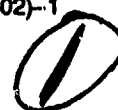AEROSPACE REPORT No.
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The Influence of Heat Treatment
of the Matrix on the Physical Properties
of Carbon-Carbon Composites

Prepared by

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The effects of heat treatment on carbon-carbon composites have been studied on small composite samples by the use of X-ray diffraction, microstructural analysis (optical and scanning electron microscopy), density measurements, and sonic resonance for determining modulus. Modulus values for small samples of three-dimensional composites give good agreement with rule of mixtures estimates when the actual fiber volume fraction of the small sample is used. Heat treatment of pyrolyzed two-dimensional laminates shows

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initially a drastic drop in modulus, corresponding to pyrolysis, decreasing density, and increasing porosity. In the graphitization temperature range, however, some increases are seen in modulus, accompanied by decreasing graphite c-spacing and increasing graphitization. Microstructural examination also shows evidence of increasing graphitization of the matrix, accompanying the increase of stiffness.

(keywords) ⇒

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CONTENTS

I. 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 strengths of the composites 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 demonstrated that efficient 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.

II. APPROACH

The ability of fibers, within a composite, to share stresses equally 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 use.[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 sample size as well as the associated matrix, transverse yarns, and and 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.

III. EXPERIMENTAL METHODS

Dynamic modulus was determined by passing an alternating current along
the axis of the sample in the presence of constant magnetic field perpendi-
cular 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 deter-
mined. 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 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 in.

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 min. 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
0.080 × 0.039 × 2.0 in.

IV. RESULTS

The value of E for part of a single yarn bundle (0.010 × 0.005 × 1.34 in.) taken from a processed three-dimensional billet (x-direction) was

$E_{measured}$ (Msi) (Single Bundle)	$E_{reported}$ (Msi) (for Multiyarn Sample)[6]
37	8.3

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

The two-dimensional laminate results are summarized in Table 1 and illustrated graphically in Fig. 1. Microstructural examination showed strong indications of graphitic structure around the fibers after the 2400°C heat treatment temperature (HTT).

Table 1. Two-Dimensional Laminate Results

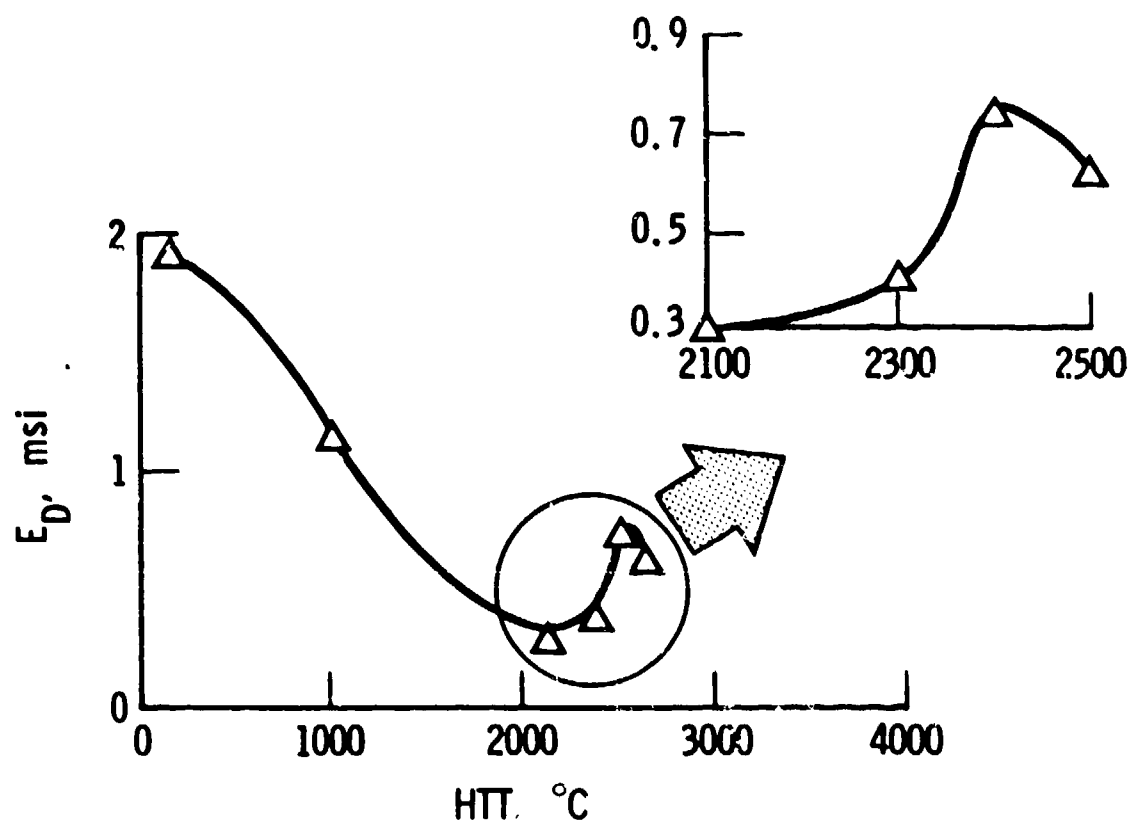| Temperature (°C)	E (Msi)	ρ(g/cc)	d_{200}(Å)
Postcured 140	1.9	1.36	-
Pyrolyzed 1000	1.15	1.19	-
2100	0.295	1.04	3.421
2300	0.40	1.09	3.400
2400	0.75	1.09	3.399
2550	--	--	3.397

Fig. 1. Dynamic Modulus vs HTT

V. DISCUSSION AND CONCLUSIONS

The E value for the single yarn from the three-dimensional billet is more than a factor of 4 higher than for multiyarn 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 used to a high degree. According to this result, the matrix to fiber bonding must be good, and the matrix is capable of transferring loads between fibers.

The two-dimensional 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 4 occurs between 1000 and 2100°C. The initial drop is caused by 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 ($\approx$ 0.010 × 0.010 in.). This small sample technique shows that graphitization heat treatment of the matrix alters the E values in two-dimensional 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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