Interphase Design for Extraordinary Nanocomposites: Multiscale Modeling and Characterization

NSF NIRT Grant 0404291

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Background and project objectives

In nanoreinforced polymers, nanotubes are typically curved and entangled as opposed to the straight, parallel fibers in traditional composites. In this project, we examine the effect of nanotube curvature and interface/interphase properties and their relationship to composite properties of interest. While improved elastic stiffness of nanocomposites has been a design target for some time, with recent good success, much less understood is the effect of nanoparticles, their morphology and connectivity on fracture toughness. Our work is a combined multi-scale experimental and theoretical effort to unravel the underlying mechanisms of strength and toughness properties of nanocomposites. The work includes molecular dynamics modeling, micromechanics, continuum and finite element analyses as well as experimental synthesis and characterization at a range of length scales to achieve this goal.

Progress

One aspect of this project has focused on understanding and modeling toughness in nanocomposites by modification to traditional composite micromechanics approaches. Our theoretical work starts from modeling single curved fiber pullout. The analysis is based on classic shear lag model for straight fiber pullout and further modifies the shear lag model by adding in fiber curvature. The complete force-displacement curve for a curved fiber is derived starting from perfectly bonded fiber/matrix system to debonding and ultimately sliding for complete pullout of fiber from matrix. It is found that curved fibers such as nanotubes require higher pullout force than straight fibers with same set of parameters. However, a constant interfacial friction stress in current analytical model is insufficient to account for the distinctions of curved fiber compared with straight fiber. Therefore we will pursue modeling the interfacial friction stress as a function of curvature and axial position. Finite element simulation is being used to define the functional form of the interfacial friction and to validate other assumptions in our analysis. The results from finite element simulation show the preliminary analytic model captures the correct distribution of interfacial shear stress qualitatively. However, the numerical results also suggest modification of some assumptions made in the derivation and incorporation of hoop direction variations which will require a more rigorous 3D model. The derived force-displacement curve for single curved fiber pullout will be transformed into bridging law in crack bridging models for our fracture analysis of nanocomposites (Fig. 1).

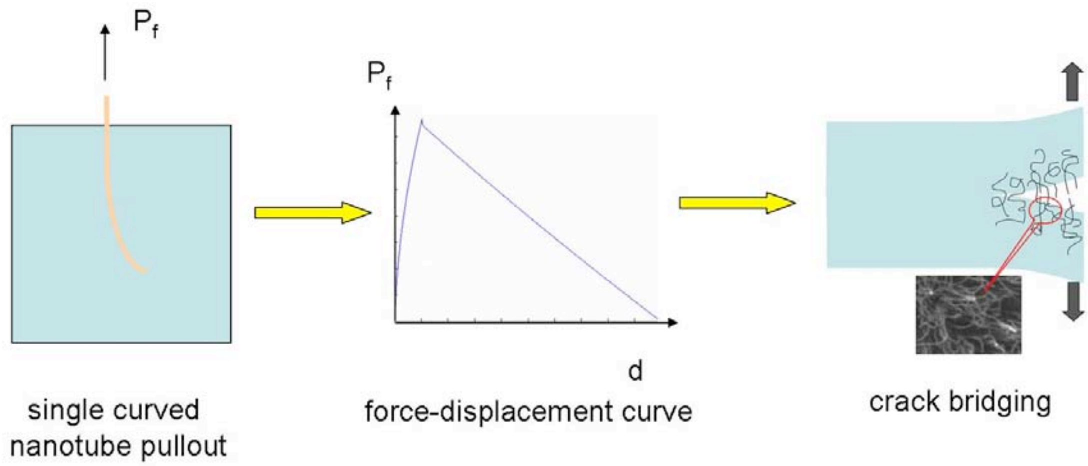

Fig. 1 Continuum analysis starting from single curved fiber pullout to the derivation of bridging law and finally crack bridging fracture analysis

In order to validate the modeling behavior, we are developing methods for testing the micromechanical behavior (albeit at the nano scale) of the composites. We are focusing on two approaches this year. The first is the use of TEM to slice the composites perpendicular to the fracture surface (Figure #2) and observe the pullout behavior of MWNT/polycarbonate composites. From the perpendicular slices, we can determine typical pullout lengths as a function of angle to the fracture surface, as a function of curvature, and as a function of interface condition. Our initial results indicate that the degree of curvature in the MWNT changes significantly during loading, and that the curvature in MWNT is small. Quantitative analysis of the behavior is ongoing. A second approach is to use a forest of nanotubes and to dip the nanotubes into a polymer (in this case epoxy), solidify the epoxy, and then complete a pullout test that provides and average pullout force and thus a calculation of the interfacial shear strength. This new test will remove some of the variability in the measurements and provide an opportunity for varying the angle of pullout and possibly the curvature of the tubes during pullout by adjusting how the nanotubes are inserted into the epoxy (Figure #3). Results will be directly used for comparison of the modeling approaches above. In addition, varying processing conditions will allow the nanotubes in the composite to have an episodic variation in morphology from alignment to a curvature of specific radius and will be used to experimentally validate the toughness value modeled for the composite.

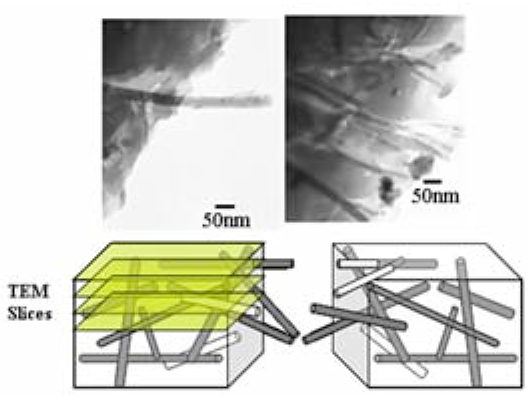

Fig. 2 TEM slices of nanocomposite fracture surfaces to examine interface and pullout effects

The above theoretical and experimental studies focus on nanotube pullout and composite fracture problems. Another interest is to understand the fundamental basis for the reinforcement for nanocomposites through the study of interaction between nanotubes and polymer at molecular level. In particular, to this point we have chosen to deal with the simplest case of spherical particles. Our results for the stress autocorrelation function (which is directly related to the time dependent modulus) show that a long time second elastic

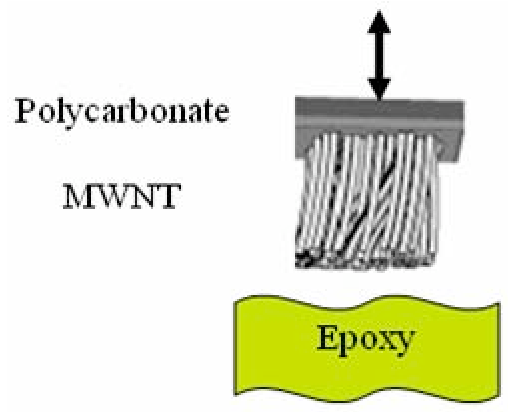

Fig. 3 Nanotube forest on SiO_2 substrate to be dipped in resin for pullout test and compared to modeling

plateau develops as one increases the content of filler (Fig. 4).

While this result is qualitatively in accord with expectations and also experiments, our unusual finding is that these results are strongly dependent on the starting state from which the simulations are begun. This conclusion is consistent with the notion that these systems do not reach their equilibrium states, or that they do not sample all relevant parts of phase space, a notion that is consistent with the appearance of extra long relaxation times in the stress autocorrelation function. To mitigate these problems we have begun to collaborate with Prof. Grant Smith (Utah) so as to implement parallel tempering Molecular Dynamics methods. This work is on going. In parallel, to study the issue of dispersion of nanotubes in polymers we have begun by simulating dilute solutions of polymers and particles so as to understand the creation of bound polymer layers on the tube surfaces. This work, which also emphasizes the non-equilibrium nature of these problems, is currently in progress and results will feed into the micromechanical modeling of fracture toughness by providing detailed properties of the interphase region surrounding the nanotubes.

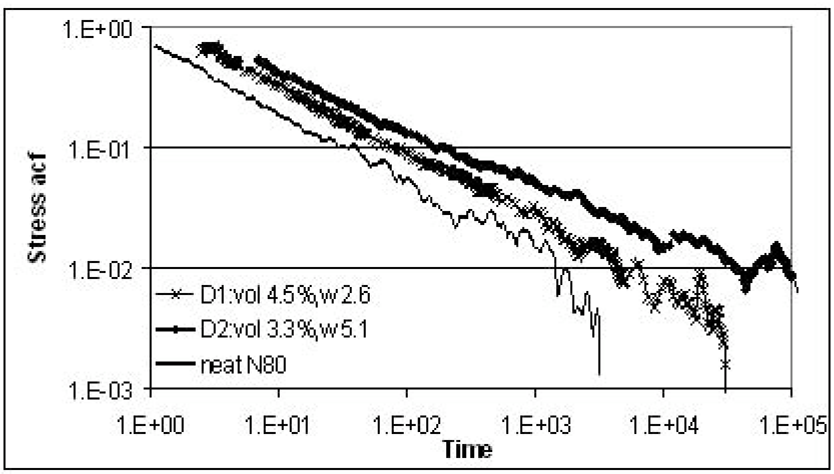

Fig. 4 Molecular Dynamics results for stress autocorrelation function (related to G') with increasing nanoparticle loading.

References

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