

# ONSET OF MECHANICAL PROPERTIES IN PITCH-BASED CARBON FIBERS

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## 1. Introduction

Otani first, then Bright & Singer [1, 2] have noticed a degradation of the preferred orientation of the pitch-based carbon fibre (PBCF) during stabilization and pre-carbonization. Beyond, a marked increase is noticed as HTT increases. More recently, Mochida's group also evidenced the same phenomenon [3]. Important transformations occur at molecular range in connection with oxygen bonding, and its removal from the lattice. In this work mechanical properties and structural characterization were performed to understand the change occurring at molecular range during the stabilization process.

## 2. Experimental

First, tensile properties were measured on a series of fibers treated in a laboratory furnace: as-spun, stabilized, then pre-carbonized every 50°C from 450 to 1100°C. For each condition at least 20 single filaments were tested and Weibull statistic was applied. A second series of carbonization was performed in industrial conditions in the same range of temperature (flash conditions). The fibers were embedded in epoxy, then cut with an ultra-microtome (less than 100nm-thick) using a diamond knife. The cross-sections were then observed by means of TEM. Sectioning gave first indices of deep rheology changes across this series. As-spun fiber was elastic, whereas after stabilization the fiber was more brittle. The pre-carbonized samples exhibited the best sectioning behavior under the shearing of the knife. At 900°C meanwhile, the so-called „sleep lines“ appeared again in connection with the orientation of molecules perpendicular to the knife [4]. Finally, at higher HTTs the carbonized fibers exhibited the expected brittle behavior known with carbon fiber sectioning.

## 3. Results and Discussion

**Mechanical properties.** A constant increase of Young's modulus was observed as the carbonization temperature was increased (Fig.1). Meanwhile, 3 different

tensile behaviors were observed. First, stabilized fiber showed an elastic linear behavior with poor performances. Then, when carbonized in-between 500 and 650°C fibres exhibited a non-linear behavior. Loading and un-loading the fibre have shown that this **non-linear behavior is fully reversible**. Also, holding the fiber under constant load (close to failure) for 8 hours have not shown any creeping. For the fibre carbonized at 600°C the strength was low (400 Mpa) but the elongation to failure still reached values as high as 4% (5.5% at 550°C). Finally, above 700°C, the classical linear behavior known for carbon fiber was obtained. Further, the stress hardening phenomenon was observed (concave up shape of the stress-strain curve).

**Microstructure.** The molecular ordering was analyzed by means of 002 darkfield TEM technique. This technique is an imaging mode by which the 2 coherent lengths  $l_a$  and  $l_c$ , (respectively parallel and perpendicular to the molecular plane) can be measured. The plot of  $l_a$  and  $l_c$  versus the carbonization temperature (Fig.2) shows that first, the coherent domain decreased in size as oxygen get bonded and during the very first stage of carbonization. With further evolving of oxygen out of the carbon skeleton, these two lengths were seen to increase.  $L_2$  which is the carbon layer diameter (mean high-resolution-TEM fringes length [5]) was seen to be constant during the stabilization and then was seen to increase after the minimum reached by the coherent domain. In this series (flash) the maximum of the elongation-to-failure was obtained for 700°C (550°C with the lab furnace). It corresponds to the maximum of the  $L_2/l_a$  ratio, which means a „crumpling“ of the individual graphene. As a matter of fact the mean diameter of the fiber ( $9.2\mu\text{m}\pm.35$ ) increased during the precarbonization and reached a maximum ( $12.5\mu\text{m}\pm.7$ ) at the same moment. As  $\frac{3}{4}$ th of the oxygen has already evolved at this point, it can be suspected that a maximum of dangling bonds (or electrons re-localization) are disturbing the flatness of the lattice. The elemental analysis has shown that an extra amount of oxygen is found in the fibers out of the furnace due to atmospheric  $\text{O}_2$  and/or  $\text{H}_2\text{O}$  physisorbed on the low-temperature

carbonized carbon (activated carbon). Thus, it is suspected that the non linear but reversible tensile behavior is likely related to the local deformations measured in the carbon lattice.

**Acknowledgements.** Dr G.J. Lavin provided the fiber, he is acknowledged for his cooperative help.

### References

1. S. Otani, Mol. Cryst.; 63, 249 (1981)

2. A.A. Bright and L.S. Singer, Carbon, 17, 59-69 (1979)
3. S. H. Hong, Y. Korai and I. Mochida, Carbon'97, Pennstate, p412
4. X. Bourrat, E. J. Roche and J. G. Lavin, Carbon, 28, 435-446 (1990)
5. X. Bourrat, „Structure in Carbons and Carbon Artifacts“, ch.1 in The Science of Carbon Materials, H: Marsh and F. Rodriguez-Reinoso, Universidad de Alicante, SP edt (1999)

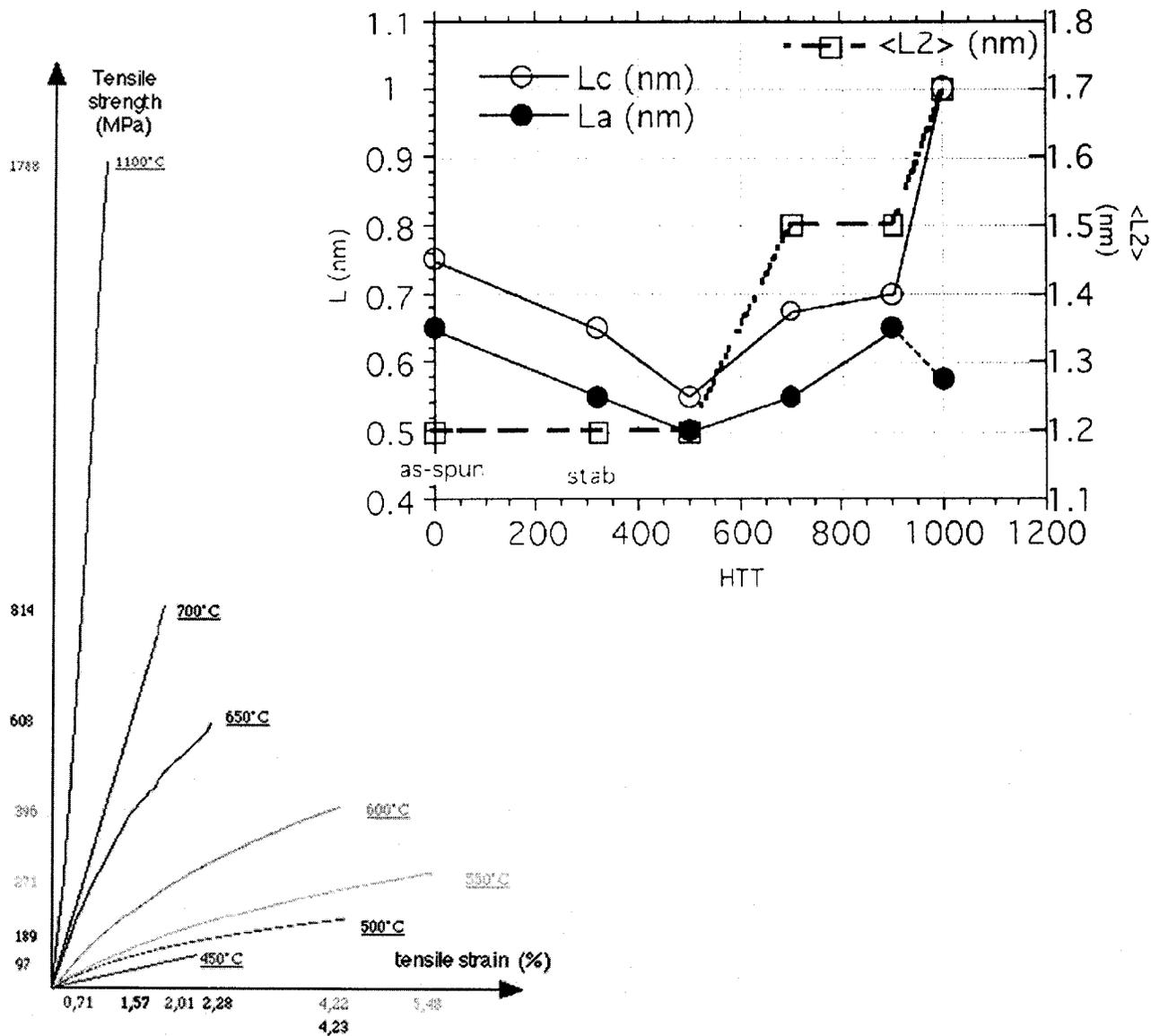


Fig.1 Schematic of the different tensile behaviors of the PBCF during carbonization.

Fig.2 Plot of  $l_a$  and  $l_c$  as well as  $l_2$  as measured by TEM [5] versus flash carbonization heat-treatment.