

CARBONIZATION STUDY OF STABILIZED PAN FIBRES

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Introduction

PAN fibers are known to be the best precursor for making the high performance carbon fibers. It was shown in earlier studies that the fibers were stabilized in temperature range of 300-400°C [1,2] and can be carbonized with very fast rate up to 1000°C resulting much improved mechanical properties [1]. The present paper describes a carbonization study of 350°C stabilized fibers between 500- 2500°C with a heating rate of 100K/min and explains some important aspects on the behavior of mechanical properties of carbon fibers with increase in carbonization temperatures.

Experimental

Courtella PAN precursor fibers of 1.1 denier having 12000 monofilaments were stabilized by heating in air to 250°C at a heating rate of 1°C/min and subsequently subjected at 350°C isothermally in air for 1 minute. Stabilized fibres were then carbonized in nitrogen with a heating rate of 100 K/min up to different temperatures in the interval of 100°C ranging from 500 to 2500°C. Resulting carbon fibres were characterized by mechanical properties, elemental analysis, XPS, Raman spectroscopy and X-ray diffraction.

Results and Discussion

Tensile strength of fibres increases continuously with increase in carbonization temperature (fig. 1) up to 1700°C to 3.7 GPa (except between 700 and 800°C) and decreases thereafter to 2.1 GPa at 2500°C. Increase in tensile strength is very sharp during the temperatures range of 1300-1500°C. On the other hand, Young's modulus continuously increases up to 2500°C to 425 GPa. This behavior of mechanical properties is similar as reported earlier[3].

Correspondingly, up to 1300°C, shrinkage in fibres both along and across the fibre axis is observed (fig.2) However, between 1300-1700°C, fibres show shrinkage only across the fibre axis (in the diameter decrease) and no shrinkage in both directions after 1700°C.

This indicates that up to 1300°C the structure development in the fibres takes place both along and across the fiber axis whereas between 1300°C and 1700°C, the changes are mostly along the lateral direction of the polymer.

Tensile strength slightly decreases during increase in temperature from 700 to 800°C. Same phenomenon was pointed in literature [4] but no explanatory study was done. Fig. 3 shows a relation between nitrogen/carbon ration (N/C) in bulk (elemental analysis) and on the surface (XPS) of the fibres with different carbonization temperatures. The N/C on the surface of the fibres carbonized to 600-900°C is found to be lower than that of the bulk, suggesting the denitrogenation on the surface started much earlier than in interiors of fibers. This delay in denitrogenation temperature on the surface and the interior may be due to poor thermal conductivity of the fibre in this region. Therefore, at 600-800°C the interior of fibres is less carbonized than surface which may create stresses in the fibers and results in decrease in the tensile strength of the carbon fibers (fig.1). Above 800°C, improvement in the thermal conductivity brings the uniformity in carbonization in the fibers and increases tensile strength again.

Raman spectrum of carbon fibers shows two bands at 1580 cm⁻¹ and 1360 cm⁻¹ (fig. 4). In the stabilized fibers, the intensity of the peak at 1360 cm⁻¹ is higher than the peak at 1580 cm⁻¹. This may be due to the oxygen and nitrogen containing groups e.g., -C=O, -COOH, -N=C, etc. in the polymer. The both bands were also not well separated. With the increase in the carbonization temperature, as the elements other than carbon go off from the polymer, the intensity of 1580 cm⁻¹ band increases and 1360 cm⁻¹ band decreases. The separation between the two bands is also increases. This behavior is more prominent above 1500°C probably due to the improvement of structure in the carbon fibres as shown by the improvement in the interlayer spacing d_{002} in the fibers after 1500°C (fig.5). Higher changes in the Raman bands and interlayer spacing during temperature increase from 2300°C to 2500°C shows increase in graphitization of fibers which is also observed in the sharp increase in the Young's modulus of the fibers (from 350 to 425 GPa as shown in fig. 1).

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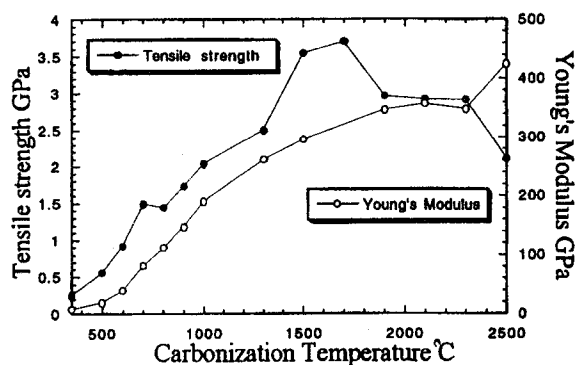


Fig. 1. Changes in tensile strength and Young's modulus of fibres with carbonization temperature

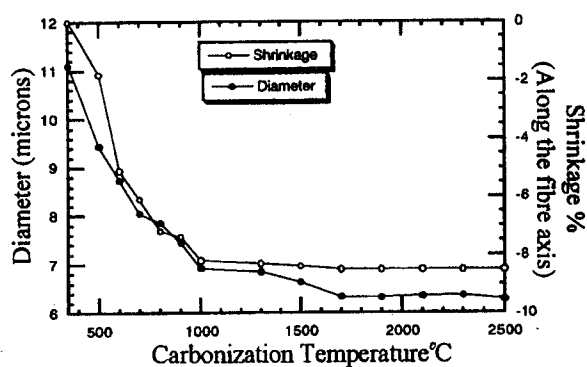


Fig. 2. Changes in diameter and shrinkage in fibres with carbonization temperature

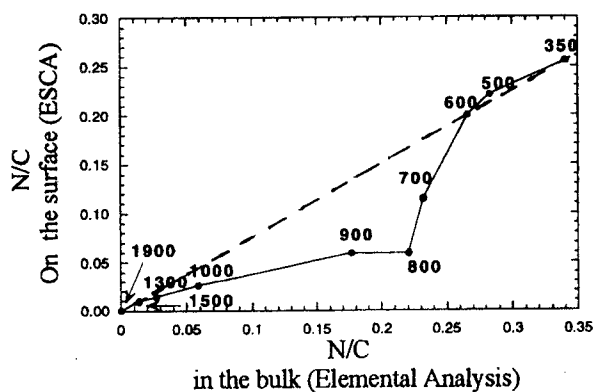


Fig. 3. Change in N/C ratio on the surface and in the bulk of fibres with different carbonization temperatures

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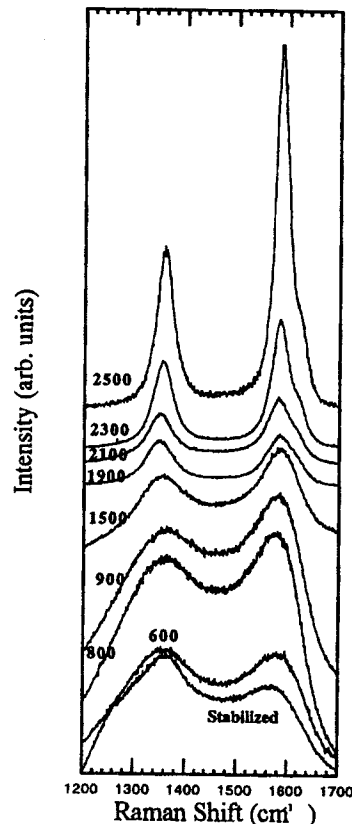


Fig. 4. Raman spectra of fibres carbonized to different temperature

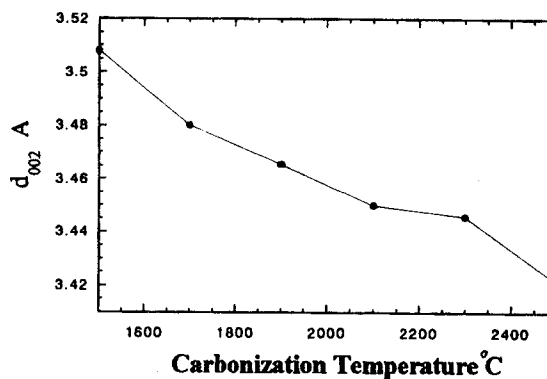


Fig. 5. Change in d_{002} of the fibres with carbonization temperature