

Title: Building and Breaking Carbon Composites with REACTER

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ABSTRACT

Carbon-based composites have become indispensable materials in aerospace and other high-performance applications, yet obtaining a detailed, nanoscale understanding of their morphology and failure mechanisms using only experimental methods remains a difficult challenge. REACTER is a versatile computational modeling tool for atomistic molecular dynamics simulations designed to model chemical reactions at the speed and length scales of classical force fields.* In this work, several recent features of REACTER were applied to the creation and subsequent mechanical testing of two classes of carbon composites: carbon nanotube (CNT) composites and carbon fiber reinforced polymers (CFRP). A network of CNTs was grown dynamically using the new ‘create atoms’ feature of REACTER. The CNT filler was embedded into a polyarylacetylene (PAA) matrix by simulated *in situ* polymerization to obtain the final composite model. To generate the second class of carbon composite, fully carbonized (graphitic) carbon fiber morphologies were created by the method of Desai et al. [1], but using the advanced reaction constraints framework of REACTER. Two fiber models were created, representing a circular carbon fiber core and a flat surface, and similarly infiltrated with resin to obtain the final CFRP structure. Failure mechanisms were elucidated by simulating mechanically induced bond breaking, as characterized by third order DFT-based tight-binding simulations, via a reaction constraint on the total potential energy of the involved atoms.

INTRODUCTION

Atomistic models provide a high-resolution, nanoscale picture of how materials behave, and their utility has long been recognized by the composites community [2]. In particular, reactive molecular dynamics (MD) simulations have been successful in modeling processes that are inaccessible with traditional MD methods, such as polymerization and polymer chain scission. Accurately predicting reaction rates and transition states must necessarily incorporate quantum-level effects, but these first-principles methods are typically limited to several hundred atoms. Various approximations have allowed reactive event modeling to be done at length and time scales typically limited to fixed-bond MD simulations, ranging from complex, highly tunable reactive force fields [3] to simpler template-based methods in which reactions are predefined and occur as stochastic functions of atomic positions or energies [4].

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The REACTER protocol is an example of the latter approximation and has been utilized to dynamically build a variety of polymeric systems, including epoxies, photopolymers, and vitrimers [5–7]. The on-the-fly nature of the protocol makes it easy to carry out *in situ* polymerization, e.g., to convert multifunctional monomers to highly interconnected networks in the presence of filler particles. Although REACTER has previously been demonstrated as a capable tool for polymerizing the matrix phase of composite systems [8], the full potential of recently added advanced features to model composite systems has not been demonstrated.

In this work, the REACTER protocol was applied to the creation and deformation to failure of large-scale (up to one-million-atoms) models of carbon polymer composites. Two classes of composites were considered, carbon fiber reinforced polymer (CFRP) and carbon nanotube (CNT)/polymer composites. Polyarylacetylene (PAA), a resin distinguished by its high-temperature stability and lack of byproducts during cure, was chosen as the matrix material. Both the filler and matrix phase were built dynamically using REACTER, which was also used to enable subsequent bond cleavage in the PAA matrix during strain. The primary objective of this work was to formulate scalable methods for building and sampling local environments of carbon reinforced composites at the atomistic scale. A secondary objective of this paper is to demonstrate that REACTER is a versatile tool capable of simplifying and accelerating common tasks encountered in building and running atomistic simulations. The authors anticipate that the open-source availability and well-documented and supported nature of REACTER will expedite workflows and help facilitate ideas for researchers in the composite modeling community.

METHODS

Overview of the REACTER Protocol

The REACTER protocol is a method for modeling chemical reactions in classical MD simulations. It is implemented in the LAMMPS MD software as 'fix bond/react' command. REACTER was designed as a flexible tool to support complex reaction mechanisms and all traditional fixed-valence force fields. REACTER requires as input three files: a molecular template of the reaction site before the reaction, another template for the post-reaction connectivity, and a 'map file' that provides a one-to-one relationship between the atoms of the pre- and post-reaction templates. The map file also specifies two 'initiator' atoms. The initiator atoms must be within a prescribed distance cutoff (or range) to initiate the reaction. During a reactive simulation, the protocol identifies initiator atoms by atom type and physical proximity, and searches the surrounding bond connectivity to ensure that it matches that of the pre-reaction template. If these, and other constraints described in the next paragraph are satisfied, the molecular topology is converted to that of the post-reaction template and the force field parameters are updated for all bonds, angles, dihedrals, improper dihedrals, and atomic charges. The sudden increase in energy that inevitably accompanies the change in bond connectivity and force field parameters can be managed by removing the reacting atoms from the

system-wide integrator and relaxing their high energy configuration with the 'nve/limit' integrator. This integrator limits the distance that atoms can move in each time step, allowing it to control the equilibration of high-energy configurations in a robust manner. After relaxation, the atoms are returned to the system-wide integrator. An up-to-date description of the growing capabilities of REACTER is provided on its LAMMPS documentation page (docs.lammps.org/fix_bond_react.html) [9] and summarized on the REACTER homepage (reacter.org) [10]. Features utilized in this work include custom reaction constraints, deletion of reaction byproducts, and creation of new atoms and incorporation of their bonded interactions at an existing reaction site.

REACTER includes a flexible framework to enforce reaction constraints, i.e., criteria that must be satisfied for the reaction to occur. Reaction constraints can be useful to delimit reactive orientations between two molecules, or for defining reaction barriers that are dependent on the local temperature or other factors. Geometric reaction constraints include the distance, angle, and dihedral angle between atoms or groups of atoms, as well as the root-mean-square deviation between the atomic positions of the local reaction site and that of the reaction template. Bespoke reaction constraints can be specified using the 'custom' constraint, which leverages the built-in variable support in LAMMPS to allow access to mathematical functions, such as random number generators, and internal thermodynamic data such as potential energy. In the present study, reaction constraints were utilized during all major stages of the simulation protocol (resin polymerization, generation of carbon fiber models, and strain to failure). While many of these options have not yet been communicated in the literature, they are fully documented and freely downloadable in recent versions of the LAMMPS software.

Polymerization of the Matrix Phase

PAA is derived from polymerization of diethynylbenzene (DEB) monomers. The simulations presented here began with a 50:50 mixture of the 1,4-DEB and 1,3-DEB isomers. Experimentally observed polymerization mechanisms of DEB include the linear coupling of two terminal ethynyl groups and the cyclotrimerization of three such moieties. Two primary types of linear ethynyl linkages have been proposed and identified, Glaser and Strauss couplings, which result in a conjugated diyne and conjugated enyne linkages, respectively. To simplify the present simulations, all linear couplings followed the Strauss mechanism. Cyclotrimerizations were modeled as a Diels-Alder reaction between the enyne linkage resulting from a Strauss coupling and a terminal ethynyl group. Both reactions are depicted in Figure 1a. A reaction distance constraint only permitted reactions to occur when a terminal carbon in an ethynyl group came within 3 Å of either another terminal ethynyl carbon or one of the carbons in an enyne group produced by a Strauss coupling reaction. Additional reaction constraints were imposed in each case to ensure the reaction was sterically favorable and that the post-reaction site was able to relax into a sufficiently low-energy configuration. The set of constraints for the cyclotrimerization step is shown in Figure 1b and Figure 1c. REACTER allows specification of the averaged positions of a set of atoms: in Figure 1b, position ③ is the average of a terminal ethynyl carbon and the two central carbons

of a Strauss linkage, while ①, ②, and ④ are the geometric centers of the three rings. The (①,③,④) and (②,③,④) angles determined whether 1,2,4 or 1,3,5 cyclotrimerization occurs (corresponding structures shown in Figure 1a). If either angle was less than 30° , cyclotrimerization was not permitted. If both angles were between 90° and 150° , then only 1,3,5 cyclotrimerization was permitted. Otherwise, only 1,2,4 cyclotrimerization was permitted. In addition, a dihedral constraint was enforced. Cyclotrimerization was permitted only if the angle between the (①,②,③) and (①,③,④) planes was less than 30° (Figure 1c). A similar angle constraint was imposed on the Strauss coupling step, to ensure ethynyl groups were oriented at $>30^\circ$ before reacting. These settings enabled stable simulations that could relax into their post-reaction configurations while reaching polymerization conversions of $>98\%$.

PAA/CNT Composite Model

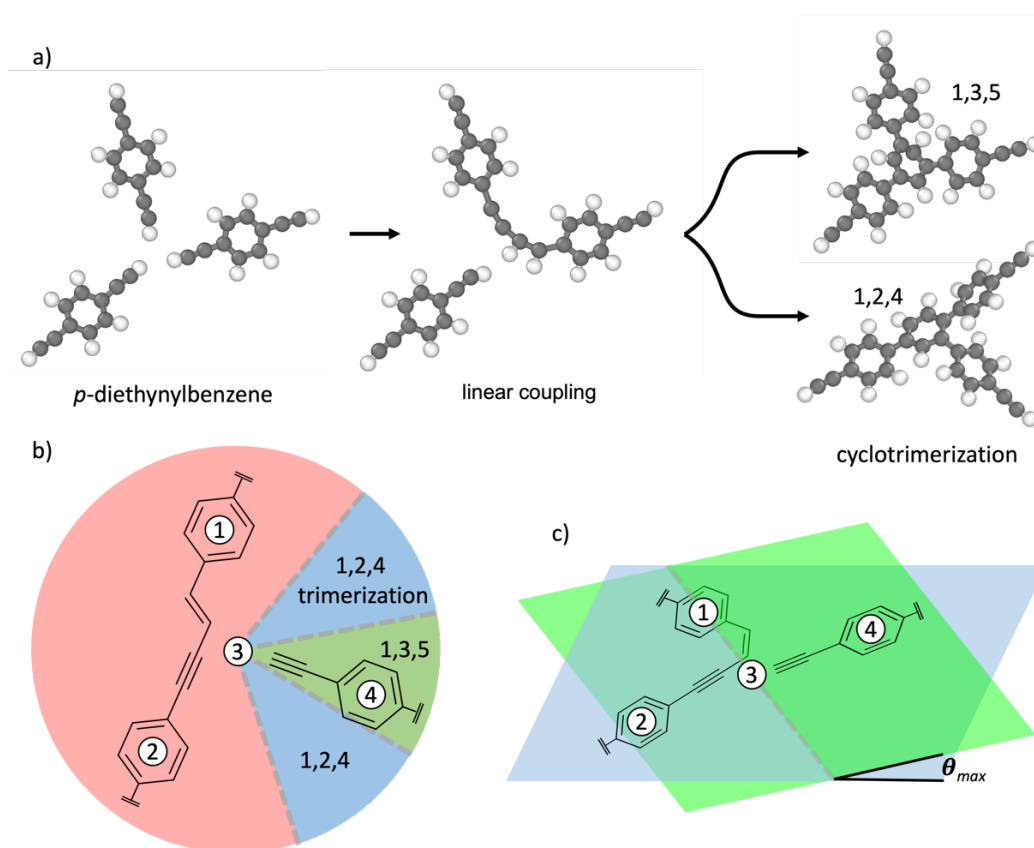


Figure 1. Overview of the PAA polymerization process. a) Snapshots of the dynamic conversion of three ethynyl groups into a linear Strauss coupling and subsequent formation of one of two cyclotrimerized isomers. b) An angle constraint determines cyclotrimerization product. c) A dihedral constraint prevents energetically unfavorable configurations from forming. Points (①,②,③) define the blue plane and (①,③,④) define the green plane.

The PAA/CNT composite was built by first creating and equilibrating the CNTs, followed by insertion of the DEB monomers and *in situ* polymerization to form the PAA matrix. The CNTs are (20,0) single-walled CNTs with a radius of 1.56 nm. The CNTs were grown dynamically using the ‘create atoms’ feature of ‘fix bond/react’ in LAMMPS. First, twenty “seed” CNTs were placed and rotated randomly in a simulation box with side lengths of 20.0 nm. Each seed is a short CNT with three layers of fused rings. The CNTs were grown by adding atoms, layer-by-layer, from both ends of the seed molecules. The pre- and post-reaction templates for CNT growth are shown in Figure 2a and Figure 2b, where edge atoms, shown in orange, are bonded to the rest of longer CNT, not shown here, in the actual simulation. The coordinates of newly created atoms were determined by optimal translation and rotation of the pre-reaction template to fit the local reaction site, and atom insertion was only completed if new atoms did not overlap with any existing atom (using a distance cutoff of 1.25 Å). This criterion for atom insertion allowed each CNT to grow until it encountered another CNT, at which point growth was arrested. After insertion, atoms were assigned for dynamic relaxation for 60 timesteps, after which another layer could be added. For the purposes of this study, no limit on CNT length

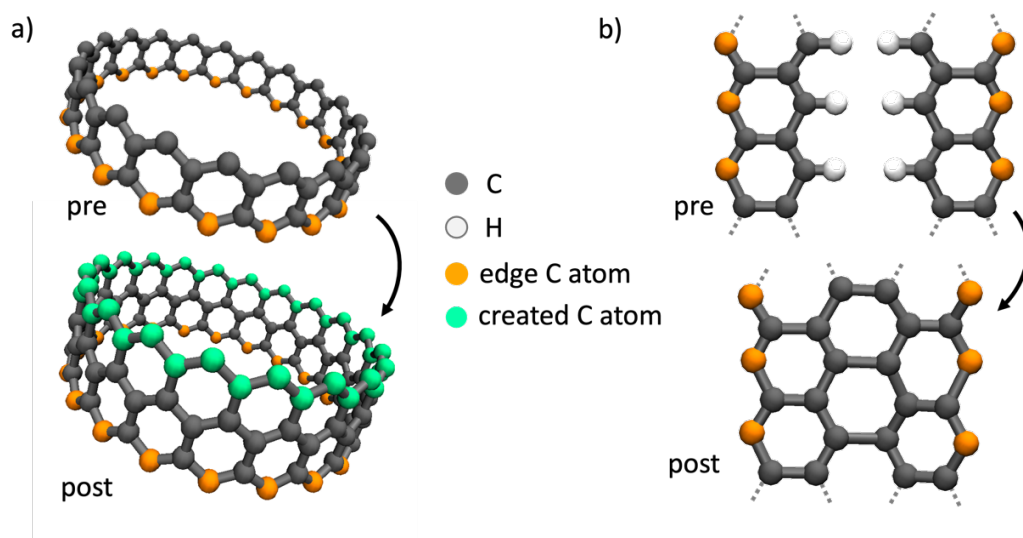


Figure 2. Reaction templates used for building carbon filler phases. a) Pre- and post-reaction templates used for growing CNTs layer by layer. Edge atoms may be connected to the rest of a longer CNT. b) Templates used to build graphitized carbon fiber models from ladder molecules. Dash grey lines indicate intramolecular bonds across a periodic boundary.

was imposed. Separately, a cell of the same size was filled with DEB at a density of 1 g/cm³ and equilibrated. The two simulation cells were then merged, and any DEB monomers found within 1.5 Å of a CNT were deleted. Finally, *in situ* polymerization was initiated using the PAA reactions described in the preceding section, achieving 98% conversion of the ethynyl groups. This process resulted in a model with ~ 575,000 atoms (~ 75,000 in CNT, ~ 500,000 in PAA), with the CNTs comprising

11.4 vol% and 18.6 wt%. The structure is shown in Figure 3c and discussed further in the results section.

CFRP Models

The approach used for building carbon fiber models in this work was inspired by the method of Desai et al. [1], who polymerized “ladder structures” comprising two fused benzene rings, that are also fused across a periodic boundary (i.e., looped), to create perfectly aligned graphitic morphologies. The multistage method they proposed requires cycles of reaction dynamics interspersed with minimization steps. Using the REACTER protocol, such models can be produced quickly via a single uninterrupted dynamics run using a fixed set of parameters. First, a molecule consisting of three linearly fused benzene rings, capped with hydrogen, and looped in the axial direction, was prepared (like the pre-reaction templates in Figure 2b, but fully hydrogenated). These molecules were then packed into a defined region at a density of 1.2 g/cm^3 to create an initial configuration for the graphitization step. The

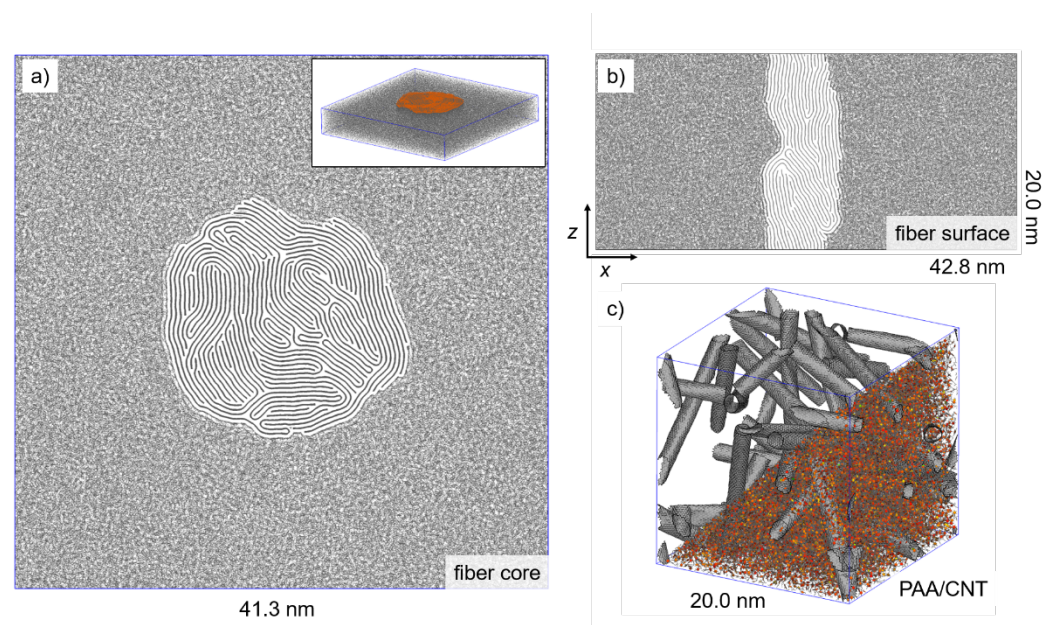


Figure 3. Final composite models used as initial configurations for mechanical testing. a) Fiber core model after packing the simulation box with DEB monomers. b) Axial view of the fiber surface composite model. The axial thickness of both fiber models is 7.2 nm. c) The CNT composite model, where DEB monomers are hidden in half the box to provide a view of the CNT phase.

pre- and post-reaction templates are shown in Figure 2b, where the edge atoms may be bonded to hydrogens (as at the start of the simulation) or carbons during later stages of the graphitization process. The hydrogen atoms present in the pre-reaction template were deleted during polymerization of the ladder structure allowing for a final graphitic structure whose edges were fully hydrogenated. Hydrogens that

remain after carbonization can then be removed or replaced with other functional groups if desired. On every timestep, the axial momentum is zeroed on a per-molecule basis, to ensure that bonding sites remain vertically aligned as shown in Figure 2b. A distance cutoff between hydrogenated carbon atoms of 3 Å was used. Additional reaction constraints are required to create a morphology reminiscent of transmission electron microscope images of carbon fiber. First, the angle between three horizontal atoms of the pre-reaction template (see Figure 2b) was restricted to be between 175° and 180°. Running the growth simulation with only this constraint resulted in a highly convoluted morphology with relatively small regions of graphitic crystallites. This deficiency was addressed by adding a second constraint that used a dihedral angle between four atoms, two in each pre-reaction template, which approximates the angle between the planes containing each pre-reaction molecule. Restricting this angle to be less than 1° resulted in the fiber morphologies shown in Figure 3a and Figure 3b. The PAA precursor (DEB) was then packed around the fiber phase, densified to 1 g/cm³, and polymerized to 98% conversion. For both fiber models, the fiber phase was ~15 vol% and ~28 wt%, with a density of 2.1 g/cm³.

Quantum-Informed Bond Cleavage

Strain-to-failure simulations were enabled by defining a heuristic bond dissociation criterion. Previously, REACTER has been used for polymer chain scission by defining a maximum allowed bond length, beyond which a given bond was deleted along with its associated multibody interactions. However, this simple criterion neglects the destabilizing effect of higher order interactions, such as out-of-equilibrium angles between atoms in the reaction site. To rectify this deficiency, the capability to use energetics-based values calculated by LAMMPS was introduced, such as the potential energy of bonded interactions (bonds, angles, dihedrals, etc.), to influence reaction probabilities. The total potential energy of a group of atoms is less susceptible to thermal fluctuations than a single bond and was found to be a reliable metric for how far from equilibrium the reaction site is. To utilize this feature, the ultimate strains of each repeat unit of PAA were first calculated with semiempirical quantum mechanical accuracy using tight-binding density functional theory (DFTB) (see Figure 4a). The potential energy of the classical force field (PCFF) corresponding to this ultimate strain was then calculated (see Figure 4b). This concept is presented in Figure 4 for the Strauss linkage motif (see the inset of Figure 4a). DFTB simulations were carried out with the DFTB+ engine, using the third order parametrization for organic and biological systems (3ob-3-1) parameter set. One periodic unit cell of the Strauss linkage was deformed at a strain rate of 0.1 ns⁻¹ and the restraining force recorded. As seen in Figure 4a, a distinct drop in the restraining force occurs as the molecule undergoes mechanically induced bond cleavage. A similar simulation was carried out for a phenyl-phenyl linkage, i.e., two directly bonded benzene rings. Five runs for each repeat unit were completed using

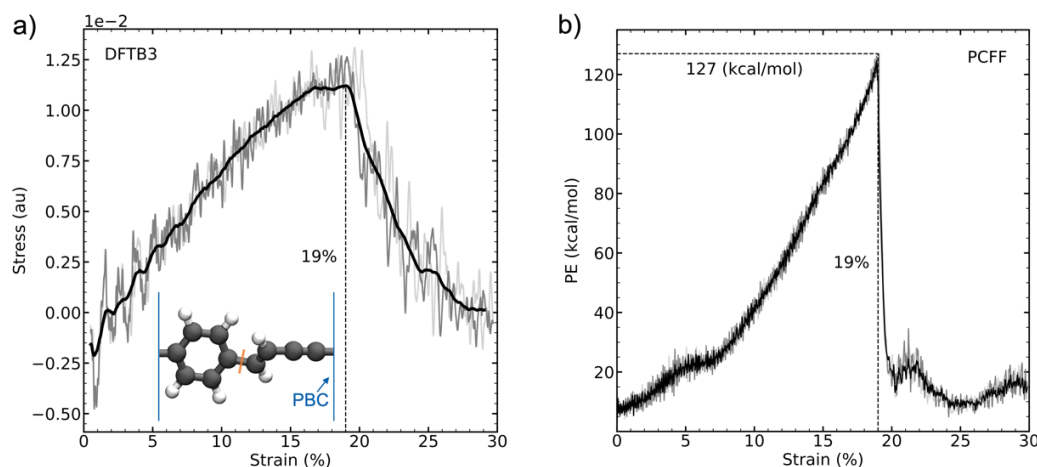


Figure 4. Method for modeling bond cleavage. a) A periodic model of the Strauss coupling product was strained using DFTB. The black line is the average of five runs initiated with independent velocities (individually plotted in gray). In all cases, the bond indicated with an orange slash (see inset) was the point of failure. b) A plot of total potential energy vs. strain for the same system using the PCFF force field. A reaction is defined to cleave the aforementioned bond after reaching an energy of 127 kcal/mol, which corresponds to an ultimate strain of 19% to match DFTB results.

independent Boltzmann distributions for the initial atomic velocities, and the same bond was observed to break in each case. In the case of phenyl-phenyl linkage, it was the link itself. For the Strauss coupling, the cleaved bond is indicated in the inset of Figure 4a.

RESULTS

To sample the mechanical response of the polymerized configurations, the ultimate mechanical properties of the neat and composite systems were probed using strain-to-failure simulations. Due to the densely crosslinked nature of the PAA thermoset, a significant percentage of the total bonds must break to reach high strain values, in contrast to the behavior of thermoplastics [11]. The energy-based criteria for bond breaking of phenyl-phenyl and Strauss couplings, described in the Methods section, were activated during deformation and found to enable stable simulations of all systems up to, and beyond, complete rupture of the material. In this work, bonds within the filler phase were not permitted to break, and no crosslinks were added between the matrix and surface of the filler particles. The three composite systems have markedly different morphologies of the filler phase, which result in different mechanical responses, depending on the strain (ϵ) axis. The two graphitic carbon models were topologically closed (bond topology is looped across a periodic

boundary) and the models were not sampled along this axis, because the fiber phases dominate the mechanical response. The fiber surface model spans the box along the z -axis, but is not looped in that dimension, and does not span the x -axis; therefore, it is fully anisotropic. The fiber core and CNT models were expected to have bi- and triaxially isotropic mechanical properties, respectively.

Neat PAA

The stress-strain response of the neat PAA system is shown in Figure 5a. The strain at failure ($\epsilon_{\max}$) was 1.2, and the ultimate strength ($\sigma_{\max}$) was 1.8 GPa. Both properties are overpredicted compared to expected values for a typical thermosetting resin, a common shortcoming of small-scale models that, as discussed elsewhere [12], also afflicts other atomistic methods, such as bond-order force fields. The total bonds broken as a function of strain is plotted in black in Figure 5b. The number of bonds broken at $\epsilon = 3$ was about 400, which is 1.6% of the original number of ethynyl groups in the pre-polymerized system. The fastest rate of bond breakage occurred just after $\epsilon_{\max}$, as evident from the derivative of the cumulative reaction count (blue curve in Figure 5b). Snapshots taken during strain illustrate the failure process (Figure 5c).

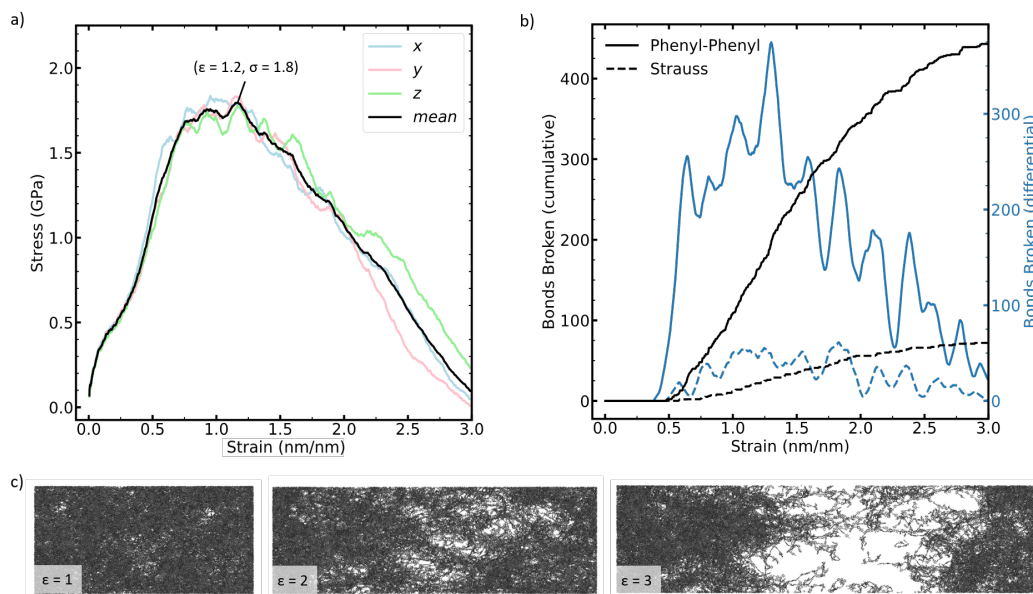


Figure 5. Neat PAA (98% polymerized) under massive uniaxial strain. a) The stress-strain curve along each axis, with the point of maximum stress labeled. b) Total bonds severed vs. strain, with a moving average of its derivative plotted in blue. c) Snapshots of the system under strain (along x axis).

PAA/CNT Composite

The polymer/CNT composite system responded to massive uniaxial strain in a markedly different manner than neat PAA, as seen in Figure 6a. First, the maximum recorded stress was 1.4 GPa, a $\sim 20\%$ drop relative to neat PAA. This decrease in tensile strength may be caused by the high loading of CNTs in this model (nearly 20 wt%). For many resins, optimal CNT loading for single-walled CNTs is often less than 1 wt%. Above that, agglomeration of CNTs and a higher density of stress concentrations can occur, weakening the material [13]. Snapshots of the system at higher strains are provided in Figure 6b. In contrast to the single, primary rupture surface observed in Figure 5c, several distinct clumps of polymer remain even after $\epsilon > 3$, an indication that there were multiple points of high stress concentration that developed during rupture. Another interesting phenomenon observable in Figure 6b, especially at $\epsilon = 3.6$, is CNT crack bridging, whereby a single CNT spans a large void and connects two polymer clumps. Crack bridging is a mechanism known to significantly increase the fracture toughness of CNT composites and laminates, as observed in scanning electron microscope micrographs of fractured composites [14], and likely contributed to the longer tail of the stress-strain curve for the PAA/CNT system. The increased failure strain is most noticeable in the x -axis trace in Figure 6a.

Another conspicuous aspect of the PAA/CNT composite stress-strain response is the high initial resistance at low strains ($\epsilon \sim 0.05$) that was observed consistently along all three strain axes of this isotropic CNT composite model. To compare the contributions of the matrix and filler phases to this peak in the stress-strain curve, the per-atom stresses were analyzed in greater detail. The axial stresses experienced by each component were calculated by summing per-atom stresses over all atoms in the phase (see Figure 7). The absolute values of per-atom stresses, when summed over a

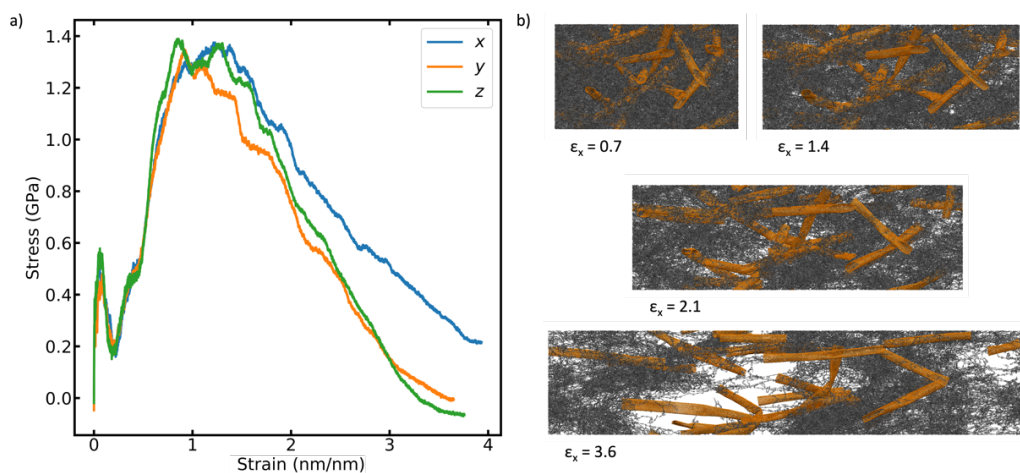


Figure 6. PAA/CNT composite under massive uniaxial strain. a) The stress-strain response of the CNT composite along each axis. b) Snapshots of the simulation during strain (x axis).

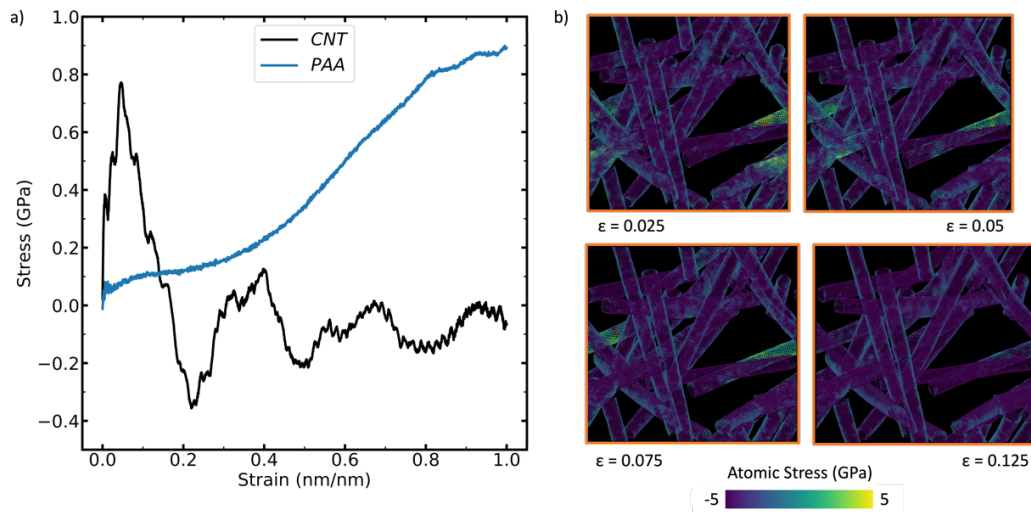


Figure 7. Analysis of the PAA/CNT composite for $\epsilon < 1$. a) Stresses calculated by summing the per-atom stresses of each phase and dividing by a uniform atomic volume of $46 \text{ \AA}^3$. b) Snapshots of the CNT phase colored by atomic stresses, smoothed using a spatial average with a cutoff of $3 \text{ \AA}$ (resin phase hidden).

subset of the simulation box, were difficult to interpret physically, due to the ambiguity of assigning per-atom volumes. Therefore, the axial component of the per-atom stress tensor was rescaled to approximately recover values observed in Figure 7a (corresponding to a uniform atomic volume of $\sim 46 \text{ \AA}^3$). As seen in Figure 7a, the total stress born by each component reveals that the CNT phase, shown by the black line, is highly loaded at low strains. The relative stress values confirm that the CNT phase is primarily responsible for the initial stiffness of the material, but this leads to several more questions about the mechanism of stress transfer between the filler and polymer matrix and the origin of negative stress (compression) and the subsequent long-period oscillations in the CNT phase, seen in Figure 7a. Interestingly, the stress is not uniformly distributed throughout the CNT network, as illustrated by Figure 7b. Very high local stresses are recorded in multiple CNTs at low strains ($\epsilon < 0.075$), but the CNT phase is not being utilized by the composite system to bear load at higher strains ($\epsilon > 0.125$). Further analysis and additional simulations will be needed to fully characterize this behavior.

CFRP

The tensile response of the fiber core composite model, which consists of more than 1 million atoms, is shown in Figure 8a. Like the PAA/CNT model, strong resistance to stretching is encountered at low strains, presumably sustained by the nested graphitic layers of the fiber phase. The nonmonotonic nature of the stress-strain curve at $\epsilon < 0.5$ hints at complex failure mechanisms within the fiber before reaching $\epsilon = 0.5$, at which point the fiber core has delaminated, nanovoids have

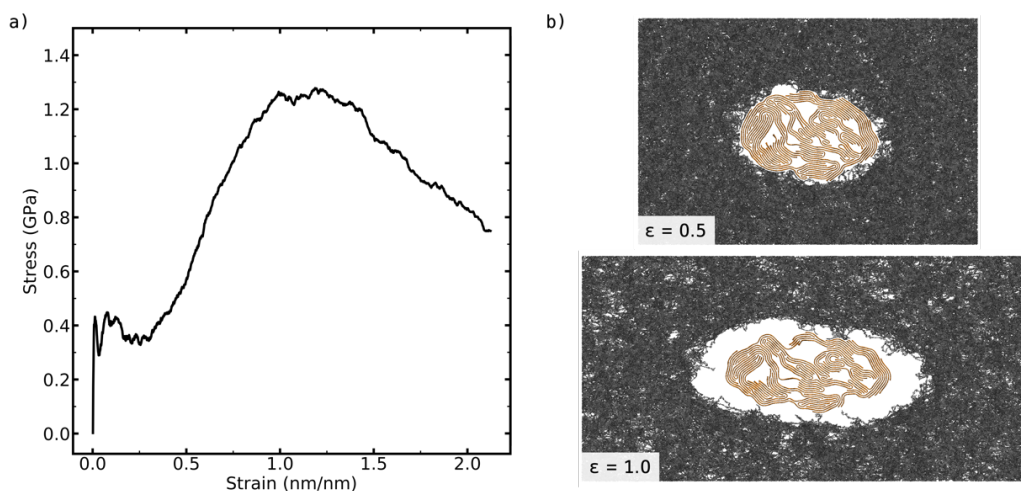


Figure 8. Subjecting the fiber core composite model to strain. a) The stress-strain response along one axis. b) Snapshots of the system at high strains show delamination of the graphitic fiber model and dewetting of the fiber-polymer interface.

appeared in both the fiber and polymer, and the polymer-fiber interface has regions that are partially or fully dewetted (see Figure 8b). It is predicted that fiber delamination is responsible for the initial peak in Figure 8a, and interface dewetting and void growth play a role in the subsequent mechanical response. At $\epsilon = 1.0$, the interface is completely dewetted and the structure of the fiber core is irreparably compromised (i.e., plastically deformed). The disintegration of the fiber core highlights a shortcoming in the current model, as such behavior is not expected in real carbon fiber. The addition of crosslinks between the graphene layers, or a more advanced model that permits misalignment of the layers along the axial direction, would increase the mechanical integrity of the fibers and lead to more realistic behavior.

The fiber surface model is found to have a highly anisotropic response to loading, as shown in Figure 9 for the two non-axial directions. Loading the sample along the x -axis still displays the peak in stress at low strains that is characteristic of these composite systems, but it is a significantly less pronounced than that of other systems. The ultimate stress was ~ 0.75 GPa, about 40% that of neat PAA, but still high for a morphology that does not have a network of covalent bonds spanning the box in that direction. Corrugation in the fiber surface assists load transfer at the interface, so this model is expected to exhibit a higher ultimate strength as compared to flat graphene sheets, for example. Along the z -axis, the system exhibits a higher initial stiffness than any system discussed thus far, reaching ~ 2 GPa and representing the ultimate stress of the graphitic phase. The extremely rapid rise in stress at low

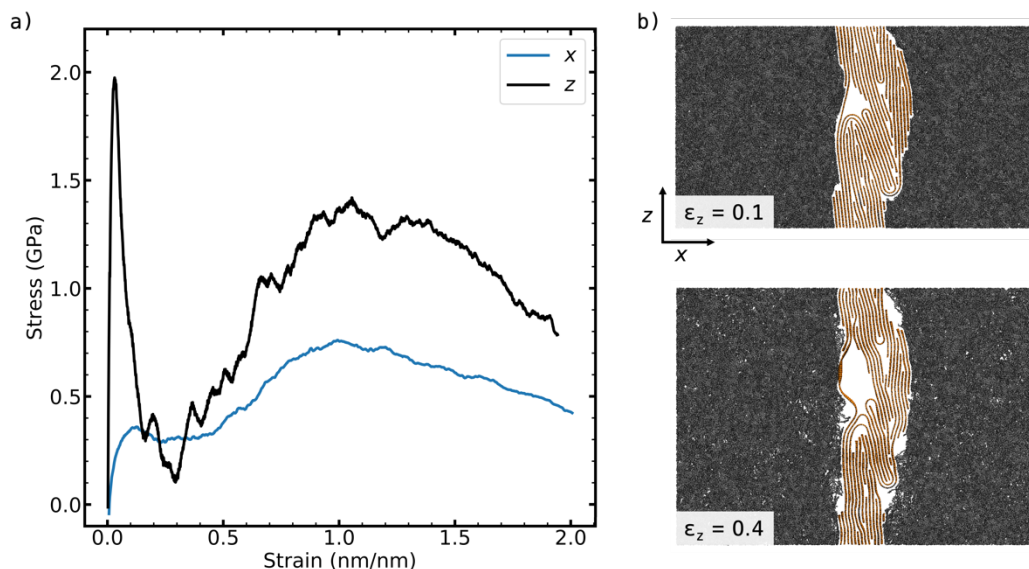


Figure 9. Straining the fiber surface composite model. a) The stress-strain response along both non-axial directions. b) Snapshots of the simulation when straining along the z -axis, for $\epsilon = 0.1$ (near the peak stress) and $\epsilon = 0.4$ (after failure of the graphitic carbon fiber phase).

strain can be attributed to the graphene sheets that, although not crosslinked and not continuous (looped) in the z direction, are highly confined by the surrounding matrix and must unfurl to allow the simulation box to expand. This deformation process is evident at $\epsilon = 0.1$, where an exterior graphene sheet was pulled taut, created a void in the fiber and compressed the nearby resin (Figure 9b). The snapshot at $\epsilon = 0.4$ illustrates the fiber structure and its interaction with the matrix after the fiber component has yielded. The secondary peak, which rises to a strength of ~ 1.4 GPa at $\epsilon = 1$, was due to the load being carried by the matrix polymer after failure of the reinforcing phase.

CONCLUSIONS

The unique suite of features provided by the REACTER protocol, a heuristic method for modeling chemical reactions in classical MD simulations, was leveraged to create large-scale carbon composite models. Both the resin and filler phases were created dynamically using the LAMMPS implementation of REACTER, known as ‘fix bond/react.’ The high-performance thermoset PAA was chosen for the resin matrix, for which the addition polymerization reactions of linear Strauss coupling and cyclotrimerization were modeled to create a highly crosslinked polymer with $>98\%$ conversion. To create a PAA/CNT composite, single-walled CNTs were grown dynamically in a layer-by-layer fashion to create a high-density CNT network, and

PAA precursor monomers were infiltrated into the network to undergo *in situ* polymerization. A second class of composite, CFRP, was modeled with a graphitic carbon phase as the filler. Uniaxially aligned graphitic carbon was produced by polymerization of ladder structures composed of fused benzene rings. For all model building steps, reaction constraints played a key role in producing the intended morphology. After obtaining equilibrated initial configurations, the composites were strained to failure using quantum-informed criteria for bond cleavage. Specifically, the repeat units of PAA were simulated using tight-binding density functional theory to determine the strain that resulted in their dissociation, and this strain was correlated with the potential energy calculated by the classical force field, summed over the bonds and angles in the reaction site. Using this quantum-informed chain scission, the large-scale models were subjected to massive uniaxial strain and their mechanical response observed.

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