

Viscoelasticity in carbon nanotube composites

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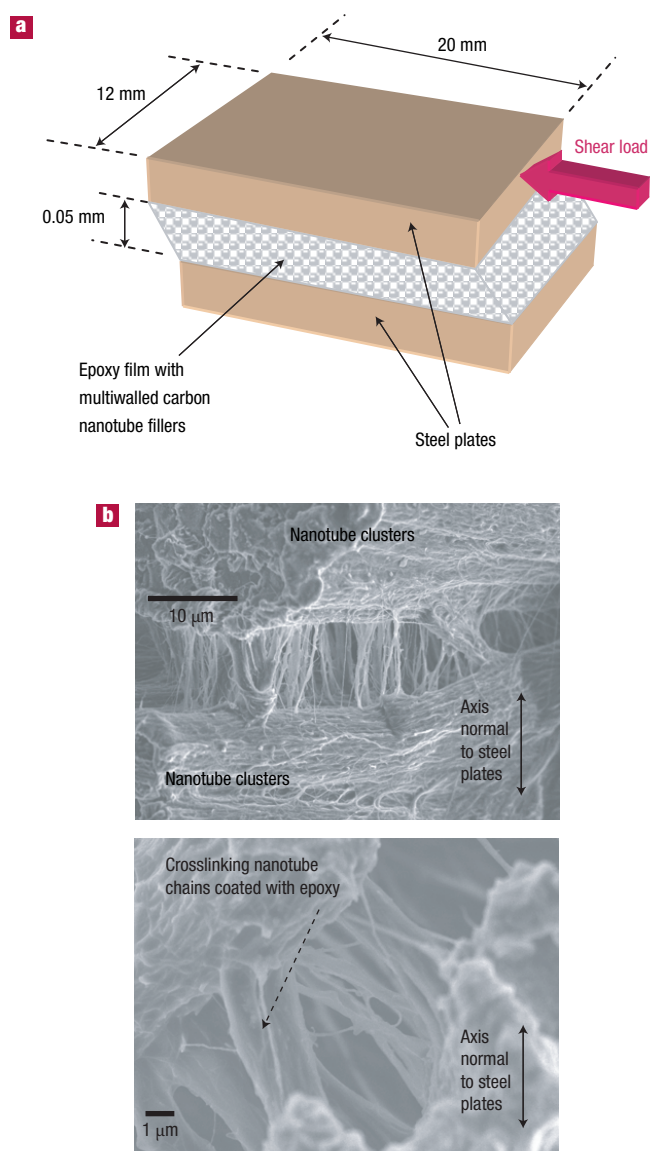
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Polymer composites reinforced by carbon nanotubes have been extensively researched^{1–4} for their strength and stiffness properties. Unless the interface is carefully engineered, poor load transfer between nanotubes (in bundles) and between nanotubes and surrounding polymer chains may result in interfacial slippage^{1,2} and reduced performance. Interfacial shear, although detrimental to high stiffness and strength, could result in very high mechanical damping, which is an important attribute in many commercial applications. We previously reported⁵ evidence of damping in nanocomposites by measuring the modal response (at resonance) of cantilevered beams with embedded nanocomposite films. Here we carry out direct shear testing of epoxy thin films containing dense packing of multiwalled carbon nanotube fillers and report strong viscoelastic behaviour with up to 1,400% increase in loss factor (damping ratio) of the baseline epoxy. The great improvement in damping was achieved without sacrificing the mechanical strength and stiffness of the polymer, and with minimal weight penalty. Based on the interfacial shear stress (~0.5 MPa) at which the loss modulus increases sharply for our system, we conclude that the damping is related to frictional energy dissipation during interfacial sliding at the large, spatially distributed, nanotube–nanotube interfaces.

Viscoelastic materials such as high-loss-factor polymers^{6,7} are rapidly gaining popularity in damping applications. Although viscoelastic damping treatments are shown⁷ to be promising, they suffer from several important limitations such as high weight penalty, compactness issues, poor reliability, low thermal conductivity and poor performance at high temperatures. In addition to passive damping, several active damping treatments^{8–11} have also been explored. These techniques offer improved damping, but they are still limited by the deficiencies of the basic polymer and incur weight and power penalties. There remains a need to develop advanced materials for damping applications that can overcome these limitations.

Figure 1 Test coupons used for damping characterization. **a**, Cross-sectional view of test specimen showing the carbon nanotube thin film sandwiched between two parallel plates. **b**, Scanning electron micrograph of the nanotube film's microstructure (viewed from an external edge after curing but before testing). Top panel shows densely packed multiwalled nanotube clusters with crosslinking nanotube chains. The nanotube clusters are oriented normal to the thickness direction of the film. Bottom panel shows high-magnification image of the crosslinking nanotube chains.



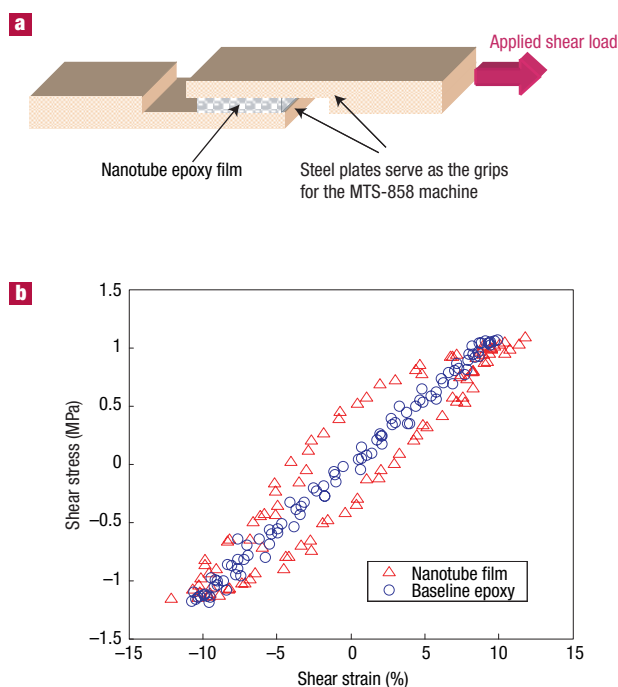


Figure 2 Viscoelastic shear-mode characterization tests. **a**, Schematic of viscoelastic shear mode testing of nanotube thin film. Tests are conducted over a range of shear strain amplitudes (5–20%) and frequencies (1–10 Hz). All tests are done at room temperature. **b**, Shear stress versus shear strain response for nanotube film and baseline epoxy at a test frequency of 10 Hz (both films have identical dimensions: 20 mm × 12 mm × 0.05 mm). The large hysteresis observed in the response of the nanotube film is indicative of energy dissipation.

The high Young's modulus and tensile strength of carbon nanotubes have generated great interest in the potential development of super-strong, super-stiff composites with carbon nanotube reinforcement fibres. Several groups^{1–4,12–14} have shown that the efficiency of load transfer in such systems is critically dependent on the quality of adhesion between the nanotubes and polymer chains. Strengthening nanotube–polymer interfaces (to prevent interfacial slip) is an area of ongoing research. Here we demonstrate that interfacial slip, although detrimental to stiffness and strength, may result in very high mechanical damping. This effect is related to the nanoscale dimensions and high aspect ratio of nanotubes, which result in a large interfacial contact area (for example, multiwalled carbon nanotubes could have a specific area¹⁵ of $\sim 100 \text{ m}^2 \text{ g}^{-1}$, compared with about $10 \text{ m}^2 \text{ g}^{-1}$ for rubber-grade carbon black and $0.4 \text{ m}^2 \text{ g}^{-1}$ for 200 μm long and 10 μm diameter carbon whiskers, both of which are competing fillers used for damping applications). This high interfacial contact area can result in high frictional energy dissipation during the sliding of nanotube surfaces within the composite. Because of their small size, nanotube fillers could be seamlessly integrated into composite systems without sacrificing structural integrity or mechanical strength. Nanotube fillers may also act as nanometric heat sinks to improve the thermal stability and heat dissipation capability of the polymer. In fact, the low mass density of hollow nanotube fillers implies that the damping enhancements could be engineered with minimal weight penalty. In spite of the enormous potential of nanotube damping materials, they have yet to be investigated in any detail. Previous investigations^{5,15} have indirectly measured the damping by sensing the bending vibrations of sandwich beams with embedded nanocomposite films.

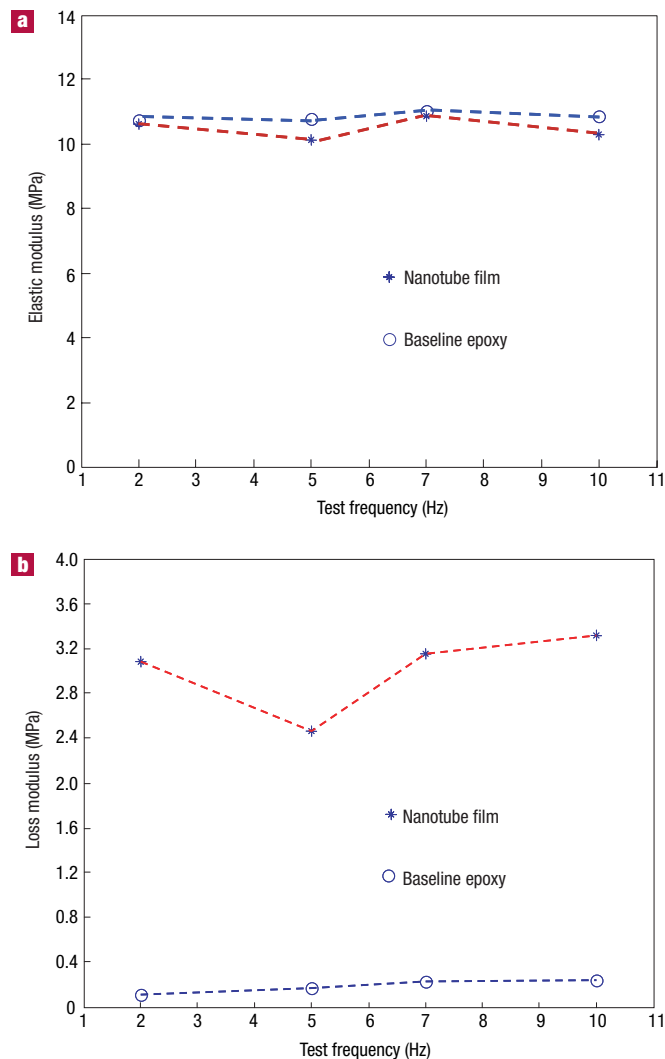


Figure 3 Complex modulus characterization results. **a**, Elastic shear modulus of nanotube film and baseline epoxy plotted as a function of test frequency. The shear strain amplitude is held constant at 10% (the nanotube and epoxy film dimensions are 20 mm × 12 mm × 0.05 mm; all tests are done at room temperature). The elastic shear modulus of nanotube film is slightly lower than that of the baseline epoxy, probably because of some void or recess formation in the composite. **b**, Loss modulus of the nanotube film and baseline epoxy plotted as a function of test frequency. The baseline (neat) epoxy has very low loss modulus and therefore minimal energy dissipation. In contrast, the epoxy film with carbon nanotube fillers shows marked increase in loss modulus (up to 15-fold increase), which indicates large energy dissipation.

Recently, Zhou *et al.*¹⁶ have also done uniaxial tests to measure loss factors of nanocomposite specimens. Here we report direct viscoelastic shear-mode testing of nanotube–epoxy thin films to characterize the complex stiffness and material loss factor.

A schematic diagram of the test coupon used for this study is shown in Fig. 1a. Dense uniform films of well-aligned multiwalled carbon nanotubes were first assembled on substrates using chemical vapour deposition of a precursor xylene–ferrocene mixture^{17,18}. The substrate consisted of SiO_2 sheets 80–100 nm thick. The individual nanotube dimensions are $\sim 30 \text{ nm}$ outer diameter, $\sim 10 \text{ nm}$ of wall thickness and $\sim 50 \mu\text{m}$ in length. The packing density of nanotubes in the film was about 10^{11} tubes per square centimetre.

The nanotube film (anchored on silica sheet) was then sandwiched between two opposing steel plates, which also serve as the grips for the MTS-858 system. The steel plates and enclosed nanotube film were bonded together using M-Bond 200 epoxy resin (ethyl-2-cyanoacrylate (80–90%) and polymethylmethacrylate (10–20%)) and cured under pressure (1 MPa) for about 10 minutes at room temperature. M-Bond 200 is a commonly used low-stiffness adhesive epoxy designed for operation between -30 and 65 °C, and the manufacturer-quoted glass transition temperature (T_g) for the cured resin is 130 °C. Characterization by scanning electron microscopy (Fig. 1b) of the nanotube–epoxy composite film reveals a fascinating network of densely packed nanotube clusters interlinked with nanotube connecting chains. This interconnectivity may play a part in delaying interfacial slip between nanotube clusters to a higher shear stress, thereby influencing the energy dissipation. Such intercluster connectivity is unusual in nanotube systems and is probably related to the pressure applied to the film during the cure cycle. The estimated volume fraction of the nanotubes within the composite film is about 50%.

Figure 2a shows a schematic diagram of the viscoelastic shear-mode testing. The sample is tested using an MTS-858 servo-hydraulic system (all tests are at room temperature). The nanotube film tested in this study has dimensions of $20\text{ mm} \times 12\text{ mm} \times 0.05\text{ mm}$. A baseline epoxy film (with no nanotubes) of the same dimensions is also tested to compare the response of the two materials. Figure 2b shows data for shear stress versus strain at a test frequency of 10 Hz and shear strain amplitude of 10% (data are shown for five cycles). The shear stress and strain are calculated from the dynamic displacement and load data measured using the linear variable differential transformer (LVDT) sensor and load cell of the MTS-858 system. LVDT displacement data were independently verified for accuracy during each test run by using an extensometer set-up. As expected, the baseline epoxy shows negligible damping (no hysteresis is observed). In contrast, the nanotube film shows large hysteresis. The area enclosed by the hysteresis loop is indicative of the energy dissipated per cycle, and this clearly indicates that damping of the nanotube film is significantly greater than the baseline epoxy film.

To quantify the damping increase, the material complex modulus²⁰ was calculated using the measured shear stress (τ) and shear strain (γ) responses. The linearized stress–strain relation can be expressed as $\tau = (G' + jG'')\gamma$, where the in-phase component (G') determines the storage or elastic modulus (real part of complex modulus) and the quadrature or 90° out-of-phase component (G'') determines the loss modulus (imaginary part of complex modulus). To obtain the storage and loss moduli, we applied sinusoidal (or oscillatory) shear strain to our sample: $\gamma = \gamma_0 \sin(\omega t)$, and we measured the resulting shear-stress response, $\tau = (\tau_0 \cos \delta) \sin(\omega t) + (\tau_0 \sin \delta) \cos(\omega t)$, where $\tau_s = \tau_0 \cos \delta$ represents the component of the shear stress that is in phase with the strain and $\tau_c = \tau_0 \sin \delta$ represents the component of the shear stress that is out of phase with respect to the strain. Note that τ_0 is the amplitude of the stress, ω is the angular frequency of the applied strain and δ is a phase angle related to the viscoelastic properties of the material. The Fourier-transform method was used to obtain the in-phase (τ_s) and out-of-phase (τ_c) components of the measured shear stress response in the frequency domain. The elastic and loss moduli were then calculated using $G' = \tau_s/\gamma_0$ and $G'' = \tau_c/\gamma_0$.

In Fig. 3 we compare the measured elastic and loss moduli of the nanotube film and baseline epoxy over the frequency range 1–10 Hz. All tests were done at room temperature and at constant shear strain amplitude of 10%. The elastic modulus (G') of the nanotube film (~ 10 MPa in 1–10 Hz frequency range) was marginally lower than that of the neat epoxy (Fig. 3a). The complex or loss modulus (G'') was more than 15 times as high (Fig. 3b) as that of the baseline epoxy. The material loss factor (ratio of loss to elastic modulus) or damping

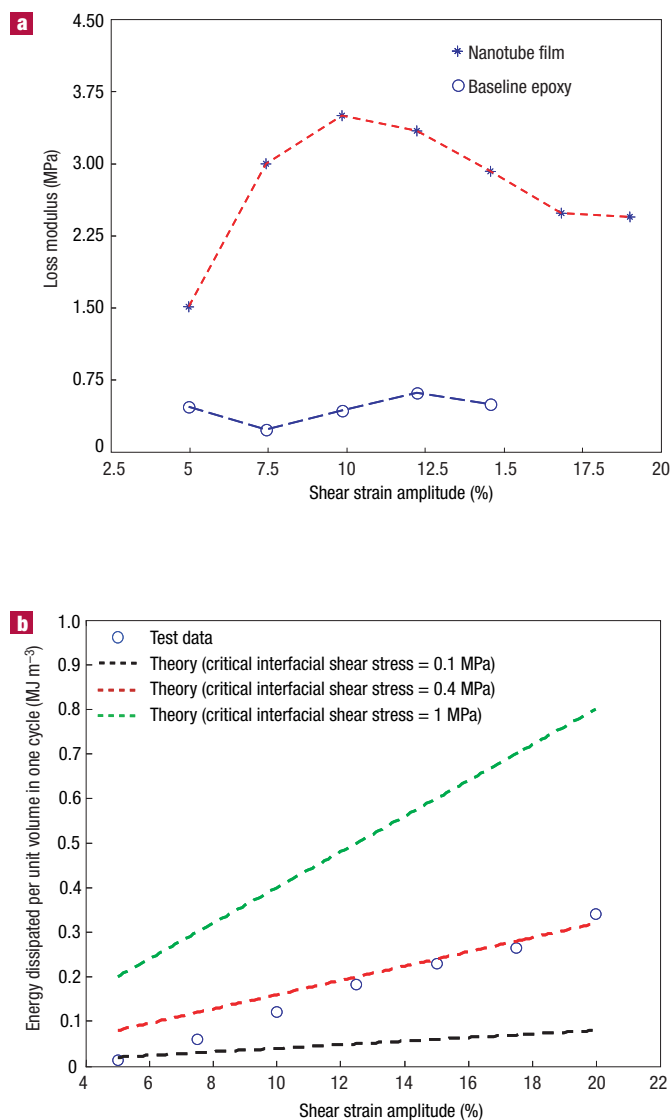


Figure 4 Effect of shear strain amplitude on damping. **a**, Loss modulus of the nanotube film and baseline epoxy plotted as a function of shear strain amplitude. Test frequency is held constant at 10 Hz (all tests are done at room temperature). The loss modulus of the nanotube–epoxy film increases markedly above 5% strain achieving a maximum value of about 3.5 MPa for shear strain amplitude of 10%. In contrast, the baseline epoxy shows very low loss modulus over the entire test range. **b**, Energy dissipated per unit volume in one cycle, plotted as a function of the shear strain amplitude. Theoretical predictions show a good match with test data (10 Hz excitation case) for a critical interfacial shear stress of 0.4 MPa, which is consistent with the hypothesis of tube–tube sliding as the main source of interfacial friction damping.

ratio of the carbon nanotube film is about 0.3 compared with only 0.02 for the epoxy. This indicates that for the particular epoxy system and test geometry used, up to 1,400% (15-fold) increase in the damping ratio can be engineered by the use of multiwalled carbon-nanotube fillers. The increased damping is obtained without sacrificing the elastic modulus (Fig. 3a) of the epoxy film. We also measured the glass-transition temperature (T_g) of the baseline (unfilled) and nanotube-filled systems using differential scanning calorimetry. The measured T_g of the nanotube-filled epoxy (129.9 °C) was very close to the measured value for the baseline epoxy (130 °C), indicating that the presence of nanotube fillers has not significantly affected its cure chemistry.

To study the effect of strain amplitude, the shear strain was varied between 5 and 20%. The tests were done at a frequency of 10 Hz and at room temperature. The nanotube film's damping behaviour is strongly amplitude-dependent and a maximum loss modulus of ~3.5 MPa (Fig. 4a) is achieved at a shear strain amplitude of about 10%. In comparison, the baseline epoxy material showed very low loss modulus over the entire test range. Amplitude-dependent damping behaviour in nanocomposites has also been reported in a recent study¹⁶. The ratio of loss modulus to elastic modulus (loss factor ~0.35) and the thickness (50 μm) of our nanotube damping film compare well with commercial viscoelastic damping polymer films^{6,7} such as 3M-ISD-130 (acrylic adhesive; 127 μm thick with loss factor of 0.38) and FasTapeTM-1191 (rubber adhesive; 280 μm thick with loss factor of 0.25). The total energy dissipated per cycle is proportional to the loss modulus of the damping material; the nanotube film has a loss modulus of about 3 MPa (Fig. 3b) in the 1–10 Hz range, which is significantly greater than the loss modulus for traditional viscoelastic polymers (0.03–0.05 MPa at 1–10 Hz). Therefore nanotube damping films may offer up to two orders of magnitude increase in energy dissipation over the best available viscoelastic polymer materials.

There are two possible mechanisms that could be responsible for the observed increase in mechanical damping: (1) energy dissipation caused by interfacial sliding at the nanotube–polymer interface and (2) energy dissipation caused by interfacial stick–slip sliding at the nanotube–nanotube interface. Before discussing these mechanisms it is important to note that for our system the energy dissipation begins to rise sharply at about 5% shear strain amplitude (Fig. 4a). This corresponds to an interfacial shear stress of about 0.5 MPa (based on ~10 MPa shear modulus, see Fig. 3a). Because there may be considerable localization of stress or strain near the nanotube inclusions, 0.5 MPa is only an approximation of the applied stress. The exact values of the localized stress and strain will also depend on the local morphology of the nanotubes relative to the loading direction and to neighbouring tubes. The discussion aims only to provide a rough estimate of the energy dissipation without attempting to address the daunting problem of more accurately assessing local stress and strain fields.

Experimental work¹⁴ indicates that the critical shear stress for the onset of slip at the nanotube–polymer interface (for polyethylenebutene) is around ~50 MPa. Experiments on other polymer epoxy systems indicate similar magnitude of shear strength (L. Schadler, personal communication). Molecular mechanics simulations²³ showed even higher critical stress (160 MPa) for slip at the nanotube–polystyrene interface. In view of these results, it seems unlikely that the critical interfacial stress for tube–polymer slip in our system would be as low as 0.5 MPa.

To evaluate the importance of the nanotube–nanotube sliding dissipation mechanism we note that the critical shear stress for interfacial slip in graphite¹⁹ is ~1 MPa. Even smaller critical shear stress, in the range of 0.08–0.66 MPa, is observed in slip experiments with multiwalled nanotubes^{21,22}. This range overlaps with the range of shear stresses where the loss modulus (Fig. 4a) increases sharply and is ~0.5 MPa at 5% shear strain. Therefore we conclude that our system may behave as follows: at low strain (<5%) very few tube–tube contacts reach the critical stress, and energy loss is small. At the critical strain of ~5% intertube sliding is activated, particularly for tube bundles closely aligned to the shear direction, and the damping shows a sharp increase. Peak damping is achieved for about 10% strain when most tubes in the film will slip. The slight decrease of loss modulus at larger strains (>10%, Fig. 4a) could be related to dynamic friction²² in multiwalled nanotubes which is shown to be lower than static friction.

To provide more quantitative support for the above discussion we show (Fig. 4b) the test data for energy dissipated per unit volume, obtained by integrating the product of the measured shear stress and the measured shear strain over one complete oscillation cycle. At high

stresses, where most of the intertube sliding is activated, the dissipated energy (per unit volume, per cycle) can be predicted by summing the product of the critical tube–tube shear stress (for onset of intertube slip) and peak shear strain over one complete oscillation period. The predicted energy dissipation per unit volume is plotted against shear strain amplitude for three different values (0.1, 0.4 and 1 MPa) of critical shear stress in Fig. 4b, along with the test data. Figure 4b shows that for 0.4 MPa critical shear stress the predicted energy loss compares well with the experimental value for shear strain above ~10%. This critical shear stress is consistent with critical interfacial slip values reported for multiwalled nanotubes^{21,22}. At strain amplitudes below 10% the theoretical prediction is an overestimate, which, as we have already pointed out, arises because the interfacial stresses are not high enough to ensure that most of the tubes will slip.

This study has shown that intertube sliding interactions in nanotube composites can be useful for structural damping. Nanotube fillers are minimally intrusive and offer the promise of improving damping without sacrificing mechanical properties and structural integrity. Nanocomposite materials could therefore advance the state-of-art in the field of polymeric damping, helping to ensure stability and low vibratory loads in a wide variety of structural components and systems.

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Competing financial interests

The authors declare that they have no competing financial interests.