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INTERFACIAL LOAD TRANSFER MECHANISMS IN CARBON NANOTUBE–POLYMER NANOCOMPOSITES

Allocation: Illinois/240 knh
PI: Huck Beng Chew[1]

[1]University of Illinois at Urbana-Champaign

EXECUTIVE SUMMARY

Carbon nanotubes (CNTs) are highly promising for strength reinforcement in polymer nanocomposites, but conflicting interfacial properties have been reported by single nanotube pullout experiments. The petascale Blue Waters supercomputing resources have enabled us to investigate the interfacial load transfer mechanisms during pullout of CNTs from poly(methyl methacrylate), or PMMA, matrices, using massively parallel molecular dynamics simulations. By building atomistic models at experimentally relevant length scales, we showed that the pullout forces associated with nonbonded interactions between CNT and PMMA are generally small, and low-density distribution of crosslinks along the interface increases the pullout forces by an order of magnitude. We identified that mechanical unfolding and pullout of single or pair polymer chains attached to the individual crosslink bonds resulted in substantial interfacial strengthening and toughening while contributing to interfacial slip between CNT and PMMA. Our molecular dynamics (MD) simulation results combined with a shear-slip model compared well with experiments and provided mechanistic insights into the design of nanocomposites.

RESEARCH CHALLENGE

Polymer nanocomposites show substantial property enhancements at much lower filler densities compared to conventional polymer composites reinforced with micron-scale fillers, which ultimately results in lower component weight. These property enhancements arise from the orders-of-magnitude higher surface-to-volume ratio of the nanoscale filler particles for interfacial load transfer. Single nanotube pullout tests are ideal measurements to quantitatively characterize the interfacial load transfer between CNT and the polymer matrix involve the use of atomic force microscopy (AFM) probes *ex situ*, or are conducted *in situ* within a scanning electron microscopy (SEM) chamber. However, conflicting interfacial shear strengths (IFSS) between CNTs and the polymer matrix have been reported by single nanotube pullout experiments conducted over the past decade. Some of these experiments have reported saturation in the critical pullout force with the embedment length of the nanotube, implying a shear lag effect that cannot be predicted by analytical models developed earlier that incorporated pure van der Waals forces. While MD simulations have the potential to provide more realistic insights, most to date have been restricted to relatively short ~10-nm model length of the nanotubes, compared to the actual nanotube embedment lengths spanning ~100 nm to several microns in experiments. The computational barrier to study all-atom models of such CNT–polymer systems at these length sales has hindered the understanding of fundamental mechanisms that could explain the experimental observations.

METHODS & CODES

Our MD simulations were performed using the open source MD code LAMMPS. We adopted the DREIDING force field potential to describe the interactions among all atoms in our single-walled CNT–PMMA system. The atomic configuration of an uncrosslinked, amorphous PMMA matrix was generated using a rapid heating and quenching technique (Fig. 1a, b) by replicating a single PMMA polymer chain generated by Polymer Modeler. The long single-PMMA chain was comprised of 500 monomers and was used to represent PMMA with a molecular weight of

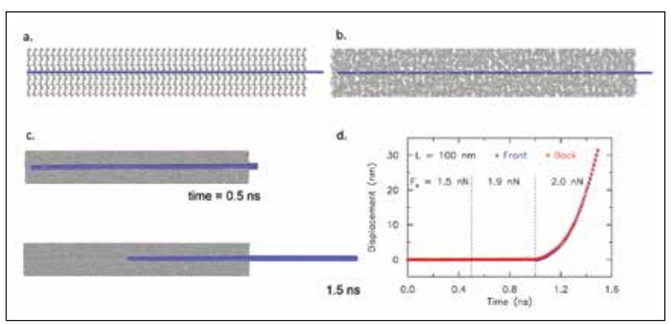

Figure 1: Atomic configurations of a 500-nm-long SWCNT (blue) in a PMMA matrix (grey) at (a) initial stage and (b) heating at 1,000K, one of multiple heating–quenching stages adopted to ensure proper condensation of the PMMA system. (c and d) Pullout of pristine SWCNT from PMMA matrix with initial lengths of 100 nm.

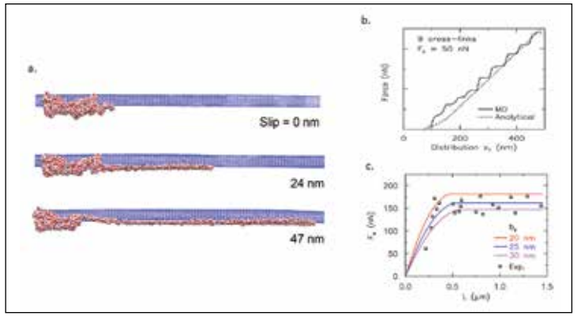

Figure 2: (a) Close-up views of polymer chains attached to crosslinks at various slip-lengths; configurations are filtered to display only the SWCNT and the crosslinked polymer chain. (b) Axial force distribution along nanotube with nine crosslinks. (c) Comparison of model predictions for nanotubes versus experimental pullout data.

50,000 g/mol in experiments. A continuous configurational bias Monte Carlo algorithm was used to randomly assign backbone dihedral angles, which ensured statistically variant representations of monomers in the chain. We equilibrated the composite system until the polymer reached a steady-state density of ~1.02 gm/cc. Quasistatic force-controlled pullout of the nanotube (Fig. 1c, d) was simulated by applying an external energy gradient and then equilibrating the system at 300K for a particular span of time.

RESULTS & IMPACT

We quantified the contribution of nonbonded van der Waals interaction and line (Stone–Wales) or point (vacancy) defects randomly present on the nanotube to the critical pullout force. Results demonstrated that the pullout forces are negligibly small compared to the ones reported by experiments, even in the presence of Stone–Wales and vacancy defects. For example, the measured force of ~3.75 nN for wavy 500-nm nanotubes translates to an average IFSS of ~0.77 MPa, which is much smaller than experimentally reported IFSS values of 3–47 MPa for CNT–PMMA interfaces. This implies the presence of bonded interactions in the form of crosslinks between the CNT and PMMA. By introducing equally spaced covalent C–C bonds/crosslinks between nanotube and PMMA monomers, and by defining a distance-based bond-breaking criteria, we investigated the pullout process and the effect of crosslink density and nanotube length. We found that to initiate nanotube pullout from the PMMA matrix, the applied pullout force must locally induce the pullout of polymer chains attached to the individual crosslinks and mechanically unfold these chains. Subsequent scission of the crosslink bonds can occur once the applied pullout force is sufficiently large. This process allows for substantial relative slip between the nanotube and PMMA matrix, which is not accounted for in classical shear lag models.

We, therefore, incorporated the mechanical behavior of chain deformation (Fig. 2a) to modify the classical shear lag model, which can now take the relative interfacial slip into account. Based on this analytical model, we predicted an evenly distributed load transfer through crosslink bonds, which results in almost linear axial force distribution in the nanotube for lower crosslink densities. This is also confirmed by our MD simulation results (Fig. 2b). Furthermore, the slip mechanism is able to capture the saturation of forces as tube embedment length increases through a transition from pure slip to slip-shear lag type of load transfer. As an outcome, the model can quantify crosslink bond distances (20nm–30nm in Fig. 2c) for previously performed nanomechanical experiments.

WHY BLUE WATERS

The Blue Waters computational capacities were necessary for several reasons. First, the number of atoms in an all-atom (with no coarse-graining) system of ~100 nm- to 500-nm-long nanotubes embedded in PMMA matrices ranges from ~0.2 to 10 million. Second, the heating–quenching process adopted to build the PMMA configurations required ~3 nanoseconds of simulation time, corresponding to 3 million timesteps for a timestep increment of 1 femtosecond. Additionally, the force-controlled pullout simulations required 0.5 million timesteps each. Such large-scale simulations cannot be performed on existing campus clusters or XSEDE resources.

PUBLICATIONS & DATA SETS

Yi, C., et al., Direct nanomechanical characterization of carbon nanotubes-titanium interfaces. *Carbon*, 132 (2018), pp. 548–555.

Bagchi, S., A. Harpale, and H.B. Chew, Interfacial load transfer mechanisms in carbon nanotube-polymer nanocomposites. *Proceedings of the Royal Society A*, 474 (2018), DOI:10.1098/rspa.2017.0705.