

## Multi-Length Scale Modeling of Highly Filled Polymer Composites

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**H**ighly filled polymer composites, including plastic-bonded explosives such as PBX-9501, are a unique class of high-value materials. PBX-9501 consists of >90% HMX particles (filler) held together by a polymer matrix (binder). Currently, there are no predictive materials science models for these materials. We are developing robust, predictive constitutive models for these composites that span the molecular to the macroscopic length scales. Using existing and emerging models, we will determine how the physics and chemistry that define the mechanical behavior at each length scale can be propagated upward to the next level.

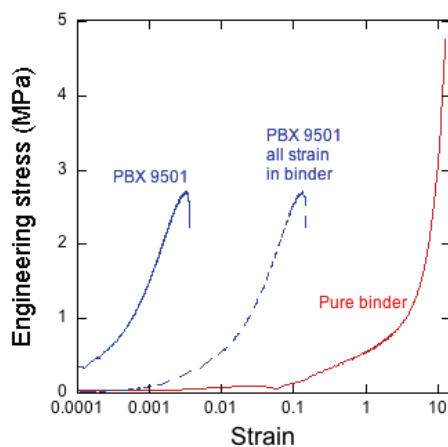
The mechanical behavior (e.g., stress-strain) of highly filled polymer composites is orders of magnitude different from the bulk behavior of its constituents. This is illustrated by compressive strain for PBX-9501, shown in Fig. 1. Over most of the strain, the stress for the pure binder material is about one tenth that in the composite material, but the strain-at-break is two orders of magnitude greater for the binder. The geometric constraints imposed by the binder adhering to the rigid filler particles dramatically change the mechanical response of the composite. Tensile experiments under cyclic deformation show that, even at low strains,

the material undergoes irreversible damage. The failure mechanisms responsible for this have their origins at the molecular level. We believe that when the local strain in the polymer network adjacent to a filler particle surface becomes sufficiently large, a polymer chain can detach from the surface, producing interfacial voids on the smallest filler particles. As the strain increases, the voids expand and propagate as cracks, ultimately causing macroscopic material failure.

It is important to model the material starting at the smallest length scales because it is here that changes due to long-term chemical aging (e.g., polymer chain scissions or oxidative cross linking) will appear. The challenge lies in developing physically faithful models for each length scale and coupling them together to achieve a computationally tractable protocol that can be implemented in Finite Element Method (FEM) simulation codes. Currently, these codes are not able to predict the effects of long-term chemical aging or thermo-mechanical insult unless all of the code parameters are explicitly fit to very specific experimental data (which are usually not available).

We represent the molecular physics occurring between the HMX substrate and the Estane with the polymer/node network model EPnet [1] (a unique asset of Los Alamos National Laboratory), using an estimate of the interfacial binding energy obtained from molecular dynamics (MD) simulations in conjunction with quantum chemistry calculations. The EPnet code treats polymer networks as an explicit collection of point-like nodes in 3 dimensions, connected by virtual chains characterized by a length distribution and a force model. The code supports void regions and will be modified to treat rigid spherical regions that are attached to the polymer network. Energy changes in the polymer network are computed by integrating the chain forces between

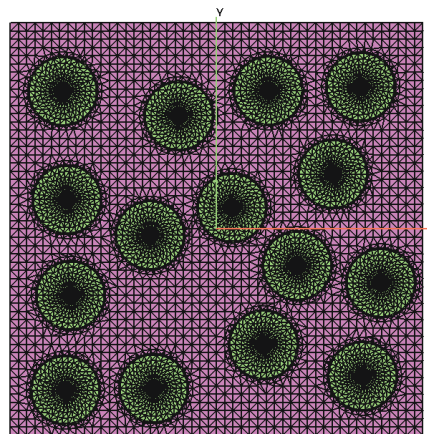
**Fig. 1.** Compressive strain for PBX-9501. Over most of the strain, the stress for the pure binder material is about one tenth that in the composite material, but the strain-at-break is two orders of magnitude greater for the binder. For the middle curve, the experimental strains for the PBX-9501 have been increased by a factor of about 40 to give the approximate strain in the binder material.



connected nodes and filler particle interfaces as the simulation cell undergoes strain. Parameters such as the chain forces will be obtained by fitting to tensile stress-strain experiments on material representative of the mesoscale region (small particles only). Void formation at the filler surface, generated in response to a tensile strain, will be studied in simulations of cells containing single spherical particles with periodic boundary conditions or single particles adjacent to a plane surface representing a large filler particle. Material failure at this length scale will occur when the void region (crack) bridges the simulation cell. A sufficient number of statistically independent network/filler particle cases will be run to determine the failure probability as a function of strain, parametric on other parameters (e.g., fill fraction).

This information will provide the input for the Probabilistic Crack Occurrence (PCO) statistical model, which is designed to connect the EPNet scale with the 2Scale FEM modeling technique. The PCO model is based on a material containing inclusions of two widely differing sizes. The small inclusions are assumed to be part of a background matrix, which is normally represented as a homogeneous substance by a standard FEM mesh. PCO is designed to reintroduce inhomogeneity in the background matrix in a controlled, statistical manner by providing a space-dependent criterion for the strain at which a crack should be opened in the FEM matrix based on the small scale properties of the material. The initial version of PCO is complete, and employs a statistical technique known as the weakest link approach. The small inclusions are assumed to follow a Poisson spatial distribution in the matrix. The solution of the model has the property that the matrix separating two large inclusions decreases in strength as the spacing between the large inclusions increases. The most likely locations for cracks to form will depend on the details of the random arrangement of large inclusions in a physically meaningful way: cracks are most likely to occur in regions with a relatively low density of large inclusions.

The largest scale of our model effort is the 2Scale-FEM analysis, which incorporates



**Fig. 2.** RVE mesh (LAGRIT) using a random spheres model distribution. Large grains are simulated by spheres and the “dirty binder” as a homogenized medium.

energy vs strain from EPNet as well as crack initiation criteria from PCO. In engineering applications using heterogeneous materials, a common approach is to start with a Representative Volume Element (RVE), the smallest domain that can be considered to have approximately constant average material properties. Here, we will determine the RVE response for a heterogeneous material (including cracking) through a Direct Numerical Simulation (DNS) using FEM in conjunction with the scheme described below. The geometry of the RVE can be constructed directly from micrographs as an idealized model in which large grains of HMX are modeled as random distribution of spheres, as shown in Fig. 2. Each constituent of the RVE is assigned a constitutive law determined from physics theories starting at the molecular level. To simulate cracking, a failure criterion for crack initiation and propagation is incorporated from the PCO analysis. The initial RVE (undamaged) is loaded until cracks occur. Cracks are propagated by stopping the FEM analysis and re-meshing the RVE with explicit crack boundaries between mesh points. The simulation is then restarted using the new geometry. The DNS at the RVE level offers the advantage of using a large variety of local microstructure of the RVE in conjunction with different types of loading conditions.

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[1] D.E. Hanson, *Polymer* **45** (3), 1055 (2004).

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