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USE OF SUBMICRON DIAMETER CARBON FILAMENTS FOR REINFORCEMENT BETWEEN CONTINUOUS CARBON FIBER LAYERS IN A POLYMER–MATRIX COMPOSITE

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Abstract—The incorporation of 0.1–0.2 μm diameter carbon filaments (0.6 vol.%) between continuous carbon fiber (7 μm diameter, 56.5 vol.%) layers in an epoxy–matrix composite during composite fabrication was found under flexure to greatly increase transverse and longitudinal tan δ values, increase the storage modulus in the transverse direction, slightly decrease the storage modulus in the longitudinal direction, and increase both longitudinal and transverse loss moduli to values as high as 2 GPa.

Key Words—Carbon filaments, carbon fibers, polymer–matrix composite, vibration, damping, modulus.

1. INTRODUCTION

Fiber reinforced composites typically consist of high modulus fibers, which have low damping ability, held together by a polymer matrix, so most of the damping in composites comes from deformation of the matrix and from fiber–matrix interfacial slipping[1]. For the case of many high performance composites the fibers are oriented such that they are aligned with the loading axis and as a result the mechanical properties of the composite are dominated by the fibers. To increase the damping capacity, it is either necessary to re-orient the fibers to new directions (which also lowers the strength of the composite) or to increase the damping capacity of the components (which for the case of organic materials will also result in a decrease of the modulus[2]). Because the properties tend to be fiber dominated, a higher damping matrix has little effect[3].

An approach for enhancing damping in composites is the addition of specialized damping polymers in the form of constrained layer sheets[3–7]. For use as a constrained layer, the damping polymer sheet is bonded to the substrate and then a constraining layer is placed over the damping polymer sheet[5]. A variation of this approach, which has received interest, is to place the damping polymer sheets between the individual lamina of a composite laminate. This approach gives large improvements in the damping capacity of the composite, but also results in a 33% reduction in the modulus[3]. The damping polymers also have a lower glass transition temperature than the matrix[4]; this may lead to a reduction in the service temperature range of the composite. Another problem associated with the use of the damping polymers is a result of the fact that, for interply use, they have to be cocured with the rest of the composite; this may lead to delamination due to residual stresses near the free edges of the composite[6].

The vibrational damping ability of carbon–fiber polymer–matrix composites are important for numerous applications, including sporting goods, anti-sonar submarines, loudspeaker diaphragms and aerospace structures. Viscoelastic layers (such as rubber) have been incorporated in or used with these composites for the purpose of increasing the damping ability, but this results in a significant decrease in the moduli of the composites.

In unidirectional composites, such as those made by pultrusion, the weak transverse mechanical properties are a disadvantage. Applications of such composites include sporting goods and the substitution of steel reinforcing bars in concrete. The problem also applies to composites made by filament winding, as the transverse weakness necessitates the use of more complicated winding patterns.

Submicron diameter carbon filaments are made catalytically from carbonaceous gases and are different from conventional carbon fibers, which are made from pitch or polymers and are typically about 10 μm in diameter[8]. The carbon filaments are not straight and are not continuous (though large in aspect ratio). The small diameter of the carbon filaments results in a large filament–matrix interface area when the filaments are used as a filler in a composite. The large interface area in turn results in good damping ability, as shown in this work. The addition of the second filler was found to enhance the damping ability in both longitudinal (long axis parallel to the continuous fibers) and transverse (long axis perpendicular to the fibers) specimens, as well as increasing significantly the modulus of transverse specimens and decreasing slightly the modulus of longitudinal specimens.

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2. EXPERIMENTAL

Composite samples were constructed from individual layers cut from a 12 in. wide unidirectional carbon fiber prepreg tape manufactured by ICI Fiberite (Tempe, Ariz.). The product used was Hy-E 1076E, which consisted of a 976 epoxy matrix and 10E continuous carbon fibers of diameter 7 μm. The fiber and matrix properties are shown in Table 1. The carbon filaments used as the second reinforcement (filler) were manufactured by Applied Sciences, Inc. (Cedarville, Ohio), and were grade ADNH. They have a diameter ranging from 0.1 to 0.2 μm, a length >100 μm and a density of 2.0 g/cm^3. In contrast to the straight morphology of the continuous carbon fibers, the carbon filaments have a bent morphology (resembling cotton wool).

The composite laminates were laid up in a 4 × 7 in. platten compression mold. The individual 4 × 7 in. fiber layers (eight per laminate) were cut from the prepreg tape. The layers were stacked in the mold with a mold release film on the top and bottom of the layup. No liquid mold release was necessary. For laminates with a second filler, the second filler material was spread out on each ply as they were laid up, producing laminates with eight layers of carbon fibers and seven interlaminar regions which contained the filament filler. A uniform layer of filament filler material (0.03 g) was assured by the fact that only a monolayer of filaments would adhere to the tacky prepreg plies. The densities and thicknesses of the laminates were 1.53 ± 0.01 and 1.56 ± 0.02 g/cm^3, and 940 and 970 μm without and with the second filler, respectively. The thickness of a second filler layer was 8 μm, as found by calculating the difference between thicknesses of laminates with and without second filler; that of a first filler layer was 110 μm. The volume fraction of second filler layers in the composite with second filler was 6%. The volume fraction of second filler in a second filler layer was 10%. The volume fraction of continuous fibers (first filler) in a composite without second filler was 52%; the volume fractions of first and second fillers in a composite with second filler were 56.5 and 0.6%, respectively. The laminates were cured using a cycle based on the ICI Fiberite C-5 cure cycle. The curing occurred at 355 ± 10°F (179 ± 6°C) and 89 psi (0.61 MPa) for 120 minutes. Afterward, they were cut to pieces of size 25 × 2.5 mm to produce both longitudinal and transverse specimens.

Dynamic testing of the composite beams was performed on a Perkin–Elmer Dynamic Mechanical Analyzer (DMA7e) in accordance with ASTM D4065. The specimens were tested in three-point bending (Fig. 1) in the temperature scan mode from 30 to 180°C at frequencies of 0.2, 0.4, 1.0, 2.0 and 4.0 Hz. These frequencies are much away from the natural vibration frequencies of the specimens. The distance between the knife-edge supports of the three-point bending fixture was 20 mm. The heating rate used for all tests was 2°C/min, which was chosen to prevent any artificial damping peaks which may be caused by higher heating rates. The test temperatures were all well below the glass transition temperature (232°C) of the matrix, so that the matrix was in a glassy state throughout the test. The loads used during testing were all large enough so that the amplitude of the specimen deflection was always over the minimum value of 5 μm required by the machine for accurate results. The loads were then set so that each different type of specimen was always tested at its appropriate stress level. For each type of specimen, results were obtained from consecutive test runs on the same sample without removing the sample from the testing machine. This was justified by separate testing, which indicated no change in the samples from run to run and that the values measured from consecutive runs on the same sample were the same as those recorded on multiple samples. The storage modulus (bending modulus) and loss tangent (tan δ) values from each test were plotted using the attached UNIX workstation. The loss modulus is the product of tan δ and the storage modulus. Values of tan δ below 10^{-4} could not be measured.

Table 1. Fiber and matrix properties (according to ICI Fiberite)

10E-Torayca T-300 (6K) untwisted, UC-309 sized PAN-based	
Fiber diameter	7 μm
Density	1.76 g/cm^3
Tensile modulus	221 GPa
Tensile strength	3.1 GPa
976 Epoxy	
Cure temperature	350°F (177°C)
Maximum service temperature	350°F (177°C) dry 250°F (121°C) wet
Flexural modulus	3.7 GPa
Flexural strength	138 MPa
T_g	232°C
Density	1.28 g/cm^3

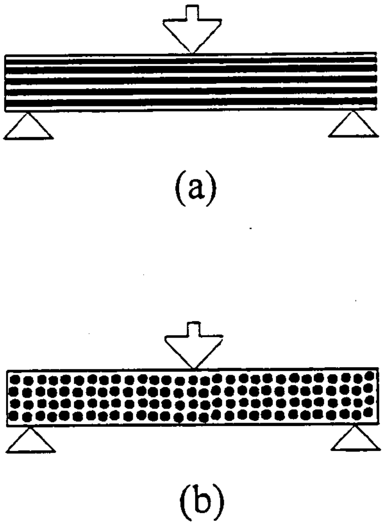

Fig. 1. Sample configuration for dynamic flexural testing: (a) longitudinal sample (fibers parallel to the page); (b) transverse sample (fibers perpendicular to the page).

3. RESULTS AND DISCUSSION

Table 2 gives the values of tan δ, storage modulus and loss modulus at 30°C for different frequencies. Table 3 gives the values at 1.0 Hz for different temperatures. Figures 2 and 3 give plots of tan δ vs temperature at three frequencies (0.2, 1.0 and 4.0 Hz), respectively, for the longitudinal and transverse laminates with second filler. Figures 4 and 5 give corresponding plots for storage modulus. Isothermal tests indicated that the noise in the plots obtained during temperature scanning was not due to the absence of a constant temperature during temperature scanning. The tan δ at 1.0 Hz increased with increasing temperature only in the transverse direction without second filler. With second filler, it increased in the longitudinal direction, but was effectively constant in the transverse direction (Table 3 and Fig. 2). The storage

8.1 Table 2. Tan δ and moduli at 30°C

	Without ~~second filler~~ interlayer			With ~~second filler~~ interlayer		
	0.2 Hz	1.0 Hz	4.0 Hz	0.2 Hz	1.0 Hz	4.0 Hz
Tan δ						
Longitudinal	0.008 ± 0.003	< 0.0001	< 0.0001	0.017 ± 0.003	< 0.0001	< 0.0001
Transverse	0.010 ± 0.003	0.090 ± 0.005	0.050 ± 0.006	0.22 ± 0.01	0.18 ± 0.01	0.14 ± 0.01
Storage modulus (GPa)						
Longitudinal	101 ± 1	97 ± 1	103 ± 1	92 ± 1	92 ± 1	93 ± 1
Transverse	7.9 ± 0.1	8.3 ± 0.1	8.2 ± 0.1	9.1 ± 0.1	9.5 ± 0.1	9.1 ± 0.1
Loss modulus (GPa)						
Longitudinal	0.8 ± 0.3	< 0.0097	< 0.0103	1.6 ± 0.3	< 0.0092	< 0.0093
Transverse	0.079 ± 0.025	0.75 ± 0.05	0.41 ± 0.05	2.0 ± 0.1	1.7 ± 0.1	1.3 ± 0.1

Table 3. Tan δ and moduli at 1.0 Hz

	Without second filler			With second filler		
	30°C	100°C	175°C	30°C	100°C	175°C
Tan δ						
Longitudinal	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.007 ± 0.001
Transverse	0.090 ± 0.005	0.120 ± 0.008	0.130 ± 0.008	0.18 ± 0.01	0.17 ± 0.01	0.19 ± 0.01
Storage modulus (GPa)						
Longitudinal	97 ± 1	96 ± 1	96 ± 1	92 ± 1	90 ± 1	88 ± 1
Transverse	8.3 ± 0.1	7.8 ± 0.1	7.8 ± 0.1	9.5 ± 0.1	8.8 ± 0.1	8.5 ± 0.1
Loss modulus (GPa)						
Longitudinal	< 0.0097	< 0.0096	< 0.0096	< 0.0092	< 0.0090	0.62 ± 0.09
Transverse	0.75 ± 0.05	0.94 ± 0.06	1.0 ± 0.1	1.7 ± 0.1	1.5 ± 0.1	1.6 ± 0.1

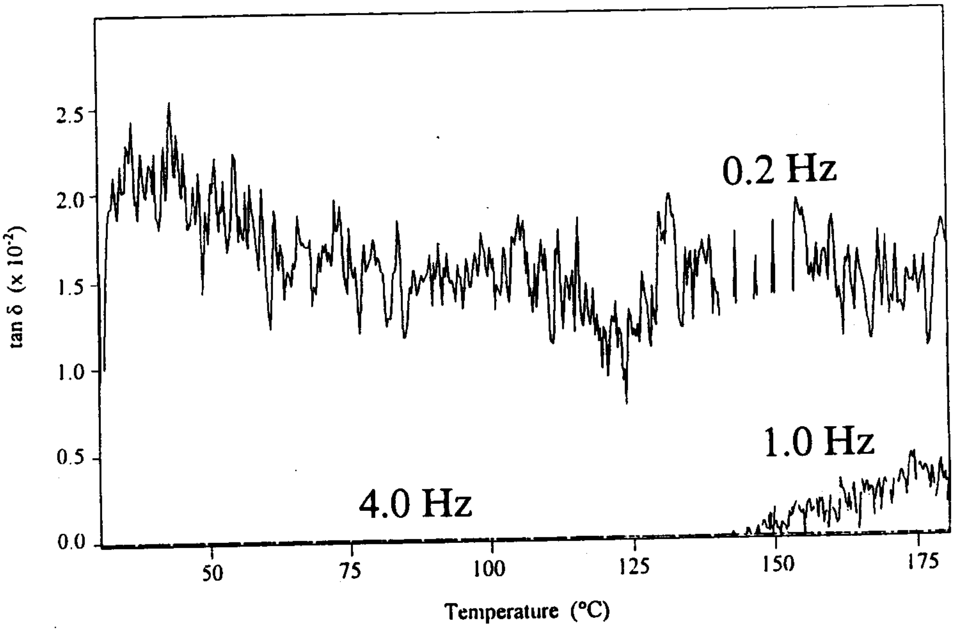

Fig. 2. Plot of tan δ vs temperature at 0.2 Hz (—), 1.0 Hz (–·–), and 4.0 Hz (– – –) for the longitudinal laminate with second filler.

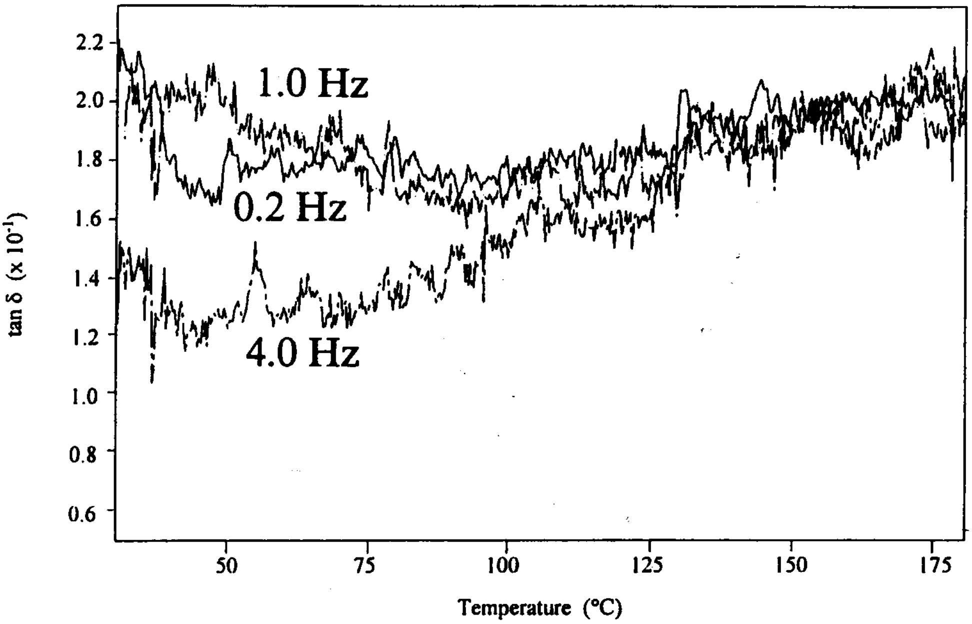

Fig. 3. Plot of tan δ vs temperature at 0.2 Hz (—), 1.0 Hz (–•–), and 4.0 Hz (— — —) for the transverse laminate with second filler.

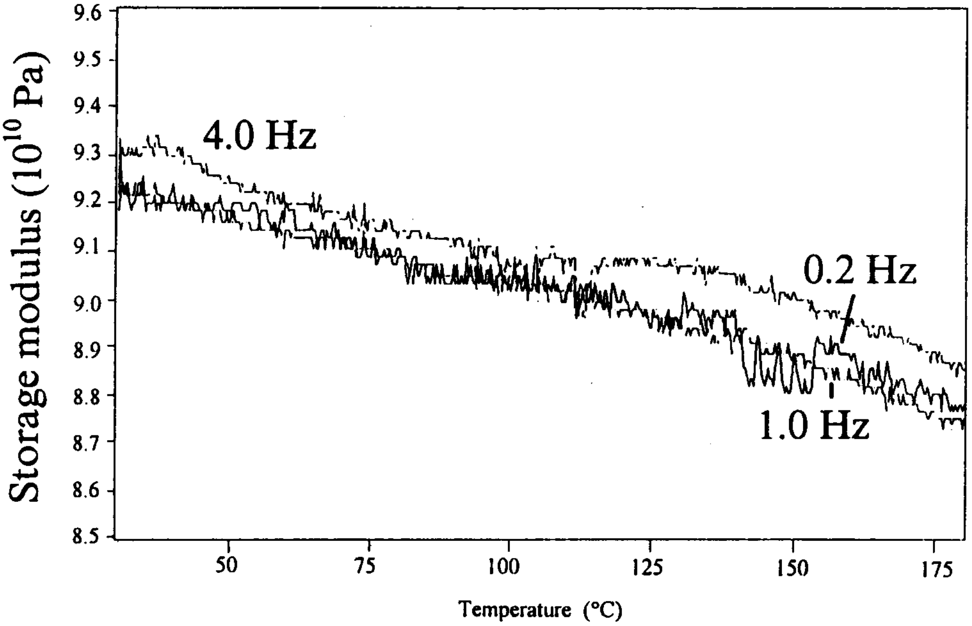

Fig. 4. Plot of storage modulus vs temperature at 0.2 Hz (—), 1.0 Hz (–•–), and 4.0 Hz (— — —) for the longitudinal laminate with second filler.

modulus decreased slightly with increasing temperature, in both the longitudinal and transverse directions, with and without second filler (Table 3 and Figs 4 and 5). The longitudinal tan δ decreased with increasing frequency for both cases (Table 2 and Fig. 3). Tan δ for the transverse direction, and without second filler, first increased and then decreased with frequency, and with second filler it decreased with frequency (Table 2 and Fig. 3). The addition of the second filler increased tan δ at all temperatures and frequencies in both longitudinal and transverse directions, though the increase was more significant in the transverse direction. The storage modulus decreased by a small fraction (5–10% at 30°C) in the longitudinal direction, but increased by a larger fraction (11–15% at 30°C) in the transverse direction with the addition of the second filler. The loss modulus was greatly increased by the second filler addition, in both the longitudinal and transverse directions, though the fractional increase was larger in the transverse direction. At 30°C and 0.2 Hz (Table 2), the loss modulus was higher in the longitudinal direction than the transverse direction when the second filler was absent, but was lower in the longitudinal direction than the

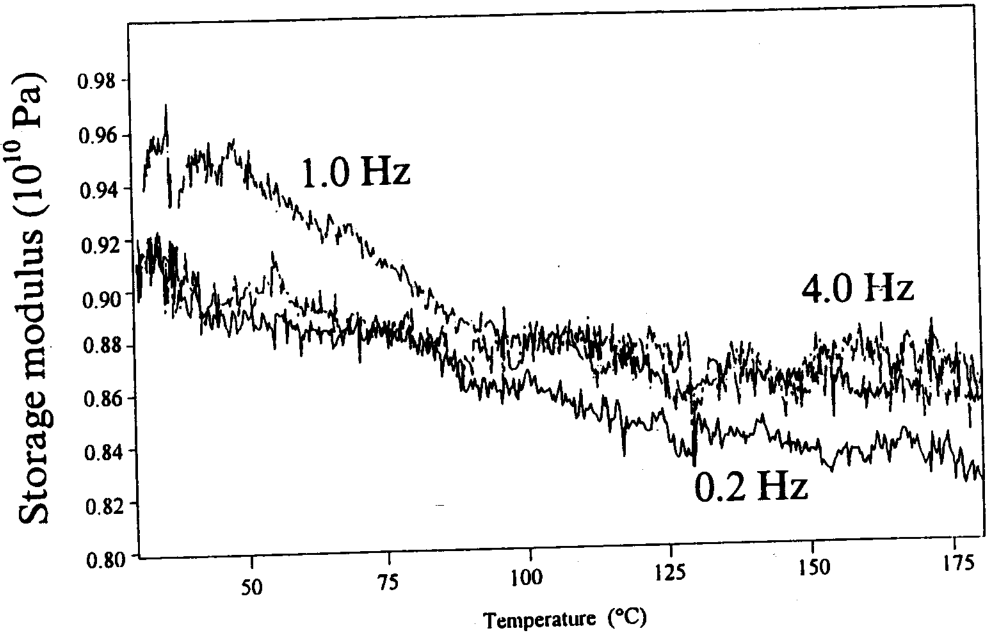

Fig. 5. Plot of storage modulus vs temperature at 0.2 Hz (—), 1.0 Hz (-·-), and 4.0 Hz (— — —) for the transverse laminate with second filler.

transverse direction when the second filler was present. For all other combinations of temperatures and frequencies in Tables 2 and 3, the loss modulus was lower in the longitudinal direction than the transverse direction, whether the second filler was present or not. When all temperatures and frequencies in Tables 2 and 3 are considered, the highest longitudinal loss modulus (1.6 GPa) was achieved with the use of second filler at 30°C and 0.2 Hz, and the highest transverse loss modulus (2.0 GPa) was achieved also with second filler at these same conditions. The combination of high loss modulus and low density makes the composite with second filler highly attractive for applications requiring high damping.

The effect on tan δ is attributed to the damping due to slippage at the filler–matrix interface and the large interface area when the second filler was present. The calculated interface area per cm^3 was 2080 cm^2 without second filler and 3744 cm^2 with second filler. The increase in the transverse storage modulus is attributed to the domination of the transverse storage modulus by the reinforcing effect of the filaments in the matrix rather than the first filler. The slight decrease in the longitudinal storage modulus is attributed to the lower storage modulus of the second filler compared to that of the first filler. The effect on the loss modulus is due to the combined effects on tan δ and storage modulus.

In a separate experiment, longitudinal samples without second filler and with different thicknesses ranging from 940 to 991 μm were tested. It was found that thickness variation had no effect on the dynamic testing results. Thus, the effects described above of the second filler addition are not due to the slight thickness increase due to the second filler addition.

4. CONCLUSIONS

The incorporation of 0.1–0.2 μm diameter carbon filaments as a second filler between continuous carbon fiber (first filler) layers in an epoxy–matrix composite during composite fabrication was found to greatly increase transverse and longitudinal tan δ values, increase the storage flexural modulus in the transverse direction, slightly decrease the storage modulus in the longitudinal direction, and increase both longitudinal and transverse loss moduli to values as high as 2 GPa. The second filler was in the amount of 0.6 vol.%, compared to 56.5 vol.% for the first filler.

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