Rheological behavior of CNT-reinforced damping materials

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ABSTRACT
Carbon nanotube-reinforced polyamide-6 composite material can enhance both strength and dynamics of many engineering structures. At 5-10 vol.% nanotube concentrations storage and loss modules of the material are in a very narrow region between $10^5$-$10^7$ Pa in a wide temperature range. Advanced damping behaviour is also observed due to nanotube reinforcing additives. Energy dissipation mechanisms and finite element approach are discussed.

INTRODUCTION
Polymer-based composite materials can significantly enhance both tensile strength and dynamics/damping performance of engineering structures by an order of magnitude. Reinforcing additives of 2 vol.% carbon nanotubes can offer further progress and nanoparticle/tube/fibre-reinforced composite materials are novel vibration damping solutions1-3 entailing placement of numerous nanoscale particles inside a vibrating material structure. A novel concept of nanoparticle-based vibration damping5,6 shows the effect that molecule-level mechanism can have on the damping. Carbon nanoparticle/fibre/tubes-reinforced materials can provide enhanced strength, dynamics and vibration damping properties over broader frequency and temperature ranges.

Carbon nanotubes can be treated as a simple nanoscale spring or combinations of damping springs due to C-C bonding6 with some advanced energy dissipation mechanisms. Thus, it opens a possibility to multiply a damping performance by billions of nanotube dampers for the next generation engineering materials that are light-weight, shock and noise resistant. Understanding the rheological properties of polymeric nanocomposites is crucial to gain a fundamental understanding of machining and structure-property relations for these materials.

MATERIALS
Thermoplastic polyamide-6.6 granular particle powder (Dupont Inc., USA) was mixed by an ultrasonic agitation procedure with multi-walled carbon nanotube (MWNT) particles supplied by Shenzhen Nanotech Co., China. Polymeric powder has granules size of 40-70 µm and purity of 90-95%. Reported density of nanotubes was approximately 1.9 g/cm³, a surface area of 250-300 m²/g was determined by the BET method1. Nanotubes were 20-40 nm in outside diameter and 50-90 nm in length, have 3±2 graphitic layers wrapped around a hollow 5-8 nm core and 80-85 vol% purity.

Carbon nanotubes were added in concentrations of 2, 5 and 10% by volume (including impurities) along with two surfactants (diphenylethylenediamine and poly-
oxyethylene-8laurylether) to aid in dispersion of CNT and polymeric particle. Volumetric concentration was calculated:

$$\varphi_{CNT} = \frac{V_{CNT}}{V_{CNT} + V_S + V_Y} \tag{1}$$

where $V$ is volume of material, CNT, S and V are indexes of carbon nanotube, surfactant and voids/purities, respectively. The materials were dried for a minimum of 2h at 100°C in a vacuum oven. One-kilogram mixes of polyamide-6.6 resin were extruded to obtain concentrations of 2, 5 and 10% nanotubes in the material at temperature of 490°F (melting point ASTM D 789). The composite material was prepared using an injection moulding and subjected to a vacuum for 10 min.

The compounds were molded into 30x30x5 mm bars for experimental measurements. Scanning electron microscope (SEM) is used to evaluate the nanotube dispersion and orientation in the polymeric matrix. CNT orientation was controlled by pressure rates at moulding.

A detailed study of microstructure specimen was carried out by conventional TEM using selected area diffraction (SAD) performed on a 200 kV microscope (model 2000, Pentax, Japan) with a point resolution of less than 0.5 nm equipped with an EDS (Model 6506, Micronix, UK) at room temperature (fig. 1).

Dynamic rheological measurements were performed using an advanced rheometric expansion system from Rheometric Scientific (USA). Experimental investigations were performed in an oscillatory shear mode using parallel plate geometry (20 mm diameter) at 300°C. Frequency sweeps between 10 and 200 rad/s were done at strains (0.2±10%) which are to be within the linear elastic range for the polymer. Specimens were placed between the preheated plates and were allowed to equilibrate for approximately 10 min prior to each frequency sweep run.

Young modulus was calculated from measurements by an indentation which resulted to $E_p=1.5-1.7$ GPa for polyamide (ISO 178) and $E_c=3.2-3.6$ GPa for CNT-reinforced material that is in agreement with others.

RESULTS & DISCUSSION

The viscous-elastic properties of the polyamide composite, storage and loss modules depend on nanotube concentration (fig. 2). The damping increase is accompanied by an increase in the viscous-elastic properties, represented by the storage modulus $G'$ and the loss modulus $G''$ (fig. 2) at higher temperatures.

![Figure 1. CNT-reinforced polyamide composite material.](image)

![Figure 2. Comparison of storage and loss modules due to CNT concentration.](image)

Pure polyamide and 2-5 vol.% reinforced composite materials reach the New-
tonian plateau at relatively low frequencies. At above 5 vol.% amount of nanotubes, the curves in fig. 2 exhibit the much greater decrease with frequency and exhibit non-Newtonian behaviour at lower frequencies. Therefore, about 5 vol.% may be regarded as a starting composition for damping.

It is worth noting that the mechanical properties fluctuate at 2 vol.% concentration (fig. 2) due to uncontrolled change in dispersion and bonding force between nanotube and polymer. This amount of CNT has lead to non-uniform relation between storage and loss modules at the concentration.

At above 2 vol.% CNT concentrations, the damping curves exhibit a much greater decrease with frequency and exhibit non-Newtonian behavior to much lower frequencies (fig. 3). Therefore, 2 vol.% may be regarded as a rheological threshold composition. The viscosity increase is accompanied by an increase in the elastic properties, represented by the storage modulus $G'$, which is much higher than the increase in the loss modulus $G''$.

The viscosity curves (fig. 4) above 2 vol.% nanotubes exhibit a larger decrease with frequency than those samples containing lower nanotube concentration. Composites containing more than 2 vol.% nanotubes exhibit non-Newtonian behavior at lower frequencies. An increase at approximately 2 vol.% nanotubes was observed in the viscosity composition curves at low frequencies. This step change may be regarded as a rheological threshold.

![Figure 3: Loss modulus of CNT-reinforced polyamide composite at 300°C.](image)

Advanced strength and viscosity (fig. 4) associated with the addition of carbon nanotubes is much higher than those changes reported for carbon nanotubes having larger diameters and for carbon black composites; this can be explained by the higher aspect ratio of the nanotubes. The viscosity increase is accompanied by an increase in the elastic properties, represented by the storage modulus $G'$, which is much higher than the increase in the loss modulus $G''$.

The rheological threshold ultimately coincides with purity, diameter and CNT concentration. This difference may be caused by the higher aspect ratio of the nanotubes used. It would be expected that incorporating CNT may affect not only the damping performance, but also the integrity under static, impact and fatigue loads.

**PREDICTION OF IMPACT STRENGTH**

Observations of rheological behaviour of the CNT-reinforced polymeric composite material showed that nanoparticles influence both loss and storage modules of the material. The damping phenomenon is complex because of the variety of other energy dissipation/fracture mechanisms involved.

![Figure 4: Viscosity of CNT-reinforced polyamide composite.](image)
pation/fracture mechanisms involved that are affecting damping/dynamics.

This phenomenon could be attributed with advanced interfacial fracture energy between the nanoparticle and polymeric chains. Particularly advanced energy dissipation in the polymeric composite can be explained by considerable interfacial fracture mechanics and bonding energy between CNT and polymeric molecular chains.

It was found that interfacial shear strength between MWNT and polymeric matrix (polyethylene–butane) at AFM pulling out or some test procedures are ranged between 50-80 G/Jm$^2$ due to high bonding fracture energy. In comparison with other nanoparticle reinforcing additives a recent study has presented a range of interfacial fracture energy values for glass fibres pulled from a variety of polymers such as polyamide 6 (44–93 G/Jm$^2$) and polyamide 6.6 (52–61 G/Jm$^2$) that may be used in a prediction methodology.

Advanced strength may be associated with chemical modification of the materials to induce strong bonding between the matrix and reinforcement phase. Thus, further possibilities to enhance damping capabilities and operational performance of the CNT-reinforced polymeric composites is to attach high molecular-weight ordered polymeric chains.

We proposed that the potential energy and energy dissipation because of the carbon-based materials can be calculated with the combined force field method and finite element modeling (fig. 5) which leads to beam torsional and nonlinear spring constants associated with carbon nanotube.

The potential energy of carbon nanotube can be calculated with the force field method. Neglecting inversion and non-bonded interactions, the potential energy of this generic force field is of the form

$$E = E_B + E_A + E_T$$  \hspace{1cm} (2)

The bond between two atoms I and J can be described by the harmonic potential

$$E_B = \frac{1}{2} k_e (R - R_e)^2$$  \hspace{1cm} (3)

which leads to the spring constant

$$c_B = \frac{d^2 E_B}{dR^2} = k_e$$  \hspace{1cm} (4)

or by the Morse function

$$E_B = D_e \left[ e^{-\alpha (R - R_e)} - 1 \right]^2$$  \hspace{1cm} (5)

which yields the nonlinear spring coefficient. The model is to estimate the spring constants and predict interfacial fracture energy in CNT-reinforced composite by using damping properties of carbon nanotube as follows:

$$c_A = \frac{d^2 E_A}{d\theta_{JK}^2} = C_{UK} \left[ \cos \theta_{\alpha} \cos \theta_{UK} - \cos (2\theta_{UK}) \right],$$

$$c_B = \frac{d^2 E_B}{dR^2} = 4D_I \left( \alpha n \right)^2 \left[ e^{-2\alpha (R - R_e)} - \frac{1}{2} e^{-4\alpha (R - R_e)} \right],$$

$$c_T = \frac{d^2 E_T}{d\phi^2} = \frac{1}{2} V_{JK} n_{JK}^2 \cos \left[ n_{JK} (\varphi - \varphi_{JK}^0) \right].$$  \hspace{1cm} (6)

where $\theta_{\alpha}=120^\circ$ and $K_{JK}=100$ kcal/(mol rad$^2$). The equilibrium angle is $\theta_{JK0}=180^\circ$, the periodicity $n_{JK}=2$ and the torsional energy $V_{JK}=25-40$ kcal/(mol rad$^2$).

Alternatively, dreiding provides a cosine form
The torsion energy can be found as

\[ E_T = E_{LIJK} = \frac{\gamma V_{JK}}{2} \left( 1 - \cos \left[ \pi n_{JK} (\varphi - \varphi^0_{JK}) \right] \right) \]  

(8)

depends on the dihedral angle \( \vartheta \) between the planes IJK and JKL (fig. 5).

It has to be considered that the bond angle energy \( E_A = E_{LIJK} \) only depends on the angle between the bonds \( IJ \) and \( JK \). Frame elements (Fig. 5a) force the adjacent bonds to rotate, but due to their bending resistance. Since this could only be prevented by additional constraints, we prefer a finite element model using spring elements (Fig. 5b).

On the other hand, the strongest interface between CNT and polymeric chains may not be an advantage for enhanced damping and require optimization. During vibration, nanoparticles interact with the material matrix and one another and, thus, dissipate energy through momentum transfer and friction. Friction and “slip-stick” motion (slip-page) between CNT and polymeric matrix is regarded as an important mechanism of vibration damping\(^7,10\). Interfacial friction and associated fracture depends on bonding force between nanotube and polymeric matrix. Shear stress may range from 0.2 to 1.2 MPa. It is still a poorly understood issue at this scale length due to many interdisciplinary aspects of this issue.

Another fracture mechanism of multi-walled carbon nanotubes at tensile loading has also telescopic-like transformation mechanism\(^11,12\), acting as a sword-in-sheath where the outer nanotube fractures followed by pullout of the interior walls. Thus, the sword-in-sheath mechanism should contribute to another “slip-stick” motion between walls of MWCNT; however, such a friction was noted to be very low\(^12\).

Overall Young modulus, impact toughness and related vibration damping of composite (fig. 6) increase as a function of stiffness and Young modulus of carbon nanotubes. These mechanical properties of CNT are associated with the length of tubes and a number of walls as every embedded graphene cylinder sheet of MWCNT may bear applied load and dissipate vibration energy due to interfacial friction and relaxation mechanisms in both polymer and nanotube\(^13\). Friction between adjacent CNT and its layers is also possible alongside polymeric chains when it is close packed by PVD deposited coating.

![Figure 6: Comparison of impact toughness and Young modulus.](image-url)

Nanotube Young modulus, diameter and length affect impact toughness of polyamide composite. The interfacial fracture energy and therefore damping/dynamic performance strongly depends on mechanical properties of nanoparticles. Carbon nanotubes may create stronger interfaces with a polymer matrix\(^14,15\) via chemical bonding and re-shaping design.

Theoretical analysis of strain-stress components at nanotube pulling out the polymeric matrix showed that local cohesion and adhesion effects should be taken in the modeling approach. Numerical simulations of local interface nanotube-matrix demonstrated sustainable growth of damping factors at wide area of interfacial contact between carbon nanotube and polymer.

The examples (fig. 7) are calculated by the model\(^17\) and the constants in Eqs. (2-8) for the range of interfacial fracture energy that decreases from 100 (in fig. 7a) to 40

\[ E_A = E_{LIJK} = \frac{\gamma C_{LJK} \left[ \cos \theta_{LJK} - \cos \theta^0 \right]^2}{2} \]  

(7)
G/Jm² (in fig. 7f) with the step of 10 G/Jm² for nanotube of 50 nm in length and 20 nm in diameter. The results correlate the experimental findings when good dispersion and high bonding forces of carbon nanotubes has been achieved.

An optimization between strength and dynamics is required for structural engineering applications of nanotechnology. Results of research work have wide-ranging technical benefits and direct relevance to an industry in the areas of transportation (aerospace, automotive, maritime), military and civil infrastructure development.

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