

Utilizing interfaces in carbon nanotube reinforced polymer composites for structural damping

Pulickel M. Ajayan · Jonghwan Suhr ·
Nikhil Koratkar

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Abstract Carbon nanotube reinforced polymer composites have been extensively researched [Shadler LS, Giannaris SC, Ajayan PM (1998) *Appl Phys Lett* 73:3842; Ajayan PM, Shadler LS, Giannaris C, Rubio A (2000) *Adv Mater* 12:750; Wagner HD, Lourie O, Feldman Y, Tenne R (1998) *Appl Phys Lett* 72:188; Thostenson ET, Chou T-W (2002) *J Phys D: Appl Phys* 35:L77] for their strength and stiffness properties. The interfaces between nanotubes and polymer matrix can play a critical role in nanocomposites for their mechanical properties, since the interfacial area is order of magnitude more than traditional composites. Unless the interface is carefully engineered, poor load transfer between individual nanotubes (in bundles) and between nanotubes and surrounding polymer chains may result in interfacial slippage [Shadler et al. (1998); Ajayan et al. (2000)] and consequently disappointing mechanical stiffness and strength. Interfacial slippage, while detrimental to high stiffness and strength, could result in very high mechanical damping, which is a hugely important attribute in many commercial applications. In this paper, we show that the mechanical

damping is related to frictional energy dissipation during interfacial sliding at the extremely many nanotube-polymer interfaces, and characterize the impact of activation of the frictional sliding on damping behavior.

Introduction

The very high stiffness and strength of carbon nanotubes have generated great interest in the research community regarding the potential development of super-strong, super-stiff composites. They are also considered the ideal reinforcement fibers for the composites due to their combination of extremely large interfacial contact area, high aspect ratio and low mass density. However, in order to fully take advantage of their exceptional properties, several challenges still remain for the synthesis of the nanotube-polymer composites. First, the mechanical properties of nanocomposites are strongly related to the dispersion of carbon nanotubes within a polymer matrix. Due to van der Waals interactions, it is very challenging to prevent the agglomeration of carbon nanotubes (especially, single-walled carbon nanotubes). Secondly, in order to tailor the properties of nanotube-polymer composites we should be able to control the orientation as well as the alignment of the nanotubes within a polymer matrix. Carbon nanotubes typically remain wavy when embedded in a polymer matrix. The impact of waviness on the effective modulus of nanotube-polymer composites has been investigated [5, 6]. In addition, several literatures [1–4, 7–10] have shown that the efficiency of load transfer in such systems is critically

P. M. Ajayan (✉)
Department of Materials Science and Engineering,
Rensselaer Polytechnic Institute, 110, 8th Street, Troy,
NY 12180, USA
e-mail: ajayan@rpi.edu

J. Suhr · N. Koratkar
Department of Mechanical, Aerospace and Nuclear
Engineering, Rensselaer Polytechnic Institute, Troy,
NY 12180, USA

dependent on the quality of adhesion between the nanotubes and polymer chains. Still, the way to strengthen nanotube-polymer interfaces (to prevent interfacial slip) is an area of on-going research.

Interestingly, several groups [11–16] have recently explored the potential of using carbon nanotubes as filler materials for improving mechanical damping in composite structures instead of achieving the super strength or stiffness. The combination of extremely large interfacial contact area (for example multi-walled carbon nanotubes (MWNT) could have a specific area [10] of $\sim 100 \text{ m}^2/\text{g}$, compared to competing fillers used for damping applications of about $10 \text{ m}^2/\text{g}$ for rubber grade carbon black and $0.4 \text{ m}^2/\text{g}$ for $200 \mu\text{m}$ long and $10 \mu\text{m}$ diameter carbon whiskers.), high aspect ratio and low mass density implies that interfacial sliding of nanotube fibers within a polymer matrix has the potential to cause significant dissipation of energy with minimal weight penalty. Another attractive feature of this concept is the nanoscale inclusions could potentially be seamlessly integrated within composite/heterogeneous systems without sacrificing mechanical properties or structural integrity. Suhr et al. [11] demonstrated that interfacial nanotube–nanotube sliding within clusters of MWNT could be used for damping enhancement. However the required loading fraction of nanotubes was quite high ($\sim 50\%$) since the weak van der Waals interaction between the nanotubes was not effective at dissipating energy. Wang and co-workers [10, 12] have also studied the damping properties of epoxy films with well dispersed SWNT fillers. In addition, Jalili and co-workers [13] have shown impressive damping increases in epoxy resins by using SWNT fillers.

In this paper we characterize the impact of activation of interfacial nanotube-polymer sliding on energy dissipation, and report that the nanotube-polymer sliding can deliver an order of magnitude ($>1000\%$) increase in loss modulus of bulk polycarbonate systems with only 2% weight fraction of SWNT fillers. The most dramatic increases in damping are reported at large strain amplitudes, when the nanotube-polymer adhesion is not strong enough to prevent interfacial slip. However to fully activate interfacial slip for a majority of the nanotubes within the composite, a large strain amplitude must be applied to the system. In practice such large strains are unlikely to be encountered and so it is important to investigate whether interfacial slip in nanotube composites can be activated at lower strain levels. In this paper it is also shown that temperature can be used to facilitate nanotube-polymer interfacial slip at relatively low strain amplitudes. We can attribute this to the increased mobility

of the polymer chain backbones in the proximity of the polymer's glass transition temperature and thermal relaxation of the radial compressive stresses at the nanotube-polymer interfaces.

This work represents the interfacial slippage, while detrimental to high stiffness and strength, between nanotube-polymer interfaces in composites can result in very high mechanical damping, which is a hugely important attribute in many commercial applications. The following sections will describe the fabrication protocols that were used to prepare the nanocomposites, the test procedure and some of key test results.

Experiment

We purchased purified HiPCO SWNTs from Carbon Nanotechnologies Inc., with an average length of $1 \mu\text{m}$ and average diameter of 1.4 nm . A solution mixing process with Tetrahydrofuran (THF) as the solvent was used to disperse the SWNT in the polymer matrix. Note that because THF is a moderate solvent for polycarbonate (Lexan 121, General Electric), it limits the interaction energy between the polymer and the solvent, and encourages the physical adsorption [14, 15] of the polymer onto the nanotube surface. The absorbed polymer serves as a surfactant for dispersing the nanotubes in the solution and then in the polycarbonate matrix, and also as a load transfer agent [14] from the bulk polymer to the nanotubes.

The as-received SWNTs were first sonicated in THF and polycarbonate was dissolved separately in THF. The SWNT dispersion and PC solution were then mixed in a ratio that resulted in the required SWNT concentration in the polymer, and the mixture was sonicated (750 W, 20 KHz) for 15 min. To obtain the SWNT-PC nanocomposite, the mixture was poured very slowly into methanol (methyl alcohol, anhydrous). The volume ratio between THF and methanol was 1:5. The composite material precipitated immediately (since methanol is an anti-solvent for polycarbonate) and was filtered and dried out under vacuum for 14 h. A compressive mold (pre-heated to $205 \text{ }^\circ\text{C}$) was used to prepare the standard tensile (dog-bone shaped) specimens. The samples have dimensions of $\sim 3.2 \text{ mm}$ in width, 3.2 mm in thickness and 63.25 mm in length. The weight fraction of SWNT in the nano-composite was varied between 1.0 and 2%. Pure polycarbonate samples (without nanotube fillers) of the same dimensions were also prepared (following the same protocol for nanocomposites) to compare the response of the two materials. The dispersion quality was checked with SEM images of the fracture surface for

SWNT-PC composite samples, showing SWNT fibers are dispersed in the polymer matrix and are pulling out of the fracture surface. Each nanotube fiber is comprised of a bundle of SWNTs (~35 nm in diameter) and appears to be coated with a polymer layer.

Viscoelastic characterization

The samples are tested at room temperature under uniaxial cyclic loading using an MTS-858 servo-hydraulic test system. Dynamic strain and stress data are measured using an MTS 632.26E-20 extensometer and the load cell of MTS-858 system. In order to characterize and quantify the damping behavior, the linearized material complex modulus [16] was calculated using the measured uniaxial stress (σ) and corresponding strain (ϵ) response. The linearized stress-strain relation can be expressed as $\sigma = (E' + jE'')\epsilon$, where the in-phase component (E') determines the storage or elastic modulus (i.e. real part of complex modulus) and the quadrature component (E'') determines the loss modulus (i.e. imaginary part of complex modulus). To obtain the storage and loss moduli, we applied sinusoidal (or oscillatory) strain to our sample: $\epsilon = \epsilon_0 \sin(\omega t)$, then we measured the resulting stress response, $\sigma = (\sigma_0 \cos \delta) \sin(\omega t) + (\sigma_0 \sin \delta) \cos(\omega t)$, where $\sigma_s = \sigma_0 \cos \delta$ represents the component of the stress that is in phase with the strain and $\sigma_c = \sigma_0 \sin \delta$ represents the component of the stress that is out of phase with respect to the strain. Note that σ_0 is the amplitude of the stress, ω is the angular frequency of the applied strain and δ is a phase angle related to material viscoelasticity. The Fourier transform method was used to obtain the in-phase (σ_s) and out-of-phase (σ_c) components of the measured uniaxial stress response in the frequency domain. The elastic and loss moduli were then calculated as follows:

$$E' = \sigma_s / \epsilon_0 \text{ and } E'' = \sigma_c / \epsilon_0.$$

Results and discussion

Figures 1a, b illustrate the room temperature behavior of the nanocomposite and baseline (pure) polycarbonate samples. The weight fraction of as-received SWNT in this test was selected as 1.5%. The maximum applied strain amplitude in the test is limited to 1.3% to stay within the elastic region of the polycarbonate. Figure 1a indicates that the elastic modulus (or stiffness) of the nanocomposite shows a gradual decrease with increasing strain amplitude, suggesting that as the

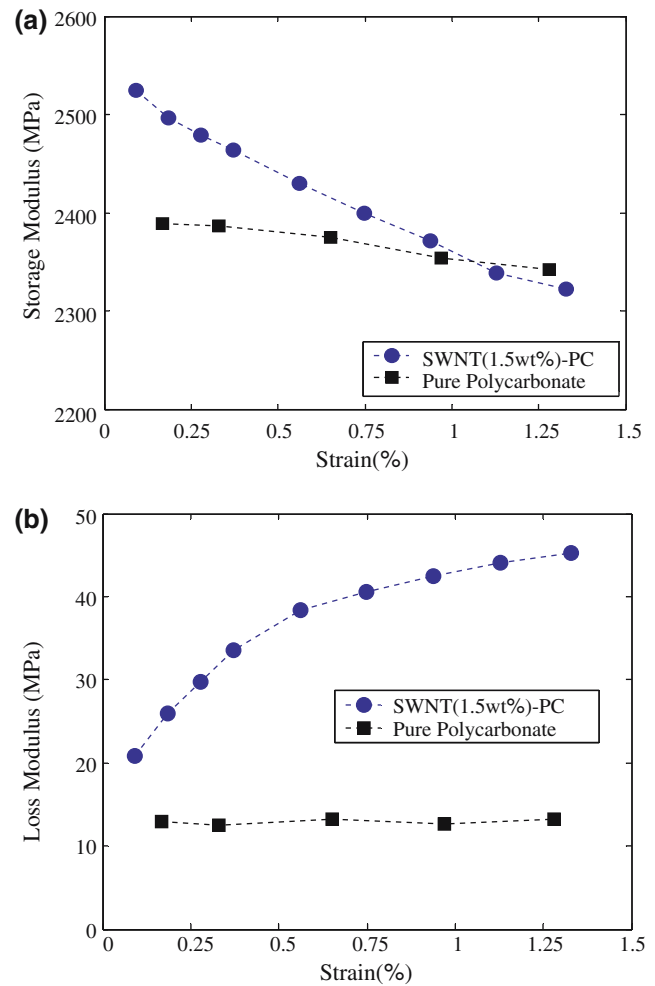


Fig. 1 (a) Elastic moduli of nanocomposite and pure polycarbonate as a function of a strain. All the tests are performed at room temperature and the test frequency is constant at 10 Hz. The weight fraction of the as-received SWNT in the composite is 1.5%. (b) Loss moduli of nanocomposite and pure polycarbonate as a function of a strain for the same test conditions. Taken from the Ref. [19]

strain amplitude is increased the critical stress for nanotube-polymer interfacial slip is reached and filler-matrix debonding (sliding) is activated resulting in a decrease in the stiffness of the nanocomposite. Note that not all the SWNT fibers are expected to fail simultaneously; since the orientation of SWNT in the polymer is random those tubes that have a $\pm 45^\circ$ orientation with respect to the loading direction tend to fail first because the build up of shear stress for these tubes is the greatest [13]. As the strain level is increased more and more of the SWNT interfaces begin to fail resulting in a progressive reduction in the storage modulus as shown in Fig. 1a. As frictional sliding at the nanotube-polymer interfaces is activated, we expect an increase in the loss modulus (damping) of

the nanocomposite. This is clearly seen in Fig. 1b which shows that the decrease in storage modulus of the nanocomposite is mirrored by a corresponding increase in loss modulus. Beyond about 1.2% strain amplitude, the loss modulus of the nanocomposite plateaus (or levels off) at about 45 MPa and is no longer very sensitive to strain. This is because interfacial slip has now been fully activated for a majority of nanotubes within the composite and further increase in strain does not serve to promote interfacial slippage. While the damping behavior of the nanocomposite (below 1.2% strain) displays strong amplitude dependence, the pure polycarbonate sample shows strain-independent loss modulus behavior (~ 12 MPa) over the entire strain range. This is to be expected since the polycarbonate chains are highly cross-linked at room temperature. Note that in the 1–10 Hz frequency range the test frequency has a small influence on the viscoelastic properties of both the nanocomposite and the pure polymer samples.

For the carbon nanotube reinforced polymer composite, nanotube dispersion is an important design parameter in terms of maximizing the frictional energy dissipation. This is because with improved dispersion of the nanotubes, the full impact of the SWNT's surface area of interaction comes into play and the effectiveness of the nanotube-polymer sliding dissipation mechanism is expected to improve significantly as a result of this. However it is very challenging to prevent the agglomeration of SWNT in a polymer matrix. The interfacial adhesion between SWNT and polycarbonate, which is caused by weak van der Waals interaction, is generally not strong enough to achieve good quality dispersion of SWNT. To help alleviate this effect, we oxidized [17, 18] as-received SWNT by sonication in nitric acid. The resulting carboxylic groups on the SWNT help to exfoliate the nanotube bundles and also the intermolecular forces caused by dipole–dipole interaction between polar groups (i.e. carboxylic acid groups on the sidewall of nanotubes and the polar carbonate groups along polycarbonate chains), lead to better quality of dispersion. Indeed, SEM images of the samples (Fig. 2a, b) confirm that the oxidized SWNT-PC composite displays significantly improved dispersion compared to the as-received SWNT-PC composite. Figure 3 compares the data for loss moduli of the oxidized and as-received SWNT-PC composites along with the baseline pure polycarbonate as a function of strain amplitude (test frequency is 10 Hz). The weight fraction of SWNT in the composite is 1.0% and 2.0%. For 1 wt% of SWNT, the oxidized SWNT-PC sample shows a maximum loss modulus of ~ 70 MPa compared to ~ 45 MPa for the as-

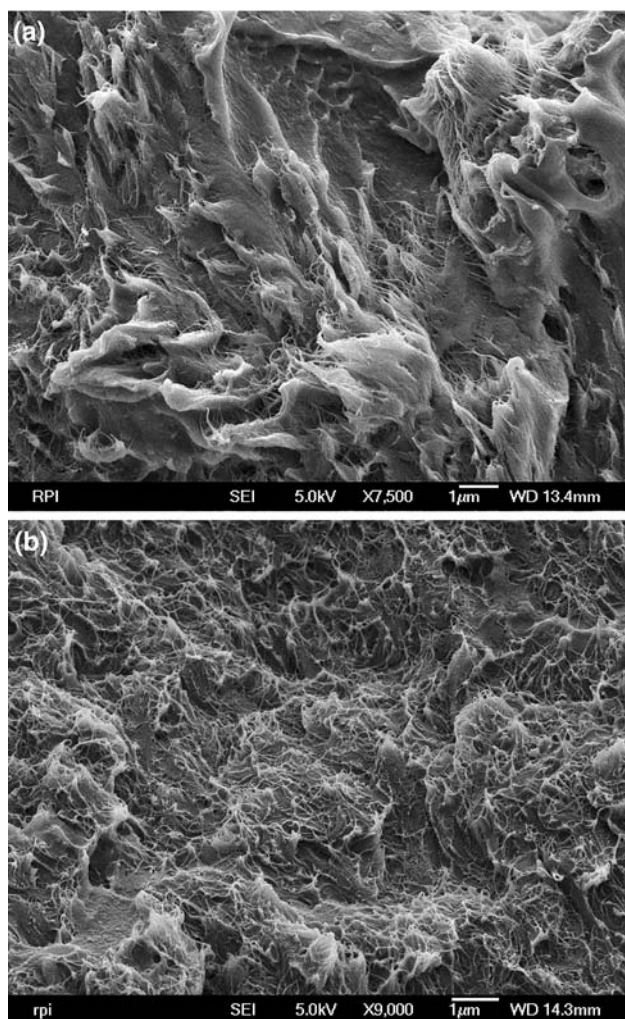


Fig. 2 SEM images of the fracture surfaces of (a) as-received SWNT-PC composite sample and (b) oxidized SWNT-PC sample. The weight fraction of SWNT in both the samples is 1%. Taken from Ref. [19]

received SWNT-PC sample: an increase of nearly 60%. Another approach to increasing the frictional energy dissipation is to boost the weight fraction of SWNTs in the composite. As seen in Fig. 3, the loss modulus of the 2% weight fraction oxidized SWNT-PC sample at 1% strain amplitude is ~ 150 MPa compared to about 70 MPa for the 1% weight fraction sample. The 150 MPa loss modulus reported for the 2% weight fraction oxidized SWNT-PC system is more than an order of magnitude greater ($>1000\%$) than the baseline PC (~ 12 MPa). Importantly the improvement in damping was engineered without compromising the elastic stiffness of the polymer; in fact the storage modulus of oxidized SWNT-PC was 10–20% greater than the pure PC sample. In addition, the same trends shown previously in Fig. 1, 3 were also observed for both SWNT-PEO (polyethylene oxide) and MWNT-

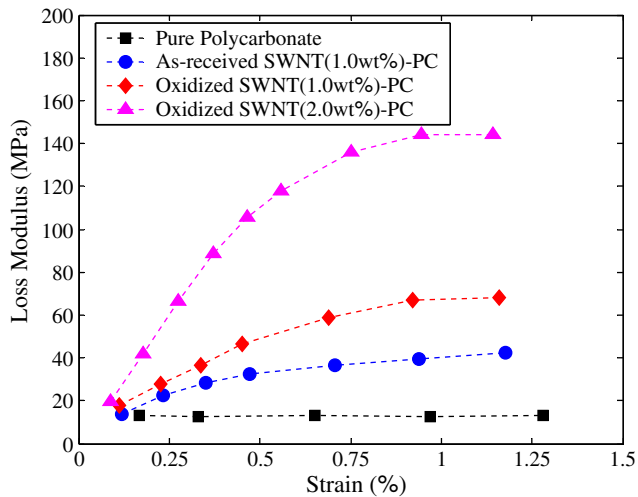


Fig. 3 Loss moduli of pure polycarbonate (no nanotube fillers), as-received SWNT-PC sample (with 1% SWNT weight fraction), oxidized SWNT-PC sample (with 1% SWNT weight fraction) and oxidized SWNT-PC sample (with 2% SWNT weight fraction) are plotted as a function of strain amplitude. All tests are performed at constant frequency (10 Hz) and at room temperature. Taken from the Ref. [19]

PC composites, indicating that the nanotube-polymer frictional sliding may be broadly applicable for the damping enhancement.

Having characterized the room temperature response, we proceeded to study the effect of temperature on the viscoelastic properties of the nanocomposite and baseline polycarbonate samples from room temperature to 90 °C in steps of 15 °C using an MTS 651.05E environmental chamber. Each temperature test was conducted at a fixed uniaxial strain amplitude of 0.35%. Test results indicate that as the temperature is raised, the storage modulus of the nanocomposite shows a marked decrease from ~2,800 MPa at 30 °C to ~2,500 MPa at 90 °C. Correspondingly the loss modulus of nanocomposite increases with temperature from ~40 MPa at 30 °C to ~75 MPa at 90 °C. It is interesting to note that the storage modulus (for 0.35% strain amplitude) of nanocomposite at 90 °C is comparable to its room temperature storage modulus at 1.2% strain amplitude. Similarly the loss modulus of nanocomposite (for 0.35% strain amplitude) at 90 °C is very close to its room temperature loss modulus at 1.2% strain. Therefore the fact that the storage and loss modulus of the nanocomposite at 90 °C and 0.35% strain is comparable to that at room temperature and 1.2% strain, suggests that increasing temperature also serves to activate interfacial slip, just as increasing the strain amplitude was shown to promote interfacial slippage. At elevated temperatures, as the glass transition temperature of the polymer

($T_g \sim 145$ °C for polycarbonate) is approached, the mobility of the polymer chain backbones is enhanced. This can weaken the mechanical inter-locking between the nanotubes and the host structure matrix making it relatively easier to activate interfacial slip at a lower strain level. Another contributing factor could be the mismatch in the thermal expansion coefficient of the SWNTs and the host matrix material, which gives rise to a radial compressive stress [17] at the nanotube-polymer interface. As temperature is increased this radial compressive stress is relieved thereby weakening nanotube-polymer adhesion and facilitating the activation of interfacial slip. This behavior at elevated temperature can suggest that temperature enhances the effectiveness of the nanotube-polymer interfacial sliding for damping enhancement in nanocomposite systems.

Conclusion

In carbon nanotube reinforced polymer composites there are several challenges to be resolved for achieving very high strength or stiffness. One of those challenges may be the slippage issue between nanotubes and surrounding polymer chains, thereby resulting in poor load transfer in a composite system. However, it is suggested that the interfacial slippage can be exploited to efficiently inject structural damping into composite systems, taking advantage of the high interfacial contact area, large aspect ratio and low density of carbon nanotube fillers. Thereby, it can imply the strong potential of nanotube reinforced polymer composites as structural damping materials for vibration and acoustic suppression in a variety of aeronautical and space vehicles, satellites, gas turbines, micro-engines and MEMS based inertial sensors used in missiles and weapon platforms.

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