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Reinforcement of small structures and critical volumes with nanomaterials may enable near-term applications that can drive longer-term research.

Structural Nanocomposites

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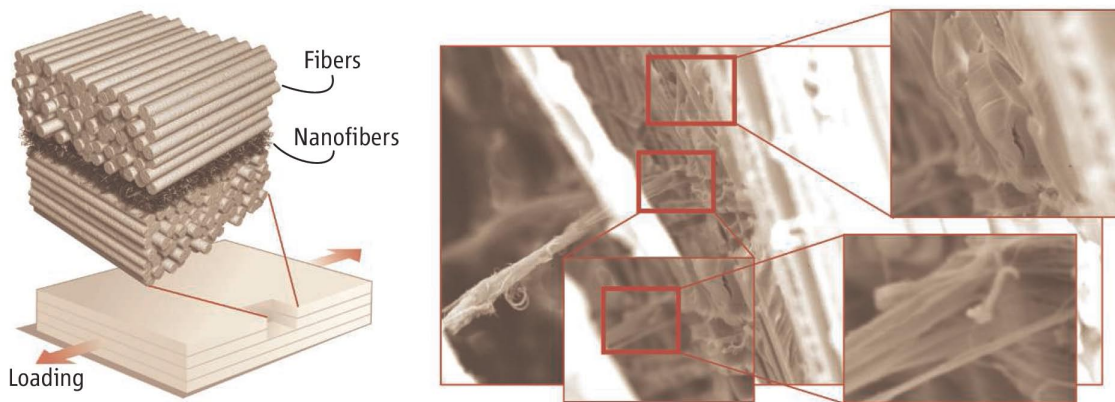
Materials scientists predict that composites made with nanoscale reinforcing materials such as nanotubes, platelets, and nanofibers will have exceptional mechanical properties. However, the results obtained so far are disappointing, particularly when compared to advanced composites reinforced with high-performance continuous fibers (1–4). The reasons include inadequate dispersion and alignment of the nanoreinforcement, low nanoreinforcement volume fraction, and poor bonding and load transfer at interfaces. Intensive work is under way, but the prospect of bulk structural supernanocomposites appears more remote now than it did just a few years ago. However, recent work shows that some applications in reinforcement of small structures may have a near-term payoff that can foster longer-term work on nanocomposites.

Most of the work on structural nanocomposites has relied on ultrastrong nanoreinforcement such as single-walled carbon nanotubes (SWCNTs) (1–3). However, the high SWCNT strength has not yet translated into bulk strength, and it is not even clear whether such translation is possible: Any attempt to create strong interfacial bonds will introduce defects into the SWCNTs that reduce their intrinsic strength. Still, multifunctional applications not relying solely on the mechanical superproperties will benefit

(4, 5). Tailorability and controlled anisotropy are other useful special features of nanocomposites. Multiscale modeling (6) will help us achieve the desired balance between various functions.

One frequently overlooked characteristic of nanoreinforcement is its small size. Various miniature and confined structures can benefit from the improved performance and tailorability of nanocomposites, including ultrathin coatings, membranes, films, and fibers; dental prostheses; structural elements in micromachines and micro- and nanoelectromechanical systems (MEMS/NEMS); thin walls in foams and aerogels; and connections in microcircuits. With the notable exception of nanoreinforced fibers (1, 2), work on the use of nanoreinforcement in microstructures has been slow, but progress is expected to accelerate with the development of more robust nanomanufacturing processes.

Another promising area of research involves solving structural problems that occur in small critical volumes, especially weak spots requiring nanoreinforcement and regions with high localized stress concentrations. Various microdefects and weak inclusions or inhomogeneities represent the former type, whereas sharp structural corners and crack tips are examples of the latter. Cases where both conditions occur simultaneously are the best candidates.



A pathway to supernanocomposites? (Left) Advanced laminated composite with nanofiber-reinforced interfacial layer. **(Right)** In situ observation of interlaminar toughening nanomechanisms including Velcro-like crack bridging by nanofibers. Photo: Yuris A. Dzenis

The use of nanocomposites in microscopic structures or critical volumes requires careful multiscale structural design as well as development of techniques to incorporate the nanocomposite in the desired microcomponents. Although the challenges may be great, the resulting applications can be achieved with considerably lower cost relative to the bulk applications, while providing substantial improvements in the overall structural performance by applying the nanoreinforcement where it is most needed and/or where there are no alternatives.

On the basis of these principles, my colleagues and I created an advanced laminated composite with nanoreinforced interfaces (7). Delamination is a severe and persistent problem in laminated composites made of anisotropic fiber-reinforced plies (8). High interlaminar peel and shear stresses near edges initiate delamination cracks that propagate along the nonreinforced interlaminar planes with little resistance. Delamination substantially reduces the load-carrying capacity and durability of advanced composites and has led to disastrous structural failures. Since the discovery and explanation of the mechanisms of delamination in advanced composites in the early 1970s, researchers have tried to improve delamination resistance. Most designs, however, resulted in cost and weight penalties.

Nanofibers or nanotubes can be used to reinforce interfaces in advanced laminated composites (7) (see the figure). Entangled nanofibers improve interlaminar fracture resistance much like the hooks and loops in Velcro. Experiments with advanced aerospace-grade carbon-epoxy composites showed that a minute quantity (less than 1% by weight) of polymer nanofibers improved the static and fatigue peel and shear interlaminar fracture toughness. We observed that crack deflection, nanofiber pull-out, plastic deformation, and crack bridging all played a part. Moreover, recent computer simulations also confirmed reduction of the edge stresses in the laminates with the nanoreinforced interfaces (9). These improvements are achieved without any measurable increase of weight or decrease of other composite properties. As delamination is known to have a detrimental effect on the overall composite performance (8), the observed improvements can be expected to lead to increases in composite strength, durability, and impact resistance. In this and similar (10) hybrid nano-micro composite designs, the small-scale reinforcement strengthens the ultrathin matrix-rich layers. These microvolumes are critical

for two reasons: They are weak (nonreinforced) and they experience high stress concentrations. The designed three-dimensional nanoreinforcement, with the combination of interlocked in-plane and out-of-plane nanofibers, successfully resolves both of these issues. The design may enable low manufacturing costs, as the nanofibers are used in ultrasmall quantities and their introduction into composites can be integrated with existing composite manufacturing technologies.

Other designs along these lines are possible. For example, fiber-matrix interfaces engineered with bonded nanoparticles show enhanced energy dissipation via a variety of mechanisms. Such interfaces modified by grown carbon nanotubes have exhibited increased interfacial shear strength (1). Nanoreinforcement of adhesive layers, contacts in sintered particulates, or grain boundaries in polycrystalline ceramics and metals can also be pursued. In general, any interface, inclusion, inhomogeneity, or interstitial volume in heterogeneous materials represents a promising nanocomposite application. This should lead the use of nanomaterials as nanoreinforcement in the near- and medium-term time frames, while providing impetus for the long-term development of bulk structural supernanocomposites.

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