JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 1939–1947 (1970)

Dynamic Young's and Shear Moduli of Graphite Fiber-Reinforced High-Temperature Matrix Resins

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Synopsis

The resonant frequencies of unidirectional graphite fiber-reinforced polyimide (Skybond 703) and polyquinoxaline resin composite beams were determined. The Timoshenko beam theory was employed to compute both the longitudinal Young's modulus (E_{11}) and the effective transverse-longitudinal shear modulus (G_{12}) from the set of resonant frequencies of the beams. E_{11}, E_{22}, and G_{12} were determined for a 64% by volume Modmor II-reinforced polyimide (Skybound 703) composite, and E_{11} and G_{12} were determined for cured and postcured Modmor II-reinforced polyquinoxaline (PQ) composites. Dynamic E_{11} and E_{22} results were found to agree with experimentally determined static flexural moduli. Voids present in these high-temperature resin composites to an extent of 5–13% by volume appeared to lower the effective shear and longitudinal moduli of the composites.

INTRODUCTION

Advanced composite materials such as carbon and boron fiber-reinforced plastics are of interest because of the very high specific modulus and specific strength properties of unidirectionally oriented, highly anisotropic composites made from these materials. In practical applications for advanced composites as structural materials, strength and stiffness are usually required in more than one direction. The design engineer can attempt to meet specific requirements by plying together layers of unidirectional material with adjacent layers oriented in a way that takes advantage of the high load-carrying capacity of the fibers. In order to design optimum laminated structures, the strengths and moduli of the unidirectional building block material must be known in the various directions.[1]

Unidirectionally oriented fiber-reinforced composites with random fiber packing in the planes transverse to the fiber axis are usually treated as macroscopically homogeneous materials with transverse isotropy.[2] Five independent elastic moduli are required to completely characterize the stress–strain properties of a transversely isotropic material. It is possible determine three of these moduli in two tests using the vibrating beam test method.[3]

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Fiber-reinforced composite beam test specimens exhibit the effects of shear deformation much sooner, i.e., at higher length-to-thickness ratios, than is the case for isotropic materials. The reason for this is that the ratio of the longitudinal Young's modulus (E_{11}) (where the beam length and fiber orientation are in the 1-direction, the width is in the 2-direction, and the thickness is in the 3-direction) to the longitudinal shear modulus ($G_{13} = G_{12}$) of the composite beam is a factor of 2 to 30 or more higher for the fiber-reinforced composite beam (depending on the fiber orientation) than for ordinary structural materials such as steel. In the vibrating beam test, shear effects are manifested by a drop in the "apparent" moduli of the beam as computed from measured resonant frequencies by the Bernoulli-Euler beam theory[4] with increasing mode of vibration (and/or frequency). The Timoshenko beam theory,[4] which includes the effects of shear deformation and rotatory inertia in the governing differential equations of motion for a vibrating beam is more appropriate for describing the behavior of anisotropic composite beams.[3] Huang's[4] solutions of the Timoshenko beam equations, which relate the beam moduli (E_{11} and G_{12}) and geometry to beam resonant frequencies, can be employed to compute both the longitudinal Young's modulus (E_{11}) and interlaminar shear modulus ($G_{13} = G_{12}$) of unidirectional carbon and boron fiber-reinforced epoxy composites.

The purpose of this paper is to present data on the moduli, E_{11}, E_{22}, and G_{12}, measured by dynamic and static methods on unidirectional graphite fiber-reinforced high-temperature resin matrix composites. The high-temperature polyimide (Skybond 703) and polyquinoxaline (PQ) matrix materials employed in this study have outstanding oxidation resistance and have potential as high strength-to-weight-ratio structural materials for applications in the 500°F temperature range.[5]

EXPERIMENTAL

Materials

Skybond 703, a polyimide resin (Monsanto Co.), and a polyquinoxaline resin[6] (Whittaker Research & Development/San Diego) having an inherent viscosity in *m*-cresol of 0.9 were the two high temperature-resistant laminating resins used as matrix materials in this study. Skybond 703 was supplied as a solution of low molecular weight (PI) prepolymer (64% solids) in N-methylpyrrolidone. Polyquinoxaline (PQ) resin, of considerably higher molecular weight, was supplied as a solution in *m*-cresol (17% solids).

Modmor Type II, with a longitudinal Young's modulus of 35×10^6 psi and a specific gravity of 1.75 (distributed by Whittaker Corporation, Narmco Materials Division), was the graphite fiber employed in this study.

After fiber collimation and resin impregnation (techniques available elsewhere[3,5]), the film-supported prepreg materials were heated slowly to 250°F and dried for 20 min to advance the PI and to remove some of the solvent prior to cutting the materials into prepreg plies. Fourteen-ply laminates (about 0.008 in./ply) were formed by hand layup procedures and placed in a trap mold with "bleeder" material (1 ply of a porous Teflon-coated fabric and 2 plies of 181 Style glass cloth) positioned at the top and bottom to permit solvent and/or products of the curing reaction to escape during cure. The laminates were cured under a pressure of 200 psi.

The Skybond 703 laminate was cured 2 hr at 270°F, 2 hr at 300°F, and 2 hr at 350°F. The laminate was postcured for 12 hr at 600°F after heating slowly from 200°F at a rate of 10°F/hr.

The PQ laminates were cured for 4 hr at 750°F after slowly heating the closed mold from 200°F to 750°F at about 60°F/min. The laminates were removed from the mold after cooling. Sections of the PQ laminates were postcured under nitrogen at 750°F for 12 hr after heating the laminate slowly from room temperature to 750°F at about 10°F/hr.

Beam test specimens were machined from the Skybond 703/Modmor II laminates with length directions parallel and perpendicular to the fiber direction. Slight imperfections in the PQ laminates in the transverse directions precluded the preparation of test beams with fibers oriented perpendicular to the length. The density and weight fractions of fiber in the composite test beams were experimentally determined and void contents of the laminates were computed using the densities of the fiber and matrix materials. The specific gravities of the Skybond 703 and PQ matrix materials were found to be 1.32 and 1.31, respectively.

Test Procedures

The test methods have been described elsewhere.[3] The resonant frequencies of cantilever composite test beams of varying length-to-thickness ratio were determined at room temperature (72°F) using a B&K Type 3930 Complex Modulus Apparatus. The longitudinal Young's moduli and longitudinal transverse shear moduli of the beams were computed from the experimental resonant frequencies and beam dimensions using Huang's solution for the Timoshenko beam equations.[4] The static flexural moduli of the same test beams were determined at varying span-to-thickness ratios by the three-point loading method.

RESULTS AND DISCUSSION

The properties of the composite test beams studied in this work are given in Table I. It was noted that the laminates fabricated from the high temperature-resistant PI and PQ matrix materials have higher void contents than usually found for epoxy matrix composites. This is a characteristic problem with matrix resins that give off volatiles during cure (solvent and/or condensation polymerization products). That postcure can sometimes add significantly to the void content of a laminate can be seen from the data for the PQ composites in Table I. Also reported in Table I are the longitudinal Young's moduli (E_{11}) of the composites which were computed from the rule of mixtures. (The moduli of the matrices were assumed to be 0.6×10^6 psi). These E_{11} values will be compared later to experimental dynamic and static results. The dynamic properties of unfilled Skybond 703 and PQ beams were not determined in this study; however, the softening temperatures for samples of the matrix materials have been determined to be 295°C and 325°C, respectively, in penetration tests using a du Pont 941 Thermomechanical Analyzer (TMA). The TMA penetration transition temperatures have been found to correlate well with mechanical and dilatometric glass transition temperatures.[7] The composites might be expected to have slightly lower softening temperatures, if all of the solvent has not been removed during postcure.

TABLE I
Composition and Fiber Orientation of Modmor II Graphite-Reinforced PI and PQ Composite Test Beams

Matrix resin	Fiber orientation[a]	Laminate specific gravity	Fiber vol fraction, vol-%	Void vol fraction, vol-%	$E_{11} \times 10^6$, psi (rule of mixtures)
Skybond	0°	1.50	0.61	0.06	21.7
703	90°				—
PQ	0°	1.51	0.64	0.06	22.7
	0°	1.39[b]	0.61	0.13	21.5

[a] Beamlength direction angle = 0°.
[b] Postcured 12 hr at 750°F in a nitrogen atmosphere.

Since the glass transition temperatures of the Skybond 703 and PQ composites are considerably above room temperature, it is reasonable to assume that at room temperature the moduli of these matrix materials are not rate (frequency) dependent over the frequency range of the vibrating beam test.

Skybond 703/Modmor Type II Composites

The resonant frequencies and the apparent and corrected dynamic longitudinal Young's moduli (E_{11}) determined for the Skybond 703/Modmor II composite beam with fibers oriented parallel to the beam length are reported in Table II for beams of varying length. The "apparent" E_{11}' values, which were computed from the experimental resonant frequencies using the classical Bernoulli-Euler beam theory, are seen to decrease with increasing mode of vibration. This decrease in apparent modulus with increasing mode of vibration is also observed to occur more rapidly as the L/t ratio of the beam is decreased. This is the expected result of transverse shear deformation in the beam. If the beam is assumed to be macroscopically homogeneous Huang's solution to the Timoshenko beam equations for a cantilever beam can be applied to find the value of E_{11}/G_{12} by computer iteration techniques which best satisfies the requirement that E_{11} should be independent of frequency for a composite beam with low internal damping (as was the case here). Since E_{11} of a composite beam is not significantly affected by the modulus of the matrix material,[2] and the modulus of the

TABLE II
Resonant Frequencies and Apparent and Corrected Dynamic and Static Moduli Determined for a Skybond 703/Modmor II Composite Beam

Vibrating beam test					Static flexural test			
			$E_{11}' \times 10^{-6}$, psi				$E_{11} \times 10^{-6}$, psi	
Beam dimensions[a]	Mode no.	f_n, Hz	Apparent	Corrected for $E_{11}'/G_{12}' = 25$	Span, in.	L/t	Apparent	Corrected for $E_{11}/G_{12} = 25$
L = 8.94 in.	1	85.3	19.7	19.8	8.0	71.1	20.0	20.1
t = 0.113 in.	2	536	19.8	20.2	6.0	53.3	20.0	20.2
w = 0.412 in.	3	1490	19.6	20.3	4.0	35.6	19.6	20.0
	4	2870	18.9	20.3	3.0	26.8	19.1	19.9
L/t = 79.5	5	4690	18.5	20.6	2.0	17.8	17.8	19.3
L = 7.04 in.	1	138	19.8	19.9				
L/t = 62.5	2	860	19.6	20.1				
	3	2390	19.3	20.5				
	4	4580	18.5	20.6				
L = 5.54 in.	1	221	19.6	19.7				
	2	1380	19.5	20.3				
L/t = 49.3	3	3740	18.2	20.1				

[a] L = Clamped length of beam; t = thickness; w = width.

fibers are not frequency dependent, this should be true even if the modulus of the matrix material is slightly frequency dependent. The corrected longitudinal moduli for the Skybond 703/Modmor II composite beam are given in Table II for a value of $E_{11}/G_{12} = 25$.

It is seen that the correction for transverse shear leads to a value of E_{11} which is constant within experimental error and independent of mode of vibration (frequency) and the L/t ratio of the beam. Values of $E/G = 22$ and 28 (i.e., 25 ± 3) also lead to E_{11}' values that are constant within the experimental error of the measurements. Hence, G_{12}, the longitudinal-transverse shear modulus of the Skybond 703/Modmor II composite, is found to be $0.8 \pm 0.1 \times 10^6$ psi. This value is reasonable and compares well with the G_{12} value of 0.75×10^6 psi measured for a 60% by volume graphite fiber-reinforced epoxy composite in torsion experiments.[8] (The comparison assumes that the epoxy and PI matrix materials have close to the same shear modulus.)

The apparent static flexural moduli determined as a function of L/t are also reported in Table II for the same Modmor II/PI composite beam. The apparent moduli are seen to decrease as L/t decreases. Corrected static moduli, i.e., corrected for transverse shear deformation[3] by taking $E/G = 25$, are also reported in Table II. Corrected static and dynamic E_{11} moduli are in good agreement with one another and about 9% lower than the value predicted by the rule of mixtures (Table I).

The dynamic and static test results determined for the Skybond 703/Modmor II composite beam in which the fibers were oriented perpendicular to the length of the beam showed that both the dynamic and static transverse Young's moduli (E_{22}) for the composite were independent of L/t within experimental error, and that the dynamic modulus was independent of the mode of vibration. This indicated that transverse shear deformation was not significant for the 90° angle fiber orientation beam, i.e., E_{22}/G_{23} was less than 8. E_{22} was found to be 0.93×10^6 psi. This comparatively low value of E_{22} obtained for the 61 vol-% Modmor II/Skybond 703 composite is probably a result of factors such as carbon filament anisotropy[9] and high void content, which operate to lower E_{22} values.

PQ/Modmor Type II Composites

The resonant frequencies and the apparent and corrected dynamic longitudinal moduli, E_{11}, found for the PQ/Modmor II composite beam, which was cured under pressure at 750°F but not postcured, are summarized in Table III. The results show that the shear correction is significant for the beam and that the value $E_{11}/G_{12} = 30$ leads to a corrected dynamic and static modulus which is independent of L/t and/or mode of vibration.

The dynamic and static longitudinal modulus data determined for the postcured PQ/Modmor II beam are given in Table IV. A value of $E_{11}/G_{12} = 30$ was also found to be the best value to use in Huang's equation[4] to produce a constant corrected E_{11} for this beam.

TABLE III
Resonant Frequencies and Dynamic and Static Moduli Determined for the PQ/Modmor II Composite Beam which was not Postcured

Vibrating beam test					Static flexural test			
			$E_{11}' \times 10^{-6}$, psi				$E_{11} \times 10^{-6}$, psi	
Beam dimensions	Mode no.	f_n, Hz	Apparent	Corrected for $E_{11}/G_{12} = 30$	Span in.	L/t	Apparent	Corrected for $E_{11}/G_{12} = 30$
L = 6.27 in.	1	176.5	20.3	20.5	6.0	53.1	19.7	19.9
t = 0.113 in.	2	1086	19.6	20.4	4.0	35.4	19.7	20.2
w = 0.301 in.	3	2960	18.6	20.4	3.0	26.5	19.2	20.0
L/t = 55.4	4	5630	17.5	20.6	2.0	17.7	16.7	18.4
L = 5.28 in.	1	246	20.0	20.2				
L/t = 46.7	2	1527	19.5	20.6				
	3	4140	18.3	20.8				

TABLE IV
Resonant Frequencies and Dynamic and Static Moduli Determined for the Postcured PQ/Modmor II Composite Beam

Vibrating beam test					Static flexural test			
			$E_{11}' \times 10^{-6}$, psi				$E_{11} \times 10^{-6}$, psi	
Beam dimensions	Mode no.	f_n, Hz	Apparent	Corrected for $E_{11}/G_{12} = 30$	Span, in.	L/t	Apparent	Corrected for $E_{11}/G_{12} = 30$
L = 6.28 in.	1	185	17.8	17.9	6.0	49.2	18.0	18.2
t = 0.122 in.	2	1137	17.1	17.9	4.0	32.8	16.7	17.2
w = 0.303 in.	3	3045	15.7	17.4	3.0	24.6	17.5	18.4
L/t = 43.0	4	5800	14.8	17.9	2.0	16.4	14.2	15.9
L = 5.25 in.	1	259	17.1	17.3				
L/t = 43.0	2	1590	16.4	17.5				
	3	4240	14.8	17.2				

The main difference between the two PQ/Modmor II beams was in the void content. The postcured beam had 13% by volume of voids compared to 6% for the unpostcured beam. The PQ/Modmor II beam with the higher void content was found to have a slightly lower Young's modulus ($E_{11} = 18 \times 10^6$ psi compared to 20.4×10^6 psi) and a lower shear modulus ($G_{12} = 0.60 \times 10^6$ psi compared to 0.68×10^6 psi) than the lower void content beam.

The presence of voids in composites made with high-temperature resins is probably unavoidable and would be expected to affect the elastic properties of the composite. Micromechanics theories[1,2,10] predict that E_{22} and G_{12} should be approximately proportional to the shear modulus G_m of the matrix material. If voids are distributed uniformly throughout the matrix material, the effective modulus of the foamed matrix, and hence E_{22} and G_{12}, would be reduced compared to a composite of equal fiber volume with no voids. Void content should not have a significant effect on E_{11} at low void contents if fiber concentration and distribution is not changed in the composite.

CONCLUSIONS

Dynamic flexural wave studies on high-modulus carbon fiber-reinforced Skybond 703 and polyquinoxaline resin composite beams showed that these highly anisotropic beams exhibit transverse shear effects at the 4th and 5th modes of vibration at L/t ratios of 100 or less. Because of this effect, it was possible to determine the effective longitudinal-transverse shear moduli of the beams as well as the longitudinal Young's moduli by applying corrections derived from the Timoshenko beam theory. Corrected dynamic moduli were found to be independent of L/t ratio and mode of vibration and in agreement with corrected static moduli as required for an elastic material. Hence, the vibrating beam test as applied here has good potential as a convenient method for studying the shear modulus of fiber-reinforced composite materials over a range of temperature and frequency.

A postcured PQ/Modmor II composite with 13% void volume was found to have a slightly lower shear modulus (G_{12}) and longitudinal Young's modulus (E_{11}) than a test sample from the same composite that was not postcured and contained 6% voids. The decreased shear modulus is expected from micromechanical theories for unidirectional fiber-reinforced composites, since voids decrease the effective shear modulus of the matrix material. High void content is also expected to affect (lower) transverse Young's modulus (E_{22}) values, and this was found to obtain for the Skybond 703/Modmor II composite.

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Received April 13, 1970
Revised May 28, 1970