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Preliminary results on rheological and damping properties of nanoparticle-reinforced materials

Maksim V. Kireitseu[1,2*]

[1]Institute of mechanics and machine reliability Academy of Sciences of Belarus,
12 Akademicheskaya str., Minsk 220012, Belarus
[2]Department of Mechanical Engineering, the University of Sheffield,
Mappin Street, Sheffield S1 3JD, the United Kingdom, e-mail: m.kireitseu@shef.ac.uk

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 10^5-10^6 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

There is a particular need for advanced vibration damping of machine structural members. The material loss factor, η_v depends on temperature while the strain energy fraction, W depends on the effective stiffness of the damping element to the structure. A typical situation is where the modulus range giving optimum material damping does not necessarily match the optimum strain energy fraction curve.

There are three types of solid material matrices available for engineering of damping structures: metals, polymers and some ceramics[1-3]. Damping and integrity of materials is complex process that has opposite requirements. Viscoelastic polymers have good damping ability, but their stiffness, performance and durability is decreased at high temperatures (above 200°C). Metal and ceramic materials have good stiffness at high temperatures, but they have low vibration damping ability in comparison with polymer-based materials. High damping and increased stiffness of a material is the best option, but it is difficult to achieve.

Carbon nanotube-reinforced polymer-matrix composite materials (CNT-PMC) are now intensively studied, notably epoxy resins[3,4], polycarbonate epoxy resin[5], polyurethane[6] and polymethyl-methacrylate (PMMA) matrix composites[7]; however, composite damping behaviour is out of control yet due to not proven manufacturing technology that may provide a dispersion and high bonding strength of the composites.

In these circumstances CNT-reinforced polymer material can survive at higher temperatures (100-200% increase) than the matrix itself. However, it still not achieves a performance of ceramics or metals at high temperatures whereas decrease in damping may be significant.

Carbon nanotube-reinforced ceramic or metal composite materials are rarely studied[8,9] due to unknown processing issues. Most successful efforts were made to obtain tougher ceramics by hot processing and sparkling-plasma sintering with carbon nanotubes. Some ceramic coatings are successfully used to enhance damping of tita-

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nium fan blades[10] and therefore, they would be recommended as a candidate material, but dispersion and orientation of nanotubes in the matrix requires optimization in term of optimized damping/dynamics properties.

For a damping system to be designed into a structure, some kind of optimisation is usually required. The availability of suitable models can greatly help in this process. Each of the damping systems considered has shown unusual properties requiring advanced modelling techniques. However, for many engineering structures (particularly where large finite element models are involved), only the very simplest damping models are practical. Methods for simplifying complicated material behaviour are currently being developed.

Recent research works[11,12] have shown that rheological modelling can be applied to stress-strain analysis at localized loading of multi-layered nanoparticle-reinforced oxide ceramic coatings deposited on both soft aluminium and hard steel substrates. When we add a polymeric layer, more complex rheological models can be developed and applied. However, a novel CNT-reinforced composite material is another challenge.

This and further research work has to be carried out because we need materials that works better over broader operating ranges and is much more durable. Thus, main goal of our joint team is the development, and validation of the computational tools and algorithms required to model/predict the damping properties of materials reinforced with nanoparticles/fibres/tubes etc. over broader operating ranges in frequency, amplitude and temperature.

MODELING

Dissipated energy, via nanotube-polymer interfacial motion, is equivalent to the shear force and the differential displacement between nanotube and a matrix[13]. An interfacial damping mechanism can be represented as shown in fig. 1.

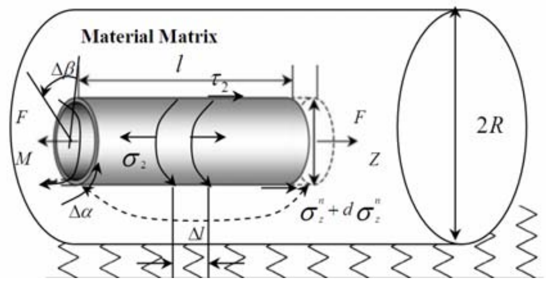

Figure 1: Interfacial damping scheme of CNT-polymer composite.

Full energy dissipation, energy dissipation and loss factor for one loading cycle can be found respectively as follows:

$$U_{diss} = \int_V (\sigma_{ij}\varepsilon_{ij}/2)dV \,,$$

$$\Delta U = 2\tau_2 \cdot (2\pi r_2 l_2^2) \cdot (\varepsilon_0 - \varepsilon_2) \,,$$

$$\eta = \arcsin\left(\frac{\Delta U}{2\pi U_{diss}}\right) \,, \tag{1}$$

where diss is dissipation energy, r is radius of nanotube (r=10–100 nm); l_2 is length of nanotube (l=20-200 nm); ε_o is strain of matrix material due to loading that can be found from experiments [13-15], τ_2 is bonding stress associated with longitude shear between nanotube and matrix material (τ_2 = 0,2-1,4 MPa depending on technology) [15], ε_2 is strain between nanotube and matrix material that can be calculated as

$$\varepsilon_2 = \frac{\tau_2 \cdot l_2/2}{E^{eq}\sqrt{\frac{G_0}{E^{eq}} \cdot \frac{1}{2\ln(R/r)}} \cdot \int_0^{l/2} \frac{\sinh(\beta(l_2/2 - z))}{\cosh(\beta l_2/2)} dz} \,, \tag{2}$$

where R is radius of representative volume of composite material, G is shear modulus of selected material ($G_0 = 0{,}2 \cdot 10^9$ Pa for polymer) and E^{eq} is equivalent module of nanotube with wall thickness t=0.34 nm and radius r=10 nm that is given by

$$\mathrm{E}^{eq} = 2\frac{t}{r}E^g \,, \tag{3}$$

where E^g is nanotube Young modulus ($E=1\cdot10^{12}$ Pa). The numerical coefficient β of Eq. (1) can be obtained in the form

$$\beta = \left(\frac{G_0 \cdot 2\pi}{E^{eq} \cdot A \ln(R/r)} \right)^{1/2}. \qquad (4)$$

Contact area between nanotubes and matrix material is given by

$$A=2V\varphi/r, \qquad (5)$$

where V is volume of matrix material (V=90%), φ is volume percentage of nanotubes with radius r=10 nm and length l=30 nm, respectively.

Stress of composite material is associated with energy dissipation and can be found from this equation

$$\sigma_2 = E^{eq}\varepsilon_2 \frac{\int_0^{l/2} \left(1 - \frac{\cosh(\beta(l_2/2 - z))}{\cosh(\beta l_2/2)} \right) dz}{l/2}, \qquad (6)$$

For viscouselastic nanoparticle-reinforced damping material, equilibrium of the damping structure can be described by the following equation in matrix form[14]:

$$M \cdot \Delta \ddot{D}^{n+1} + C^n \cdot \Delta \dot{D}^{n+1} + K^n \Delta D^{n+1} = \Delta F^{n+1}, \qquad (7)$$

where the superscript n and n+1 are the incremental steps; M is the mass matrix; C_n and K_n are the damping and stiffness matrices at the n^{th} step, respectively. The vectors ΔD^{n+1} and ΔF^{n+1} are displacement and force at the $(n+1)^{th}$ step, respectively. The average value of surface strain is used to represent structural deformation.

The mass and stiffness matrices for the full system are obtained as

$$M = \begin{bmatrix} m_1 & 0 \\ 0 & m_2 \end{bmatrix};$$

$$K = \begin{bmatrix} k_1 & 0 \\ 0 & k_2 \end{bmatrix} + k_v \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + i k_v \eta_v \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}. \qquad (8)$$

The complex modulus matrix of nanoparticle-matrix interface loaded along the axes, Z (if assumed dynamic loading at two degree of freedom) can be written as

$$C = \begin{bmatrix} a_1E_x(1+\eta_{xi}) & a_1E_x(1+\eta_{xi}) & a_1E_x(1+\eta_{xi}) \\ a_1E_y(1+\eta_{yi}) & a_1E_y(1+\eta_{yi}) & a_1E_y(1+\eta_{yi}) \\ a_1E_z(1+\eta_{zi}) & a_1E_z(1+\eta_{zi}) & a_1E_z(1+\eta_{zi}) \sim \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \sim G_{xy}(1+\eta^i{}_{xy}) & 0 & 0 \\ 0 & G_{xy}(1+\eta^i{}_{xy}) & 0 \\ 0 & 0 & \frac{E_x}{2(1+\nu_3)} G_{xy}(1+\eta^i{}_{xy}) \end{bmatrix}, \qquad (9)$$

where ν is Poisson ratio in three-dimensional space (x, y, z), a is coefficient defined as follows

$$a_1 = \frac{1-\nu_1\nu_2}{1-\nu_3^2-2\nu_1\nu_2-2\nu_1\nu_2\nu_3}; \quad a_2 = \frac{\nu_3+\nu_1\nu_2}{1-\nu_3^2-2\nu_1\nu_2-2\nu_1\nu_2\nu_3};$$

$$a_3 = \frac{1-\nu_3}{1-\nu_3-2\nu_1\nu_2}; \quad a_4 = \frac{1-\nu_1}{1-\nu_3^2-2\nu_1\nu_2}; \quad a_5 = \frac{1-\nu_2}{1-\nu_3^2-2\nu_1\nu_2}.$$

A two degree of freedom double mass system (fig. 2) was used in this study to represent the CNT-reinforced material. The system can be considered consisting of two independent systems: CNT-matrix phase and polymer material with own natural frequencies.

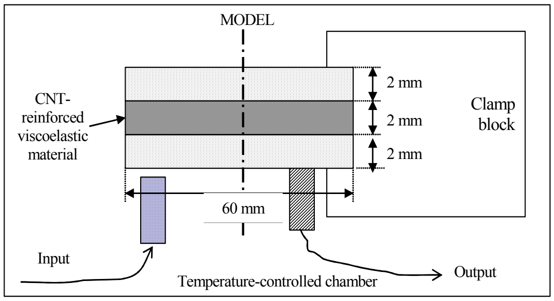

Figure 2: Damping double mass system and experimental setup.

In order to validate some basic rheological concepts novel vibration damping design solution was analytically modelled and simulated via FEM-based code created in MSC.visualNastran for Windows XP.

EXPERIMENTS

Polyamide (polymer A) and polymethylmethacrylate (Polymer B) granular particle powder (Dupont Plastics, USA) was mixed by an ultrasonic agitation procedure with single and multi wall carbon nanotubes (SWNT and MWNT) supplied from Shenzhen Nanotech Co., China. The amount of 20vol.% E-glass ceramic microparticles (d=2-4 μm) were used to compare an effect of reinforcing additives in the polymeric material. Polymeric powder has granules size of 40-70 μm and purity of 95%. For both models material properties of polymers were used to represent the viscoelastic elements while the metal parts had the properties of titanium alloy.

Multiwall 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. Single wall nanotubes were 10-15 nm in diameter and 20-30 nm in length and 95 vol.% purity. Nanotubes were added in concentrations of 10% by volume along with a surfactant (polyoxyethylene8laurylether) to aid in dispersion of CNTs and polymeric particles. The materials were dried for a minimum of 2h at 100^oC in a vacuum oven.

The composite materials were prepared using an injection moulding and subjected to a vacuum for 25 min. The compounds were molded into 60x60x2 mm bars for experimental measurements.

A vibration damping and impact test procedure has been initially developed to quantitatively evaluate the performance of CNT-reinforced polymer matrix composite system. The test procedure uses a sandwiched specimen (fig. 2) simulating a fan blade made of Ti-6Al-4V titanium alloy.

Loss factor were determined at standard vibration shaker tests with clamped specimen[10]. During testing, the specimen is supported along both ends and on one edge. The shaker used in this test is designed to simulate the most important features of a full-scale fan blade at a low cost.

The test procedure has been used to evaluate a number of different sandwiched specimen containment concepts, including two sandwich systems and two composite systems. Shock loads are applied as a prescribed acceleration of the lower surface and the response is calculated (in the vertical direction) in the centre of the upper mass for model (fig. 2).

Resonance frequencies, the mode shape and damping at each mode were determined by laser vibrometry at standard vibration shaker tests in Bruel & Kjaer vibration system. The clamping block is fixed so that friction losses and extraneous damping is minimized. The data acquisition and control of the electro-dynamic system is based on the Computer Measurement System. The resonance frequency is determined from peaks on a frequency response curve for each of the experimental methods.

RESULTS & DISCUSSION

To validate the modelling approach in terms of computational efficiency and computer-based implementation we have used the Materials Algorithms Project originated in the University of Cambridge, UK (www.msm.cam.ac.uk/map/) and continued at our institutions, concentrating on tailoring an engineering design concept and modeling approaches for damping/dynamics.

Advanced workbench tools are being developed by CASE tools (Rational Rose) and C++ programming language. Basic finite element code for damping behavior previously discussed was implemented in MSC.visualNastran to study the potential of energy dissipation mechanisms enveloping dispersed nanoparticles for the toughening of polymer matrix.

In each integration point of the 1,234 four-nodded bilinear elements, a local coordinate system is generated. The 1-direction corresponds to the direction of the eigenvector. The 2-directions are chosen perpendicular to the 1-direction and in the plane of the FE mesh. The resulting stress field of material 1-directions should be perpendicular to the nanoparticle/matrix interface and parallel to the left and lower symmetry boundaries. It also satisfies anti-symmetric compatibility conditions along the radial boundary. The differences between these orientation sets seem to be small; the influence on the deformation mode that is obtained is substantial.

Experimental findings (fig. 3) and modeling suggests that high damping performance is achieved at polymeric matrix with a core ≤1 GPa modulus, 20-40 nm diameter, nanotubes in a matrix of 3 GPa. Added carbon nanotubes clearly increase loss factor of polymeric material and operational temperature range.

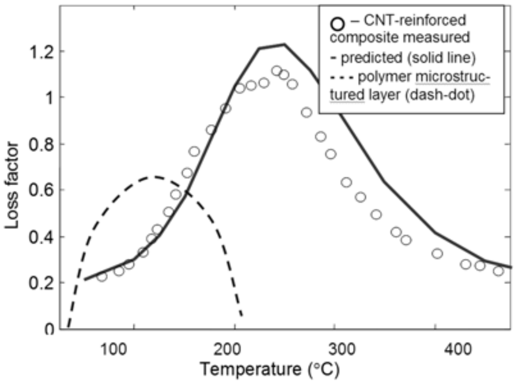

Figure 3: Comparison between measured and predicted loss factor properties under non-rotating conditions.

The amplitude-frequency characteristics were calculated using a finite element mesh in MSC.visualNastran finite element program and the damping model (Eqs. 1-9) where used to estimate the damping properties of the composite. This program is used to determine the resonant frequency of different mode shapes given the specified conditions. Modal points will be the main area of interest to determine the modal force.

The modal analysis of the final nanotube lay-up selection for clamped specimen showed that the lowest eigenfrequency is about 20 Hz. Mode 1F and 2F clamped specimen – comparison of predicted and measured damping and finite element mesh of the model, with carbon nanotube fraction f = 10%, is shown in Figure 4.

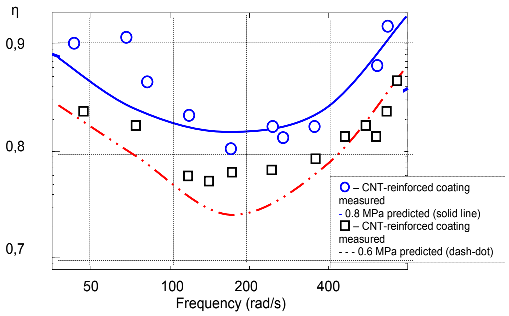

Figure 4: Loss factor – comparison of predicted and measured damping.

Two shear stress have been taken in the model. Obviously, that 0.8 MPa shear stress will result in higher interfacial fracture enegry that is being used for vibrational enegry dissipation and thus, leading to higher loss factor of the composite. However, over 0.8 MPa interfacial strength is reported[6] between nanotube and polymeric molecules.

Frequency sweep (fig. 4) demonstrated that the composites and tested specimen is sensitive in damping performance at 200 rad/s. This value would be a critical and to be investigated in more details. It is worth noting that statistics of the experimental outcomes is widely plotted in fig. 4 that showed no solid conformity in the composite processing.

Referring to the data (fig. 5), at 10 vol.% nanotube concentration the composite achieved Young modulus of 2 GPa and loss factor of over 1.1 in the temperature range up to 250°C. Mixture of E-glass and carbon nanotubes is also beneficial for strength and damping considerations. The nature of degradation and energy dissipation mechanisms is not obvious from the results. These composites being reinforced with nanoparticles, it is expected that degradation is primarily the result of matrix degradation.

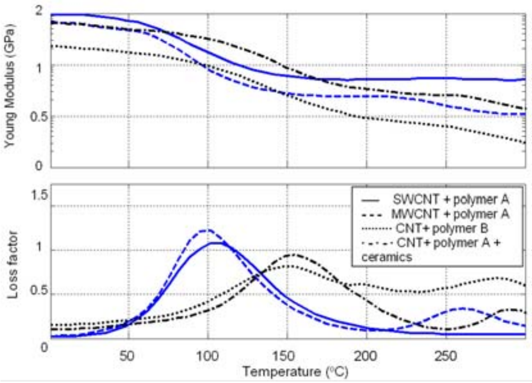

Figure 5: Damping properties of 10vol.% CNT-reinforced composite.

The peak damping of CNT-polymer damping composite occurs around 100°C (fig. 5) and 150°C for CNT and reinforcing E-glass ceramic microparticles added in polymer. It is worth noting that multi-walled nanotubes slightly decrease modulus of the material in comparison with single-walled CNT. The phenomenon may be associated with the greater number of possible energy dissipation mechanisms of MWCNT among that are telescopic-like transformation, buckling and kinking.

The mixtures based on thermoset polymer B show lower peak levels of damping due to the volume of reinforcing particles; however, it is less sensitive to temperature. The presence of CNT-reinforced polymeric damping material clearly reduces the modulus and also introduces a second transition around 250°C that coincides with the softening point of the polymeric material. Young modulus values in the range 0.2 to 2 GPa can give the highest core strain energy. The presence of high levels of polymeric B composite reduces the modulus below the desirable range. CNT-reinforced composites on the other hand, maintain Young's modulus levels thereby improving the overall damping achieved.

Advanced damping material and fan blade design concepts could be introduced as follows:

1) Volume and weight of filler material should be minimized. In large civil engines, the blades are hollow and usually have stiff rib-like metallic structures in order to increase the rigidity and maintain cross-sectional profile of the blade. The filled fan concept is to replace this metal structure with CNT-reinforced foam simultaneously acting as a strengthener and a damping element.

2) CNT-reinforced damping coatings has considerable adhesion and adds significant damping to titanium fan blades. Ceramic coating is desirable in high temperature applications, but its damping level is lower than that of polymeric ones. Another problem is fracture and fatigue of hard coatings on dynamic blade.

Further improvements can be made to both the materials and to the blade design. In its simplest form, the CNT reinforcement concept is simply a fan blade coated or filled with a suitably selected damping material.

CONCLUSIONS

It would be expected that incorporating CNT may affect not only the damping performance, but also the integrity under static, impact and fatigue loads. While hard balloons are desirable for maximising stiffness and damping, CNT-reinforced polymeric ones may be better for the damping and integrity.

Study of the damping behavior of CNT-reinforced polymeric material has been undertaken using the interfacial damping computational model to nanoparticles - matrix interaction. At preliminary point, it was validated that a concept of using CNT as vibration damping element would be worth using in manufacturing and material designs.

Carbon nanotubes could be particularly promising cost-decreasing reinforcement material for polymeric materials and sandwich-like structural composites in both foamy and bulk state. Results of the research work provide a platform for the development of nanoparticle-reinforced damping materials that are light-weight, vibration and shock resistant. The outcome of the research work is expected to have wide-ranging technical benefits with direct relevance to industry in areas of transportation (aerospace, automotive, rail) and civil infrastructure development. However, the goal is aerospace applications and next generation of turbine engine fan blades with CNT-based ceramics and metal damping technology.

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REFERENCES

1. Ferry, J.D. (1970), *“Viscoelastic properties of polymers”*, John Wiley & Sons, New York, p. 120-180.

2. Bhushan, B. (2004), “Handbook of Nanotechnology”, Springer-Verlag, New York, p. 1220.

3. Cooper, C.A.; Cohen, S.R.; Barber, A.; Wagner, H.D., *Appl. Phys. Lett.* **2002**, *81(20)*, 3873-3878.

4. Koratkar, N.; Wei, B.; Ajayan, P.M., *Compos. Sci. Technol.* **2003**, *63*, 1525–1531.

5. Zhou, X.; Shin E., Wang K.W., Bakis C.E., *Compos. Sci. Technol.* **2004**, *71*, 1825–1831.

6. Barber, A.H.; Cohen S.R.; Kenig, Sh.; Wagner, H.D., *Compos. Sci. Technol.* **2004**, *74*, 1931–1937.

7. PoEtschke, P.; Fornes, T.D.; Paul, D.R., *Polymer* **2002**, *43,* 3247-3255.

8. Harris, P.F. In *Carbon Nanotubes and Structures*, Cambridge Univ. Press: UK, 1999; p. 440

9. Talay, T. In *Systems Analysis of Nanotube Technology,* NASA, Washington, D.C., 2000; p. 240.

10. Patsias, S., Saxton, C., Shipton, M. (2004), *Materials Science and Engineering* A 370, 412-416.

11. Kireitseu, M.V. (2003), *Particulate Science and Technology* 20(3), 20-33.

12. Kireytsev M.V. (2003) Journal of Engineering Physics and Thermo-physics 76 (1): 178-187.

13. Kelly, A. (1970), *Proceedings of the UK Royal Society* A 344, 287–302.

14. Chandra, R. (2003) *Journal of Sound and Vibration* 262, 475–496.