_s = 1.5$ and $U_s = 67.22$. Chains can cross only by breaking bonds.

Geometry. The complete system consists of a polymer network between two walls with separation h. The (111) direction (z-direction) is perpendicular to the walls. Each wall is composed of particles in two layers of an fcc lattice with nearest neighbor distance 1.204. The wall particles are bound to the lattice sites by a harmonic spring with spring constant 100. The potentials for the wall particles are identical to the bead potentials.

Procedures. The dynamics of the system is performed at constant temperature using the Langevin thermostat. The integration time step is 0.005. Epoxies form highly crosslinked molecular networks with each strand consists of only a few monomers. Typically a bead corresponds to 2 or 3 monomers [4]. A bead-spring model with two beads per strand is the best match for highly crosslinked epoxies. To create a random network R similar to epoxy networks, a liquid mixture of two bead and three bead molecules is crosslinked dynamically. The three bead molecule has a sixfold functional crosslinker bead already bonded to a two bead strand. All beads have identical potential parameters. After equilibrating the mixture, crosslinkers are first bonded to the walls. The crosslinkers are bonded to strands until at least 95% of all possible bonds are made. Afterward, the temperature is reduced below the glass transition temperature (0.5) to 0.3. The tensile pull is performed by moving the walls apart at constant velocity. The tensile and shear stresses are calculated from the total wall force.

RESULTS

Random Networks. In Fig. 1 the stress-strain curve for bond set 1 is shown for both walls pulled at a wall

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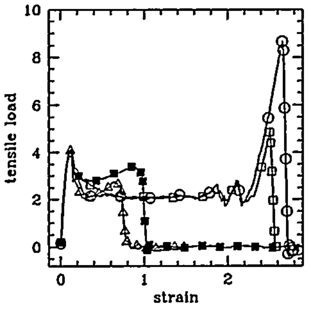

FIG. 1. The stress-strain curves for the random network (solid squares) and the ordered networks O1 (squares), O2 (triangles), and O3 (circles).

velocity of 0.01. The yield stress is about $\sigma_y = 4$ and the yield strain is 0.1. The stress drops suddenly and complete failure occurs at $\epsilon_f = 1.0$ and $\sigma_f = 3.4$. The first bond breaks at $\epsilon_f = 0.62$. Between $\epsilon = 0.82$ and 1.0 all the bonds between the network and the bottom wall break resulting in failure. Almost all broken bonds occur at the interface. Bonds in the bulk of the random network are not stressed. In fact, strains large compared to macroscopic measurements are required before any bonds are stressed and broken. To understand this, the molecular deformation sequence was determined by examining configurations. At low strains, the near neighbor cage is plastically deformed producing the yield behavior. This deformation involves only LJ interactions and determines σ_y. Once the monomers have moved beyond their initial local position, further applied strains tighten the strands of the network. In the plateau region, bond lengths are rarely stretched. The bonds begin to stretch only after strands are pulled taut which requires large local strains. Most of the stretched bonds are interfacial bonds. Subsequently, these bonds break and the interfacial failure occurs. This sequence of molecular deformations corresponds to the deformation zones (DZ) seen experimentally [5]. The local strain at a DZ is much larger than the external applied strain. System R and even other simulated systems 10 times larger are still smaller than the typical DZ for epoxies let alone a complete system.

An upper limit to the strain at which scission must occur is given in the minimal path lengths P of the network. In fact, the simulations show that the average P is a good estimate of the failure strain. For a site on the bottom wall to which the network is bonded, there are many paths through the polymer network to the top wall. The shortest path defines P for that site. Conversion of P into a strain can be done via the relation, $\epsilon_P = (P-h)/h$. For $\epsilon > \epsilon_P$, some bond within the minimal path must break. P has been calculated for all bonding sites on the bottom wall. The average P over all such bonding sites is typically about $2h$. In the absence of another constraint, this implies the system can be strained almost 100% before significant scission. For system R the path with the smallest P has $\epsilon_P = 0.84$, and by $\epsilon = 1.1$ all the paths' must break. These values are consistent with the major onset of scission and ϵ_f for R given above. Thus, scission is determined by a global, not local constraint.

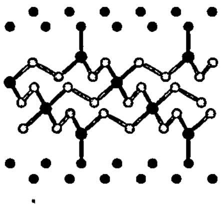

FIG. 2. Schematic of the ordered network O1.

Ordered Networks. To provide a simpler model for theoretical treatment and to further test the connectivity constraints, an ordered network is constructed. The ordered network is designed to minimize the connectivity constraints yielding in large minimal paths. When a tensile pull is applied to the ordered network, all strands are expected to become taut before any bond breaking occurs. The failure strain will be much larger than for R. As in R, the ordered network is sixfold coordinated with two monomers between each crosslinker. The network is constructed using the body centered cubic (bcc) lattice as a template (Fig. 2). Crosslinkers are the central particles in the bcc cells yielding a sixfold lattice. The z-direction is the (111) lattice direction. There are two (111) planes each with 3 sites in the bcc cell. These sites represent strands which form a zig-zag path between crosslinkers. This path is adjusted to achieve the correct density. The system is also created at $\rho = 0.8$ and then equilibrated to $T = 0.3$ and zero load.

The stress-strain curve is shown in Fig. 1 for the ordered system O1 with one bond per crosslinker to the wall as in R. The yield stress is identical to the random network's. As expected, failure occurs at a much larger strain, $\epsilon_f = 2.5$. The strain for the fully taut configuration where bonds begin to stretch is 2.3 as calculated directly from the geometry.

The number of bonds to the solid surface are indentical in systems O1 and R, but O1 has a much larger failure stress. Because the O1 network completely opens before bond breaking occurs, more bonds break simultaneously and the failure stress is larger than in R. The ideal fracture stress is

$$\sigma_{\rm id} = F_{br} * N_b/A \qquad (3)$$

where F_{br} is the force to break a bond, N_b is the number of bonds to the wall, and A is the wall area. O1 and R have $N_b = 60$ and $\sigma_{\text{id}} = 6.5$. The fracture stress of O1, $\sigma_f = 4.9$ is much closer to the ideal value than R's value (3.4). For R, interfacial bond breaking occurs over a strain range of 0.18, but for O1 the range is just 0.005. Thus, at any given strain fewer bonds are broken in R, and the instantaneous stress of the bond forces is significantly smaller than for O1.

The reason for interfacial failure is especially clear for O1. There is only one bond between the wall and crosslinkers, but three bonds between these crosslinkers and the rest of the network. In system R this is a consequence of the wall geometric contraints. Thus, fewer bonds maintain the stress. Consequently, they stretch more and break first yielding interfacial failure.

Constructing an ordered network with three bonds per crosslinker to the wall (O3) can be done. By positioning interfacial crosslinkers above the the middle of the triangles of the wall fcc layer, the crosslinks can bond to each particle in the triangle. There should be no preference to failure at the interface. Given that the interface is a small fraction of the system, failure is likely to occur within the network—cohesively.

The stress-strain curve for O3 (Fig. 1) is similar to the O1 case. The difference is mainly that the failure stress is larger ($\sigma_f = 8.7$), since there are more bonds to break. However, σ_f is larger by only a factor of about two, not three like the ideal value, $\sigma_{\text{id}} = 19.5$. For O3, the bonds break over a larger range of strain.

Large strains occur in O1 and O3, because of the lack of constraints between strands connecting crosslinkers in neighboring planes. A network with some strands connecting next nearest neighbor planes of crosslinkers should have fundamentally different behavior. Such an ordered system (O2) was constructed. One of the three strands extending downward from every crosslinker is switched to connect to a next nearest crosslinker. The stress-strain curve (Fig. 1) exhibits failure at a *lower* strain and stress than R. This lower strain agrees with the calculated strain $\epsilon = 0.6$ for the taut path of connected next nearest neighbor crosslinkers.

Thus, by manipulating only the network connectivity, the failure stress and strain can either be less than or greater than random network values. The fundamental point is that the network connectivity is a critical factor controlling the nature of interfacial fracture of highly crosslinked networks bonded to a solid. The connectivity defines the minimal paths which determine the failure strains. The connectivity effects the dynamical sequence of bond breaking and thus the failure stress. The tendency for adhesive fracture instead of cohesive fracture is because of the relative deficit of interfacial bonds, i.e. the interfacial connectivity.

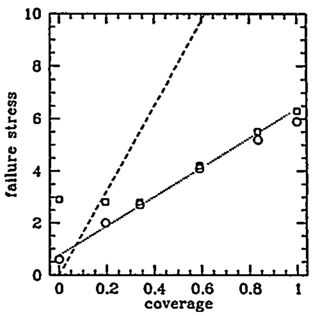

FIG. 3. Failure stress vs. strain as a function of curvature: tensile pull (squares), shear (circles). Dashed line is ideal bond fracture stress. Dotted line is fit to shear data.

Interfacial strength. The number of bonds across the interface is an important quantity affecting interfacial fracture. The dependence on N_b can be examined in a controlled manner by forbidding bonds to occur in a subset of the wall surface. Experimentally, coating the surface with SAMs prevents chemical bonding [6]. In the simulations, we simply forbid bonds in a chosen region on the wall. The area of the wall surface coverable by bonds is denoted C. Figure 3 shows the failure stress data under tensile pull and shear. At large C the failure stress is proportional to C, even though $\sigma_f \neq \sigma_{\text{id}}$. In the tensile stress-strain curve at all C, there is a yield stress $\sigma_y = 4.0$ and a plateau stress, $\sigma_p = 3.0$. These stresses are due to the van der Waals interactions. For a range of C near 0, the failure stress equals σ_p. Thus, bond fracture stress is small at these C. In general, since sequential bond breaking reduces the stress, σ_f is much less than the ideal stress.

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[1] A. Kinloch and R. Young, *Fracture Behavior of Polymers* (Applied Science Publishers, London, 1983).
[2] R. Wool, *Polymer Interfaces: Structure and Strength* (Hanser, Munich, 1995).
[3] *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford, New York, 1995).
[4] K. Kremer and G. Grest, *ibid* Chap. 4.
[5] M. Glad and E. Kramer, J. Mats. Sci. **26**, 2273 (1991).
[6] See work by M. Kent *et al.* in this volume.