The Influence of Heat Treatment of the Matrix on the Physical Properties of Carbon-Carbon Composites

by

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Introduction

Carbon fibers have unique mechanical properties that permit the design and application of composites for special lightweight, high strength and stiffness purposes, especially at high temperatures.

The properties of composites made with graphite fibers have not kept pace with the fiber development. In recent years the fiber strengths approach 700 Ksi and the modulus 140 Msi which is almost theoretical compared to graphite single crystal properties. In contrast the composite's strengths are 30 Ksi and moduli are in the range of 10 Msi. Possible reasons for these discrepancies have been attributed to fiber inhomogeneities, yarn misalignment, and bonding between filaments and matrix.[1]

Little attention has been given to the influence of matrix microstructure between filaments and yarns. Earlier work by Fitzer, et al.,[2] has shown a high utilization of fiber mechanical properties can be obtained in unidirectional composites with a carbon matrix. More recently, the thermal expansion, energy absorption and fracture toughness have been shown to be independent of the microstructural characteristics of the matrix.[3] In all these studies, relatively large samples were used. Consequently a more exact interpretation of the causes of the variations is difficult because of large numbers of possible competing factors that could influence the results. Therefore this investigation was undertaken using very small samples and measuring modulus of elasticity (E) as a function of heat treatment and sample size.

Approach

The ability of fibers, within a composite, to equally share stresses depends on the relative modulus differences between the fibers and the matrices (including the interface bonding). The more graphitic the matrix, the greater the ability to distribute the forces between fibers resulting in their improved utilization.[4] The dynamic E was selected as a sensitive indicator of the fiber-matrix interaction.

Techniques for preparing and measuring E of the samples were developed to minimize their size with intent of determining the elastic moduli of the "building block" of a composite, namely a yarn with its associated matrix or a few yarns and the interstitial matrix. In this manner an attempt was made to minimize the larger defects that occur between yarns or plies, thereby improving the ability to interpret the results.

Experimental Methods

Dynamic modulus was determined by passing an alternating current along the axis of the sample in the presence of constant magnetic field perpendicular to the direction of the current. The resulting interaction between these two fields placed a transverse force on the sample. By altering the frequency of the current, the vibrational resonances of the sample were determined. By knowing the mass and geometry of the sample, the modulus could be calculated. Verification of the method was determined by preparing small samples of graphite, type ATJS, and finding E to be 1.2 Msi[5] as compared to ≈1.1 for large tensile samples.[5]

Single yarn samples were taken from a fully processed and graphitized 3D carbon-carbon composite, woven by FMI, processed by GE and characterized by SORI.[6] Sample sizes were about 0.010" × 0.010" × 1.34".

All samples were examined microscopically for evidence of a graphitic structure. These samples were cathodically etched and observed with the SEM. Furthermore, the heat treated samples were examined by X-ray diffraction to determine if any appreciable differences occurred in the d_{002} spacings. Modulus values were measured for the purpose of determining if E for yarns is similar to E for billets, when the volume of fibers is taken into account by the rule of mixtures.

Laminates made from plies of WCA cloth and prepregged with a resole resin were heat treated for 15 minutes to various stages of processing and cut into thin beam samples. These samples were measured by vibrational resonance methods to evaluate the influence of matrix microstructure. Sample sizes were .080" × .039" × 2.0".

Results

The value of E for part of a single yarn bundle (.010" × .005" × 1.34") taken from a processed three dimensional billet (x-direction) was compared to the value for large tensile samples.[5]

$$\frac{E_{measured\ (Msi)}}{37} \qquad \frac{E_{reported\ (Msi)}}{8.3}$$

The microstructural examination showed the matrix between fibers to be graphitic with a sheath-like structure around the fibers.

The 2D laminate results are summarized in the following table

	E (Msi)	ρ(g/cc)	d_{200}(Å)
1. Post cured (140°C)	1.9	1.36	-
2. Pyrolyzed (1000°C)	1.15	1.19	-
3. 2100°C	0.295	1.04	3.421
4. 2300°C	0.40	1.09	3.400
5. 2400°C	0.75	1.09	3.399
6. 2550°C	--	--	3.397

Microstructural examination showed strong indications of graphitic structure around the fibers after the 2400°C heat treatment temperature (HTT).

Discussion and Conclusions

The E value for the single yarn from the 3D billet is more than a factor of four higher than for multi yarn specimens pulled in tension. From microstructural examinations of the single yarn specimens it would appear that approximately 57% is filled with fibers. If the rule of mixtures is obeyed, E should be 31 Msi whereas the measured value is about 37 Msi. The comparison, although not exact, is sufficiently close to indicate the filaments in the yarn are being utilized to a high degree. According to this result, the matrix to fiber bonds must be good and the matrix is capable of transferring loads between fibers.

The 2D composite study showed HTT does affect the matrix which in turn alters the composite's properties. A slight drop in the modulus is seen after 1000°C pyrolysis. A further drop in E of about a factor of four occurs between 1000°C and 2100°C. The initial drop is due to the carbonization of the matrix, and the subsequent change accompanies the approach of graphitization. This demonstrates that the modulus of the fibers is being less fully utilized. The loss of matrix material reduces the transfer of load between filaments up to 2100°C. The continued increase of E above this temperature is attributed to the matrix and filaments becoming more graphitic. This combination of fiber and matrix produces a stiffening of the composite.

In conclusion, a method has been developed for measuring the E of samples with a cross section of one yarn (≅.010" × .010"). This small sample technique shows that graphitization heat treatment of the matrix alters the E values in 2D composites. Both these results demonstrate further study is needed to understand better the influence of the matrix on the physical properties of the yarns or the building blocks of the composite.

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References

1. K. Wolf, R. E. Fornes, J. D. Memory, and R. D. Gilbert, Chem. and Phys. of Carbon, Vol. 18, pp. 93-138.

2. E. Fitzer, W. Huettner, and L. Maniocha, Carbon, Vol. 18 (1980) 291.

3. R. A. Meyer, S. R. Gyetvay, and A. B. Chase, Ext. Abstr., 16th Biennial Conf. on Carbon, pp. 506-507.

4. R. A. Meyer, "The Contribution of Matrix to the Performance of Carbon Fibers in Carbon-Carbon Composites,", Am. Chem. Soc. Symposium, St. Louis, April 8-13, 1984, to be published.

5. C. D. Pears and H. G. Sanders, AFML-TR-69-204, Southwest Res. Inst., Feb. 1970.

6. H. E. Littleton and C. D. Pears, AFML-TR-77-48, Southwest Res. Inst., April 1977.