

# The Effect of Heat Treatment on the Structure and Properties of Mesophase Precursor Carbon Fibers

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**Abstract.** Pitch precursor carbon fibers were heat treated to study structural development and properties. Crystallite size and preferred orientation developed more rapidly with increasing heat treatment temperature than with PAN precursor carbon fibers. However, the trends were quite different for the two series of pitch fibers studied. Observed moduli were compared with moduli calculated from preferred orientations and the models of Reynolds and Sharp or Ruland. Neither model produced acceptable results. Finally, the strains to failure observed in the fibers correlated extremely well with crystallite size. High strength fibers require small crystallite sizes.

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Two series of mesophase pitch precursor carbon fibers were annealed upto temperatures of 2400°C for 5 minutes. Structure was evaluated by x-ray diffractometry and SEM fractography. Then, the fibers' mechanical and electrical properties were correlated with the structural development. Both the E and B fibers had smooth outer surfaces but the fibers were devoid of large pie shaped cracks. There was some indication of corrugated radial structure. The radial structure became more prominent and shear slip steps became larger with increasing heat treatment temperature. The unwrinkling of crystallites seen in the fracture surfaces indicates an increase in basal plane perfection and a decrease in interlayer pinning which is in agreement with x-ray and mechanical properties.

Crystallite development,  $L_c$ , was calculated by the Scherrer formula from the (002) diffraction peak after correction for the baseline, Lorentz Polarization Factor and machine broadening. Orientation of the crystallites was determined from the full width at half maximum (FWHM) of an azimuthal scan on a collimated bundle of fibers. The raw data asymptotically approached  $Z=10.5^\circ$ . This value was used as an estimate

of peak broadening due to fiber collimation errors. Peak width was corrected for this broadening by variance subtraction.

Crystallite stack height of the E-series fibers increased gradually with increasing treatment temperature to 2000°C then rose much faster above 2000°, Fig. 1. This sudden rise was probably due to the increased mobility of carbon atoms within the graphitic lattice above 2100° and permits faster annealing of defects and alignment of crystallites. Stack height of the B fibers increased gradually with temperature through

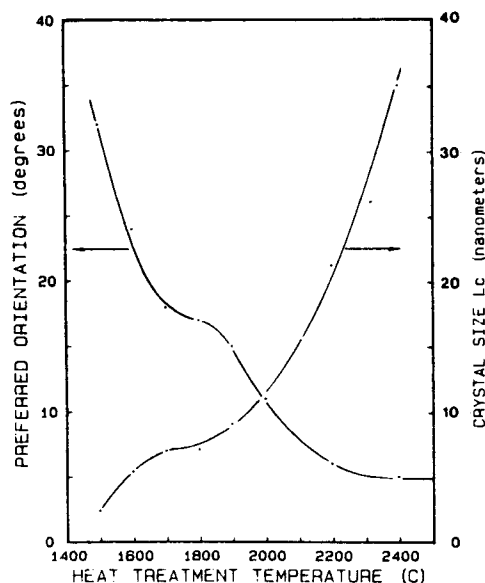


Fig. 1 Preferred orientation and crystallite size versus HTT for mesophase precursor carbon fiber.

2200°C. The inhibition of rapid crystallite growth between 1800°C and 2200°C indicated a material which did not graphitize as easily as other fibers[1]. Preferred orientation increased, i.e.,  $Z_c$  decreased, with increasing heat treatment temperature, Fig. 1. The trend was not so smooth for the B fibers. A crossplot of  $100/Z_c$  vs.  $L_c$ , Fig. 2, showed the parallel development of preferred orientation and crystallite stack height. The same physical phenomena apparently dictate stack height growth and preferred orientation development. Preferred orientation, of the B fibers increased faster as a function of  $L_c$  than that of the E fibers indicating that the B fibers contained smaller, more faulted domains which apparently align along the fiber axis faster than they coalesce into crystals.

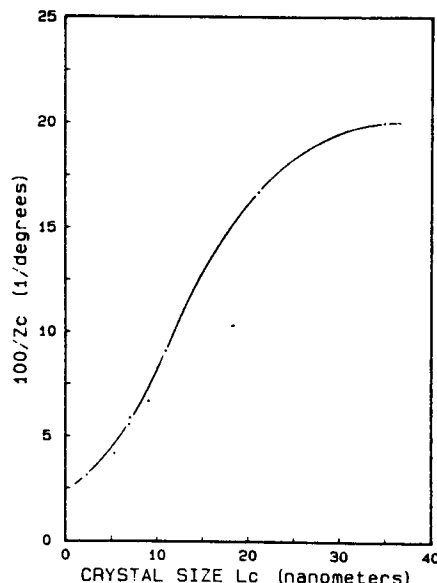


Fig. 2 Correlation of inverse of FWHM of preferred orientation with crystallite size for a mesophase precursor carbon fiber.

Improvements in mechanical properties followed similar trends as structural parameters. Tensile modulus of the E fibers smoothly increased with heat treatment temperature (HTT), Fig. 3. The B fibers' modulus increase with HTT was neither as well defined nor as steep. The difference between single crystal graphite and fiber modulus as a function of HTT predicts a minimum temperature of 3100°C to produce a perfectly aligned fiber. Two of the more accepted models for relating preferred orientation to modulus were proposed by Reynolds and Sharp[1] and Ruland[2]. Reynolds and Sharp related crystallite orientation and modulus by

$$\frac{1}{E} = s_{11} \cos^4 \bar{\phi} + s_{44} \sin^2 \bar{\phi} \cos^2 \bar{\phi}$$

$s_{11}$ ,  $s_{44}$  - compliance of single crystal graphite  
 $\bar{\phi}$  - avg crystallite orientation

A is a parameter which changes with the model ultrastructural deformation:  $A=1$  for the uniform stress model; and  $A=0$  for uniform strain. Assuming  $s_{11}=6.79 \times 10^{-9} (\text{psi})^{-1}$ ,  $s_{44}=1.724 \times 10^{-6} (\text{psi})^{-1}$  and  $\phi$  is  $(Z_L/2)$ , the parameter, A was determined

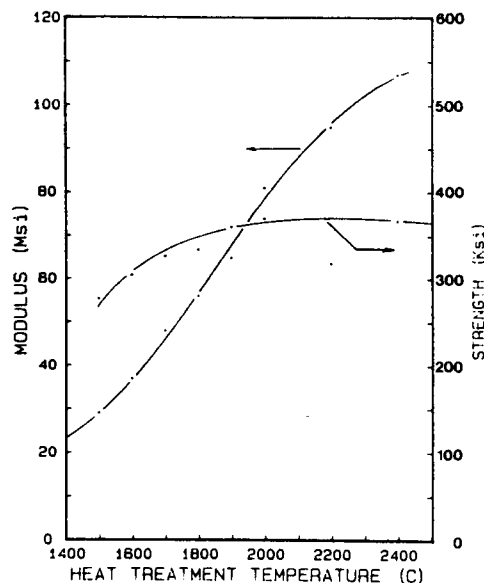


Fig. 3 Modulus and strength versus HTT for a mesophase precursor carbon fiber.

for the annealed pitch fibers. A for the B fibers rises gradually with increasing HTT indicating an apparent increase in interlayer pinning.

A for the E fibers rose gradually with temperature to 2000°C and then jumped. The sudden rise in A indicated an apparent sharp increase in interlayer pinning or a rapid increase in the density of crystal defects, which is just the opposite of what might be expected from  $L_c$  vs HTT. Ruland's model assumes that the distribution of crystallite orientation is the Poisson kernel

$$q(\phi) = \frac{1-q}{1+q^2 - 2q \cos 2\phi}$$

$q$  is the orientation parameter. The FWHM of this distribution for various values of  $q$  was determined and used, with  $Z_c$ , to estimate the value of  $q$  for these fibers. The orientation parameters  $l_z$  and  $m_z$  for each fiber were computed:

$$l_z = \frac{\pi}{4} \frac{\sqrt{lq}}{\tan^{-1} lq} \quad m_z = \frac{1+q}{1-q} l_z$$

and used in the governing equation of the Ruland elastic unwrinkling model:

$$\frac{1}{E} = s_{11} l_z + m_z k$$

The elastic unwrinkling parameter,  $k$ , is a compliance that described the resistance of the undulating graphite ribbons, within the fiber, to straightening. Previous authors have implied that  $k$  is constant for a given type of fiber and that it equals approximately  $25 \times 10^{-8} (\text{psi})^{-1}$  for rayon based fibers[3] and  $49 \times 10^{-8} (\text{psi})^{-1}$  for Thornel P-VSB-32-0 mesophase pitch based fibers[4]. The fibers produced here had  $k$  values between 5 and  $25 \times 10^{-8} (\text{psi})^{-1}$ . Among the annealed E fibers, those with the highest modulus had the lowest values of  $k$  and  $k$  steadily increased as  $E$  dropped below 50 Msi. There was no obvious trend for  $k$  among the B fibers but  $k$  of the B fibers was higher than that of the E fibers. These variations in  $k$  would indicate that pinning is less extensive

in the low modulus and B fibers, again opposite the expectations from the x-ray data.

Tensile strength also improved with increasing heat treatment temperature to 2000°C. However, there was a great deal of scatter in the strength data making it difficult to quantify  $\sigma=f(\text{HTT})$  for  $T < 2000^\circ\text{C}$  or even qualify  $\sigma=f(\text{HTT})$  above 2000°C. Strain to failure steadily decreased with increasing treatment temperature for both B and E series fibers. For a given treatment temperature, the B fibers  $\epsilon_f$  was 0.1 - 0.2% higher than that of the E fibers. A strong correlation between crystallite stack height and strain to failure exists, Fig. 4. A small crystallite size is required for high strain to failure and small changes in crystallite size between 4.0 and 10.0 nm can produce large changes in strain to failure.

In summary, the E fibers produced here develop significantly higher  $L_c$  at low treatment temperatures. Two models were used to try to correlate physical and mechanical properties.

A new model, based on crystal mechanics, which can account for varying transverse microtexture is being developed to better describe the fibers' mechanical behavior.

#### References

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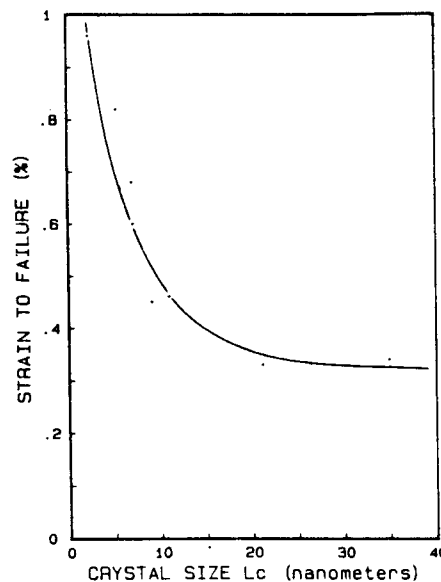


Fig. 4 Relation of strain to failure to crystallite size for a mesophase precursor carbon fiber.