

Deformation and Failure of Polymer – Layered Silicate Nanocomposites: Coarse Grained Computer Simulations

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INTRODUCTION

For many high performance applications, the impact of nanofiller on strength and failure, not only the retention or increase of modulus, is a key consideration in many technology insertions, such as for automotive and packaging applications. Much has been, and is being, investigated on the impact of nanoparticles on stiffness (modulus), but only recently have the effects of clays, tubes, and other nanofillers on failure of the polymer been recognized and understood. Unfortunately, our understanding of the failure initiation and the role played by nanocomposite morphology is scattered and empirical at best.

Bright-field TEM images¹ of the fracture of a polystyrene / montmorillonite-clay nanocomposites at 10% strain are shown in figure 1. The crazed fracture path departs from a straight path typical of unfilled / neat polystyrene, instead exhibiting jumps to follow a path predominately through the (weak) polymer/silicate interfaces. Moreover, catastrophic failure occurs at a much smaller craze-thickness next to the fillers in the nanocomposite (ca. 2 μm) resulting in a reduction of the strain-at-break.

Coarse-grain computer simulations have been undertaken to investigate the nature of the failure mechanism in polymer-silicate nanocomposites and its dependence on the strength of the interface between the polymer and the silicate sheets.

SIMULATION METHODOLOGY

These simulations follow the general methodology of previous calculations of the formation process of polymer-layered silicates, reported elsewhere². A coarse-grained model³, implemented in the LAMMPS⁴ molecular dynamics engine, was used. The model captures the essence of an atomistic system without the computational cost of atomistic molecular dynamics. The polymer and silicate sheets are represented as spheres (diameter = 1σ) connected by an anharmonic FENE (Finitely Extensible Nonlinear Elastic) potential. Polymers are represented as chains of these spheres; sheets are square arrays of spheres. A pair of square sheets, each with 900 beads (30 beads on edge), was immersed in a homopolymer above the entanglement molecular weight (chain length = 100 beads). The total number of beads was adjusted so that the overall system density during equilibration was $\rho^* = 0.8$. Simulations were carried out at reduced temperatures of 0.1 and 1.0, both below the Tg of the polymer. Typical simulation box dimensions before elongation were approximately: $70\sigma \times 70\sigma \times 70\sigma$, with 284,372 total beads. The stiffness of each sheet was controlled by two stiffness parameters; $K_{\pi} = 25\epsilon$ for 180° bends and $K_{\pi/2} = 25\epsilon$ for 90° angles. Two fcc packed walls were placed at $X=0\sigma$ and $X=70\sigma$ and the cell was stretched in the X direction. Periodic boundary conditions were used in the Y and Z directions. Polymer-sheet interactions in the case of a strong interface had interaction $\epsilon_{PS} = 2\epsilon$ and in the case of a weak interface $\epsilon_{AS} = 0.5\epsilon$. Nonbonded interactions between other components were set to 1ϵ . The simulations consisted of a multi-step equilibration stage utilizing the micro-canonical (NVT) ensemble, followed by a constant strain isothermal ensemble (N ϵ T). The subsequent data collection (production) stage comprised over 20 million MD steps for each simulation using the N ϵ T ensemble at a constant strain rate in the X dimension.

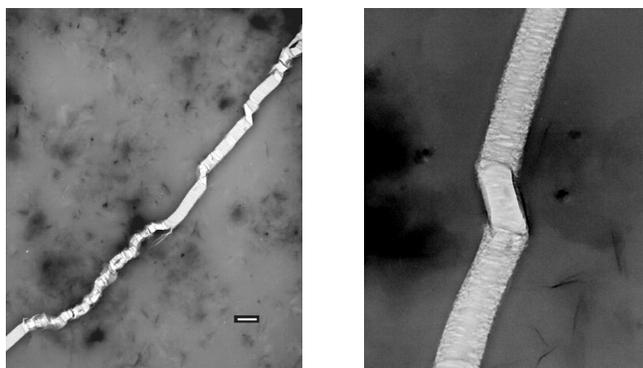


Figure 1. TEM micrographs of craze-fracture of polystyrene-silicate nanocomposite (adapted from reference 1).

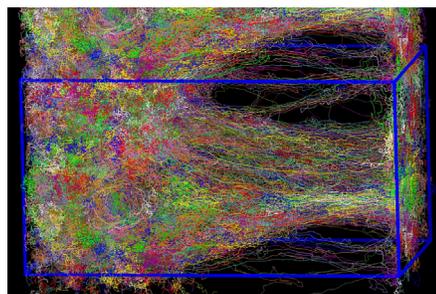


Figure 2. Computer simulation of failure mode of neat homopolymer.

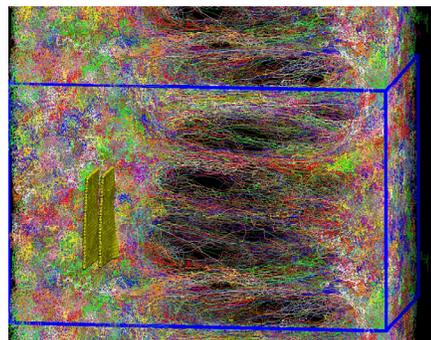


Figure 3. Computer simulation of polymer-silicate nanocomposite with a strong polymer-sheet interface.

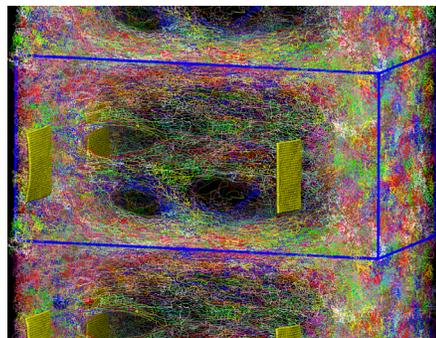


Figure 4. Computer simulation of polymer-silicate nanocomposite with a weak polymer-sheet interface.

DISCUSSION

Insight into the molecular mechanisms of failure and design principles for stronger nanocomposites can be gained from molecular modeling approaches. Where there exists no filler particles, failure in the neat polymer occurs in a uniform fashion across the simulation box, with the development of extended strands of polymer as shown in figure 2. In contrast, in the presence of layered-nanofillers failure occurs earlier, in a more haphazard manner, consistent with the experimental observations. The failure occurs differently depending on the strength of the interface between the polymer and the silicate sheets. For a strong interface, failure occurs in the polymer matrix in regions distant from the filler particulates, as shown in figure 3.

When there is a weak interface between the polymer matrix and the silicate sheets, failure occurs between the filler particulates (figure 4), reminiscent of the experimentally observed behavior seen in figure 1. Further, the weak interface pushes polymer to the bulk region between the sheets and walls and between sheets and their periodic images, as seen in figure 5 which shows the density profiles across the simulation box.

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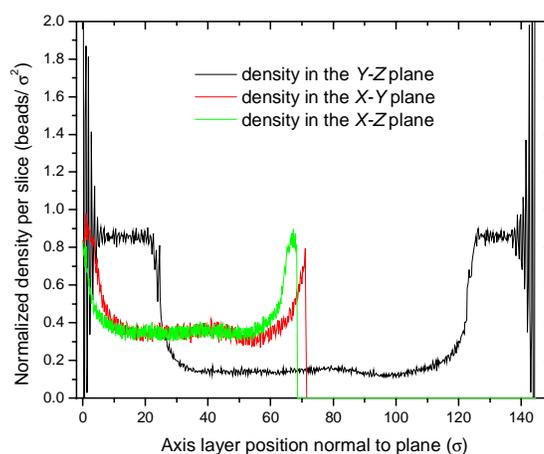
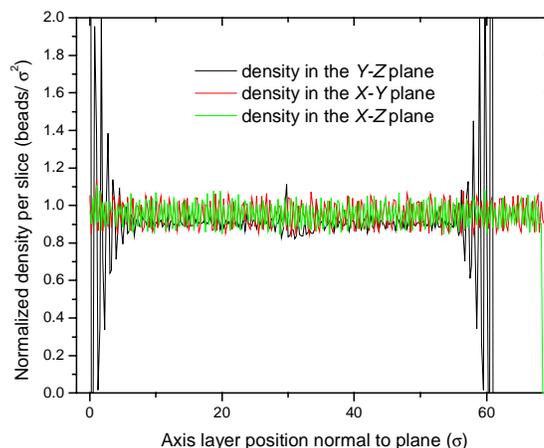


Figure 5. Density profiles across the simulation box initially (top) and at the end of the computer simulations (bottom) of the system with a weak interface.