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Enhanced Composite Plate Damping Using Intercalated Graphite Fiber

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The increased vibration damping capability of bromine-intercalated graphite fibers has been recently reported. Continuing investigation of the use of such fibers in structural composite materials has demonstrated increased flexural damping of unidirectional, brominated P-100 graphite/epoxy composites. Damping was measured at temperatures ranging from -120 to $+30°C$ and at frequencies from 50 to several 100 Hz. As expected on the basis of constituent fiber and matrix damping characterization, the observed damping was both temperature- and frequency-dependent. The peak modal damping ratio observed for pristine fiber composites was 0.8×10^{-3}, whereas that exhibited by the brominated fiber composites was 1.6×10^{-3}. Theoretical predictions of composite specimen modal damping ratios based on known fiber and matrix properties are in reasonable agreement with experimental data. Discrepancies may be due to imperfect intercalation or to the effects of the fabrication environment on intercalation stability. Analytical results obtained for additional cases and materials indicate that 1) contrary to state-of-the-art design principles, the damping of quasi-isotropic composites made using intercalated graphite fibers could be dominated by fiber damping instead of matrix shear damping; and 2) damping levels of significance could be achieved.

Nomenclature

ζ = modal damping ratio (fraction of critical damping)
Ψ = damping capacity ($= 4\pi\zeta$ for small damping)

Introduction

VIBRATION damping is essential to the attainment of performance goals in advanced engineering systems. In common built-up structures that operate in the atmosphere, air damping and joint damping typically dominate system damping. However, material damping can also be an important contributor to overall damping in many applications, such as precision spacecraft structures. Although considerable effort has gone into the development of high-damping nonstructural materials for use in aerospace vibration control, associated weight penalties, outgassing, and temperature sensitivity limit their use. The development of light, thermally stable *structural* materials that also display high damping is an area of current research with potential for high payoff.

Continuously reinforced graphite composite materials are well-suited for use in precision structures because of their superior mechanical and thermal properties—properties such as high modulus, high thermal conductivity, low density, and low coefficient of thermal expansion. Because the damping of these materials is often assumed to be negligible, it is rarely measured. Today, however, because of its practical importance, more efforts are being directed towards understanding, measuring, and increasing composite material damping.

In general, damping in a composite material may be considered as the sum of the damping in the constituent materials weighted by the relative contribution of each to total strain energy. Because the fiber modulus is typically much greater than that of the matrix material, most of the strain energy of deformation is found in the fiber. Efforts to increase composite material damping are therefore well-focused on the high-leverage graphite fibers.

Previous research has addressed the development of a method to increase the vibration damping properties of graphite fibers used in structural composite materials to a level of engineering significance. Initial results[1] indicate that intercalation may be an effective means of accomplishing this goal. In this earlier work, a resonant flexural free-decay method was used to directly measure the temperature-dependent damping of single graphite fibers. Figure 1 compares the damping of pristine and bromine-intercalated (20% by weight) P-100 graphite fibers at a frequency of about 200 Hz and over a temperature range from -200 to $+100°C$.[1] The peak modal damping ratio of the intercalated fibers is about 0.22% (damping capacity about 3%), a level approximately 15 times that of the pristine fibers.

Of prior interest primarily for demonstrated increased electrical conductivity, other researchers report that important material design properties such as modulus, strength, and thermal conductivity change only slightly following bromination.[2]

A considerable body of work exists on the subject of the dynamic properties of graphite-reinforced composites.[3-6] This work generally neglects the contribution of fiber damping to composite damping in favor of that due to matrix shear. Although this approach is perhaps justifiable for commercially available high modulus graphite fibers, with inherent damping ratios generally below 0.02% (damping capacity below 0.25%),[7,8] it would lead to serious errors if applied to composites made from bromine-intercalated graphite fibers.[9]

The remainder of this paper describes the results of a recent experimental investigation of the inherent vibration damping capacity of composite specimens made using pristine and bromine-intercalated P-100 graphite fibers. Although preliminary experimental results have been previously reported,[9] comparisons to theoretical expectations were not attempted.

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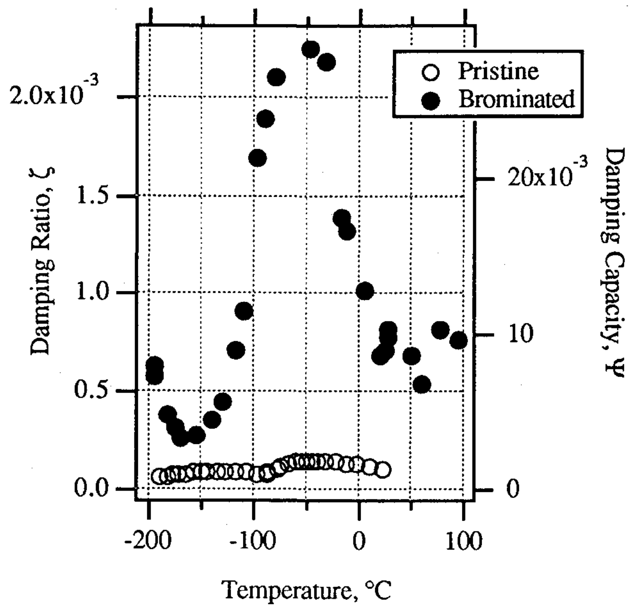

Fig. 1 Temperature-dependent damping of pristine and bromine-intercalated P-100 graphite fibers.

Recent progress on a theory that adequately accounts for the contribution of the fiber to observed composite damping permits a more complete discussion of the experimental results than was previously possible.

Experiment

Composite specimens were fabricated from both pristine and bromine-intercalated P-100 graphite fibers.[9] The temperature-dependent vibration damping properties of the specimens were measured using a resonant flexural test apparatus. The dynamic properties of a neat resin specimen were also determined. The following subsections briefly describe the specimens and the test method in more detail.

Specimens

Pristine P-100 graphite fiber was obtained from the manufacturer without sizing or shear treatment. Some of this P-100 fiber was intercalated with bromine to approximately 18% bromine by weight. The bromine intercalation process is relatively simple, involving fiber immersion in a bromine atmosphere at room temperature for a period of about 48 h. E705 epoxy was used as the matrix material for initial composite specimens, whereas, in anticipation of future higher-temperature work, neat resin specimens were made from 3501-6 material. The two matrix materials were expected to exhibit damping of the same order of magnitude over the range of temperatures and frequencies considered.

The initial specimens were beam-like of four-ply, unidirectional construction with the fibers aligned with the long axis of the beam. Composites contained either pristine or intercalated fiber, but were otherwise nominally identical. Each measured approximately 150 mm (6 in.) long by 12.5 mm (0.5 in.) wide by 0.5 mm (0.020 in.) thick, with a fiber volume fraction of approximately 50%.

Experimental Apparatus and Procedure: Narrow-Band Sine Sweep Frequency Response

The composite beam specimens were characterized using a facility that had been previously developed for studies of the flexural and torsional damping of graphite/aluminum (Gr/Al) and carbon-carbon (C-C) composites.[10] This facility is more fully described elsewhere.[9]

The damping of cantilevered beam-like specimens undergoing forced flexural vibration was determined using a frequency-response technique. The forcing frequency was swept slowly through a narrow band in the vicinity of a specimen resonant frequency. With the force level fixed, the frequency-dependent response level was noted, and damping was determined by curve-fitting the frequency-response function to estimate the location of various natural modes of vibration in the complex plane. For small damping, the modal damping ratio is approximately the negative of the real part of the complex pole divided by the magnitude of the imaginary part.

Figure 2 illustrates the apparatus used for damping testing. A specimen was cantilevered by clamping it to a relatively massive copper block. The block provided a mechanical and thermal "seismic mass," with high stiffness, large mass, high heat capacity, and high thermal conductivity. The position of noncontacting magnetic drivers and sensors could be adjusted to any point along an instrumentation beam parallel to the specimen and at any distance from the specimen.

The specimen and instrumentation beam were enclosed in a copper tube to minimize thermal radiation exchange of the specimen with the external environment. Channels through the block and around the tube allowed liquid nitrogen (LN_2) to cool the block, tube, and specimen to temperatures near $-150°C$. A resistance tape heater was used to raise the temperature to near $+150°C$. Thermocouples on the instrumentation beam, both near the root and near the end, are used to infer the temperature of the specimen. Thermal calibration runs verified that specimen and instrumentation beam temperatures are very nearly the same at nominal rates of temperature change ($<2°C/min$).

The fixture was placed in a vacuum chamber to eliminate contributions of air damping. A combination signal general/signal analyzer was used to force a specimen and record its response. A narrow-band sine sweep method was found to yield the best data and was subsequently used as the baseline test technique.

In making a low temperature to room temperature run, the temperature was first reduced to the low extreme by pumping LN_2 through the cooling channels, then increased towards room temperature while data were taken. At low temperatures, no heating augmentation was needed to raise the temperature. With only conductive and radiative heat transfer from the rest of the fixture, the thermal time constant of the system was about 7 h, providing temperatures that were quite stable over the course of a damping measurement (less than 5 min).

Based on results obtained for an aluminum specimen, the accuracy of the test technique was estimated to be better than 2×10^{-5} (in nondimensional units of modal damping ratio). This "calibration" specimen was sized so that a thermo-elastic damping peak of known magnitude would be apparent among the measured low-frequency modes. The largest damping ratio measured for the aluminum specimen was about 1.8×10^{-3} (at high temperature), and the smallest was about 7×10^{-5}.

Theory

Considerable effort has gone into the development of analytical design tools for predicting composite material damping. The tools developed to date appear to account adequately for the contribution of the fiber to observed composite damp-

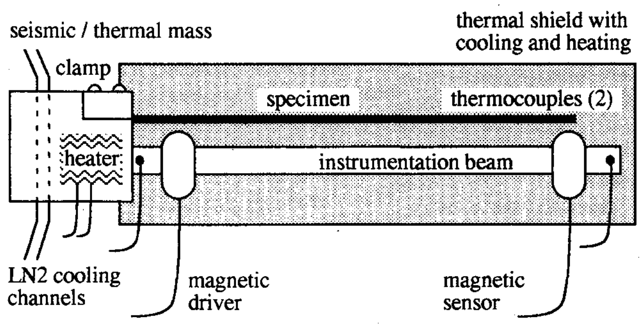

Fig. 2 Flexural damping test apparatus.

ing. Table 1 summarizes some of the key features of the analytical approach,[11] and the remainder of this section describes them in more detail.

Other researchers have typically based predictions of composite *laminate* properties on measurements of *lamina* properties. In this work, predictions of the damping of laminated graphite fiber composite plates in flexure are based on measured damping of the constituent fiber and matrix materials. To our knowledge, this procedure has not been used in the past, possibly because graphite fibers have been generally assumed to contribute little to composite damping or because inadequate constituent property data are available. However, the approach here offers the kind of flexibility that will be needed by those who design advanced composite materials for use in dynamic applications.

Predictions of composite lamina elastic and dissipative properties are based on the composite cylinders assemblage model[12] in combination with the complex modulus treatment of damping. A key aspect of this approach includes consideration of the highly anisotropic nature of the graphite fiber—the work of Datta et al.[13] has been extended, using complex moduli. Accounting for the transversely isotropic fiber properties is important for accurate prediction of composite transverse and shear properties, and it has the added benefit of allowing isolation of the effects of the fiber longitudinal loss modulus E''_{11}, which has been experimentally measured.

Note, however, that this approach generally requires user input of five fiber elastic moduli and five loss moduli in addition to two matrix elastic and two loss moduli. Obtaining accurate data for fiber and matrix materials will be a significant challenge for the materials designer of the future. On the other hand, contributions to composite material damping may well be dominated by only a few loss moduli. In fact, the typical approach to analysis of composite damping assumes that matrix shear is the only significant contributor. In this work, the additional damping due to longitudinal fiber deformation is also considered.

A higher-order composite plate theory[14] was used to account for the effects of transverse shear as well as transverse normal stresses. In addition, complex moduli were employed throughout the process of laminate property generation. Other approaches[3-5] typically work exclusively with real moduli and reasonably neglect transverse normal stresses.

Consideration was restricted to the flexural vibration of flat rectangular panels using a (global) Ritz method for numerical determination of panel natural modes. Complex eigenvalue routines were used to estimate natural frequencies and damping directly. Other approaches[3-5] have used both Ritz techniques and more flexible finite element methods to determine modal frequencies and the distribution of modal strain energy

Table 1 Key features of the theoretical approach

Feature	Typical approach
Lamina properties based on lamina test data or on fiber-matrix data using micromechanics; transversely isotropic fiber and isotropic matrix; all moduli may be viscoelastic; modeled using complex moduli.	Test data only; isotropic, lossless fiber.
Laminate properties determined from complex lamina moduli and stacking geometry. Complex properties used.	Lamina complex moduli not used.
Higher-order deformation theory accounts for transverse shear, rotatory inertia, and normal stress effects.	Similar, use real moduli.
Modal damping ratios for structures determined directly using complex eigenvalue routine; Rayleigh-Ritz (RR) method used with simple geometries.	Modal strain energy with lamina loss factors; both FE and RR.

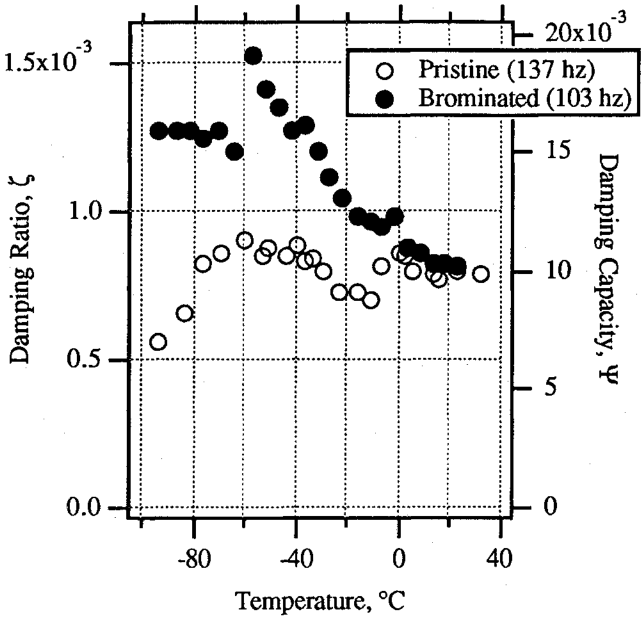

Fig. 3 Temperature-dependent damping of P-100 and bromine-intercalated P-100 composite beams.

among individual lamina. These approaches indirectly obtain modal damping ratios using the modal strain energy (MSE) method with (experimentally determined) lamina loss factors.

Several disadvantages of the MSE approach suggested the direct use of a complex eigenvalue approach. These disadvantages include the fact that damping estimates are made on the basis of the strain energy distribution associated with the undamped mode shapes. For very light damping, this is of little concern, but it is potentially important when the damped mode shapes may differ substantially from the undamped shapes.

This analytical approach has been tested against our own limited data and against some of the data published by Lin et al.[3] The agreement with available frequency and damping data is quite good.

Results

Two composite specimens were characterized using the flexural damping test apparatus, forced in their fundamental bending mode of vibration. Both specimens used the E705 matrix material; one used pristine P-100 fiber and the other used brominated P-100. As illustrated in Fig. 3, the bromine-intercalated graphite composite specimen exhibited considerably higher damping than the pristine graphite composite specimen, especially for temperatures near $-60°C$. The peak damping ratio observed for the pristine fiber composites was 0.8×10^{-3} (damping capacity of 1%), whereas that for the brominated fiber composites was 1.6×10^{-3} (damping capacity of 2%).

Properties for the constituent materials were sought and obtained from a number of sources. Pristine fiber elastic and physical properties were obtained from a recent manufacturer's research report.[15] Longitudinal fiber damping data previously obtained for both pristine and brominated fibers[1] were used for analysis purposes. Manufacturer's data for E705 epoxy matrix material elastic properties were used, but no damping data were available for this material.

As previously noted, in anticipation of future higher-temperature work neat resin specimens were made from 3501-6 material. The two matrix materials, E705 and 3501-6, were expected to exhibit similar damping over the range of temperatures and frequencies considered. Figure 4 summarizes the damping data obtained for the 3501-6 material.

Note that the peak modal damping ratio observed for this matrix material is about 2.5%, more than 10 times that of the

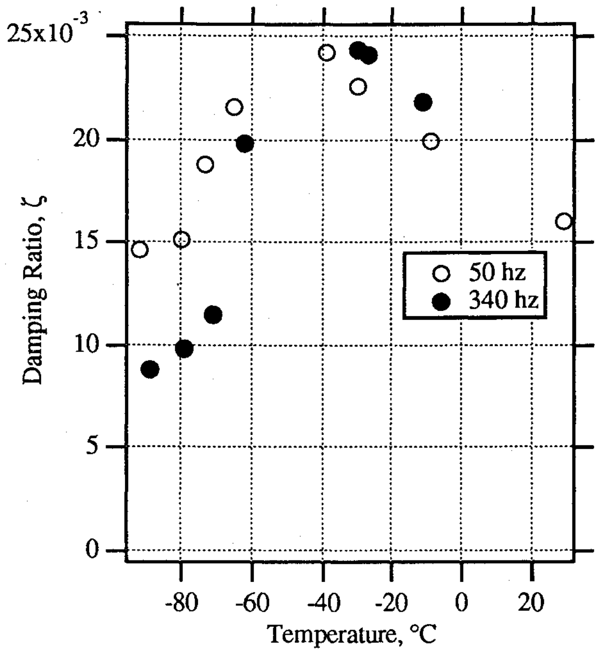

Fig. 4 Temperature- and frequency-dependent damping of 3501-6 resin beam.

brominated fiber and more than 100 times that of the pristine fiber. For the purpose of composite damping prediction, the observed matrix damping was assumed to result entirely from the matrix shear loss modulus.

Measured composite damping is at least qualitatively consistent with expectations based on knowledge of the relative damping of pristine and intercalated graphite fibers. In particular, peak damping of the brominated fiber composite material is observed at a temperature corresponding to peak damping of the brominated fiber.

Using the composite design tools previously described, analytical predictions were quantitatively compared to experimental results. Predictions of composite material damping were generated for both pristine and brominated fiber composites, at two temperatures. One temperature was $-60°C$, close to that at which peak brominated fiber damping is observed, and the other was 20°C, approximately room temperature.

Table 2 summarizes the theoretical results obtained for the lowest bending and torsional modes of vibration for the cases of interest, and it compares them with the experimental data.

Note that the experimentally determined modal damping ratio for the first bending mode of the pristine fiber composite specimen is small, but about twice as high as that expected from the theory (using the 3501 matrix properties). The source of the additional damping is unknown, but it is possible that some other mechanism not considered in the theory is contributing to the measured damping. An example might be a case in which slight imperfections in the specimen or its alignment in the test fixture results in a fundamental vibration mode that involves coupled bending and torsion—as the preceding table shows, the modal damping ratio predicted for the first torsion mode is about 40 times that of the bending mode. A little twist in the experimental mode shape would produce a relatively large contribution to damping.

On the other hand, the experimental value for the damping of the brominated fiber composite material is lower than expected. This might be explained by imperfect intercalation of the original fiber material, as the properties of each batch were not monitored in detail and some inconsistencies have been observed in the past. Alternatively, the discrepancy could be due to migration of the bromine intercalant from the fiber to the matrix during composite fabrication; intercalant stability is known to be lower at temperatures above 100°C (Ref. 16). As the fiber damping is roughly proportional to the concentration of intercalant, composite damping would be reduced accordingly in either case. These issues must be resolved before a transition to applications can be expected.

Table 2 Comparison of experimental and theoretical composite modal damping ratios

Composite	T, °C	Experimental (E705 matrix) ζ, %	Analytical (3501 matrix) ζ, %
Pristine fiber (1B)	−60	0.08	0.04
(1T)		——	1.62
Brominated (1B)	−60	0.16	0.25
(1T)		——	1.66
Pristine fiber (1B)	+20	0.076	0.03
(1T)		——	1.16
Brominated (1B)	+20	0.083	0.09
(1T)		——	1.17

Note also that the damping theory predicts that, when the matrix shear damping loss factor is higher than the fiber longitudinal modulus loss factor, the damping of the flexural modes will increase with mode number. This reflects the increasing contribution of shear deformation with mode number, as a larger fraction of the modal strain energy is found in the matrix material. This phenomenon manifests itself as a change in modal frequency as well as damping.

The effect of increased fiber damping is likely to be even more pronounced for other composite systems, such as Gr/Al metal matrix composites (MMC), that use a matrix material with damping much lower than that of the epoxy used in this work. In fact, calculations made using our composite design tools indicate that modal damping ratios for a Gr/Al panel would increase significantly with the use of brominated graphite fibers. They start at about 0.03% for longitudinal flexure and 0.05% for twist (consistent with available data)[10] and increase to about 0.21% and 0.11%, respectively, with brominated fibers. Stability of the intercalated graphite at the high temperatures encountered during MMC fabrication, however, is a serious concern.

C-C composites are another promising material system in which bromine intercalation might be useful for increasing inherent vibration damping capability. Instead of using pre-intercalated fiber, such composites could be intercalated following high-temperature graphitization, avoiding exposure that would otherwise drive off the intercalant. There might be near-term applications to space radiator components of satellite thermal control systems.

In anticipation of verifying future experiments and to investigate the damping of material configurations of interest to aerospace designers, the natural frequencies and damping of some square symmetric plates of various constructions ($[\pm 45]_s$, for example) were estimated. Different possible assumptions concerning contributions to composite damping were investigated, including: 1) matrix shear only (state of the art); 2) baseline graphite fiber in extension only (quite low, as generally assumed); 3) bromine-intercalated fiber in extension only; and 4) a combination of matrix shear and bromine-intercalated fiber extension.

The results indicate that intercalated fibers can be the dominant contributor to composite damping in all lowest-frequency modes, depending on the matrix material used.[11] This would not be expected from consideration of state-of-the-art composite damping design principles.

Conclusions

Increased damping of a graphite/epoxy composite material through the use of a graphite fiber with enhanced damping has been demonstrated. Fiber damping was increased through bulk modification of the graphite via bromine intercalation. The results are qualitatively consistent with expectations based on fiber damping properties, but the quantitative agreement with constituent-based theoretical predictions needs to be improved. To this end, better intercalation process monitoring and tailored composite fabrication techniques are recommended. In addition, complete characterization of constituent material properties is essential, and this is likely to be one of the biggest hurdles to the development of a constituent-based composite material damping design methodology.

Additional theoretical results indicate that the damping of composites made using a combination of typical matrix materials and bromine-intercalated graphite fibers could be dominated by fiber damping and increased to a level of engineering significance. The design and verification of such composites would require the development and use of new analytical tools.

In summary, intercalation may be an effective means of increasing the vibration damping properties of graphite-reinforced structural composite materials to a level of engineering significance. The availability of such tailored materials would have significant implications for engineering structural design.

Acknowledgments

Pristine P-100 graphite fiber was obtained from Amoco Performance Products, Inc., Atlanta, Georgia. Some fiber was intercalated with bromine by Intercal, Port Huron, Michigan. Composite specimens were fabricated by SPARTA, Inc., San Diego, California. The composite beam specimens were tested at SPARTA and the Pennsylvania State University.

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