WIDE, HIGHLY ORIENTED MESOPHASE PITCH-BASED CARBON TAPES: MECHANICAL PROPERTIES OF THE TAPES AND OF TAPE-DERIVED CARBON "SPRINGS"

A. Antonarulrajah, A. Westwood*, E. Galanopoulos, A. Eagles, J. Sansom and B. Rand
School of Process Environmental and Materials Engineering,
University of Leeds, Leeds, LS2 9JT, UK

**Corresponding author e-mail address:* a.v.k.westwood@leeds.ac.uk

SUMMARY

Highly oriented carbon tapes have been produced from mesophase pitch with thickness 10-20μm and width of *ca.* 1mm. The tapes show thickness shrinkage of 36% but only small width reductions of around 2% upon carbonisation. Increasing the heat treatment temperature resulted in an increase in the apparent density of the tapes. X-ray texture analysis for the transverse area of tape heat treated to 1600°C indicate that the predominant molecular arrangement is parallel to the tape's main surface although there is evidence of some tilting of the molecular planes in relation to the surface of the tape. The tapes were highly flexible after carbonisation at 1000°C despite the fact that their transverse areas were comparable to that of *ca.* 150 conventional carbon fibres. The strength and Young's modulus of these tapes compare favourably with those of commercial high performance carbon fibres of much lower transverse cross-sectional area. Continuous springs with diameters as low as 1-2mm were successfully formed from the carbon tapes. The potential of these carbon springs to act as biocompatible endovascular supports (or "stents") is currently being investigated with respect to their introduction / deployment and their in-situ behaviour within coronary arteries. As part of this study, the mechanical properties of the carbonised springs have been investigated. Following carbonisation to 1000°C, the springs were highly extensible and flexible with elastic extension to >2000%, in the case of 10mm diameter springs. Longitudinal spring stiffness measurements show "hardening" and "softening" behaviour upon extension for 0.70mm and 0.32mm-wide springs, respectively. Springs of 0.70mm wide tape show a radial compressibility of over 40% (reduction in diameter) and a radial strength of 0.04N/mm. These springs also remain intact upon twisting through more than 1000° in both clockwise and anticlockwise directions. The successful forming of springs and their subsequent mechanical performance can be greatly affected by the presence of various defects in the tape, as observed in SEM studies.

INTRODUCTION

Highly-oriented mesophase pitch-based carbon tapes have been developed with thickness 10-20μm and width of *ca.*1mm. The apparent density of the tape increased with heat-treatment up to ~ 1.9g/cm^3 at 1600°C and the preferred microstructural orientation was maintained. Optical microscopy, FEG-SEM and XRD pole figure analyses showed that the discotic mesogens in the tapes are aligned parallel to the tapes' main surface, and that the orientation was improved by heat treatment offering the potential for development of very highly graphitic structure. The graphitic nature of the tapes was demonstrated by X-ray powder diffraction results. The tapes can be shaped into highly flexible springs with diameter <2mm. The potential of these carbon springs to act as biocompatible endovascular supports (or "stents") is currently being investigated with respect to their introduction / deployment and their *in-situ* behaviour within coronary arteries. As part of this study, the mechanical properties of the carbonised tapes and springs will be presented including tape tensile properties, longitudinal spring strength / modulus and radial compressive strength and fatigue behaviour of the springs.

EXPERIMENTAL

2.1 Tape spinning and shaping

Mesophase pitch-based carbon tapes were produced from AR-MP-H naphthalene-derived synthetic mesophase pitch (*ex* Mitsubishi Gas Chemical Corporation) which has 100% anisotropic content and a softening point of 237°C. The mesophase pitch tape was prepared by melt extrusion and drawing followed by stabilisation and heat treatment. The apparent density of the tapes was measured by helium pycnometry using an AccuPyc 1330 pycnometer. Proprietary techniques were used to shape the tapes into springs with diameters as low as 1-2mm.

2.2 Tape structural characterisation

Polished surfaces and cross-sections of the carbon tapes were studied using a Nikon Optiphot cross-polarised light microscope in reflectance mode. The optical microscopy techniques used are reported elsewhere [1-3]. CamScan Series 4 and FEG-SEM scanning electron microscopes were used to study orientation within the carbon tapes. X-ray powder diffraction measurements were performed using nickel filtered CuK_α X-rays. X-ray texture scans were conducted in a texture goniometer using CuK_α radiation with a Schulz reflection-specimen holder, in which the source and detector were positioned at the fixed 2θ Bragg angle for reflection from the (002) planes.

2.3 Tape mechanical testing

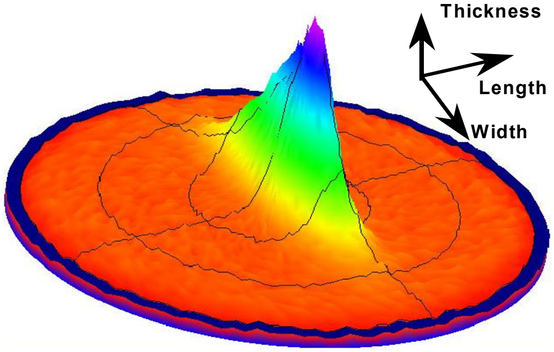
Tensile and radial compression testing was carried out on a SM50 MAYES mechanical testing machine. Longitudinal spring extension was measured using a 5N Spring-Balance and a 300mm ruler to measure the load and the extension of carbon-tape spring simultaneously. Qualitative torsional testing was carried out by fixing the ends of the spring sample twisting to a pair of flat circular surfaces which were perpendicular to the spring longitudinal axis and twisting one surface relative to the other surface whilst avoiding any longitudinal stretching of the spring.

RESULTS AND DISCUSSION

3.1 Tape microstructure

The liquid crystal mesophase pitch retains planar micro-domain units composed of discotic planar molecules in both its molten and solid states. Such micro-domains are closely and nematically packed in the solid or molten states. Shear stress during melt spinning deforms the micro-domains in the mesophase pitch and aligns them parallel to the tape axis, forming fibrils. Following stabilisation and carbonisation, the tapes show thickness shrinkage of 36% but only small width reductions of around 2%. Increasing the heat treatment temperature resulted in an increase in the apparent density of the tapes. The density of the stabilised tape was 1.35g/cm^3. After treatment to 1000°C, the apparent density increases to 1.75g/cm^3 and after treatment to 1600°C, the apparent density reaches 1.89g/cm^3, comparable to that of "graphitised" carbon fibres.

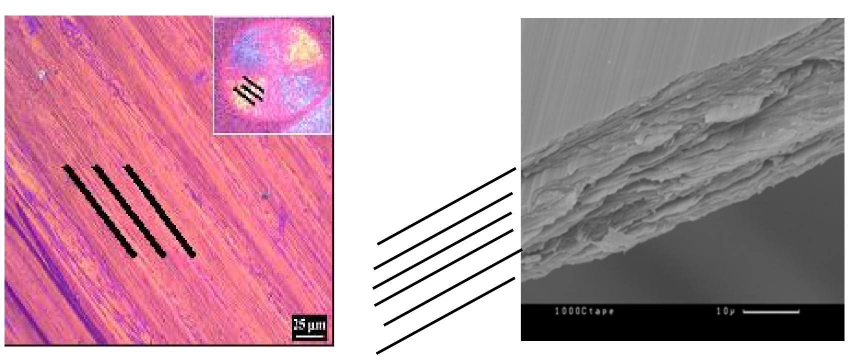
Figure 1 shows an X-ray pole figure for the transverse area of tape heat treated to 1600°C. The high intensity contours in the central region indicate that the predominant molecular arrangement is parallel to the tape's main surface. Nevertheless cross-polarised optical microscopy of the tape (figure 2) shows evidence of some tilting of the planes in relation to the surface of the tape. SEM images (figure 3) obtained for carbonised samples also agree with the information derived from the optical microscope images and the pole figures. X-ray diffractograms of the powdered tapes also show increasing graphitisation as heat-treatment progresses.



<u>*Texture misorientation (HWHM) angles:*</u>

21° about the length axis
6° about the width axis

Figure 1. X-ray pole figure of carbon tapes following heat treatment to 1600°C



Figures 2 and 3. Optical and scanning electron micrographs of transverse sections of carbonised tapes

3.3 Mechanical properties of carbon tapes

The tapes were highly flexible after carbonisation at 1000°C despite the fact that their transverse areas were comparable to that of *ca.* 150 conventional carbon fibres. The strength (>1GPa) and Young's modulus (*ca.* 150GPa) of these tapes compare favourably with those of commercial high performance carbon fibres of much lower transverse cross-sectional area. The development of tape strength with increasing heat treatment temperature is shown in figure 4.

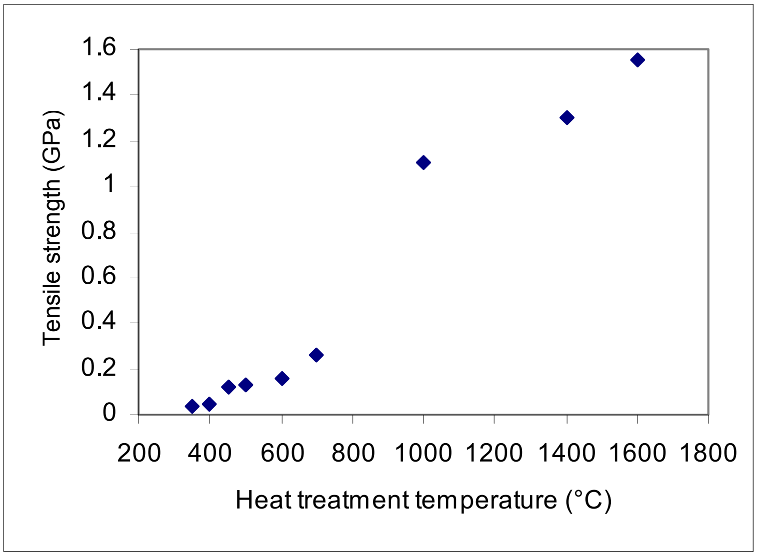


Figure 4. Tensile strength *vs.* heat treatment temperature of carbon tapes

3.5 Mechanical properties of carbon tape springs

Continuous springs (figure 5) were successfully formed from the carbon tapes.

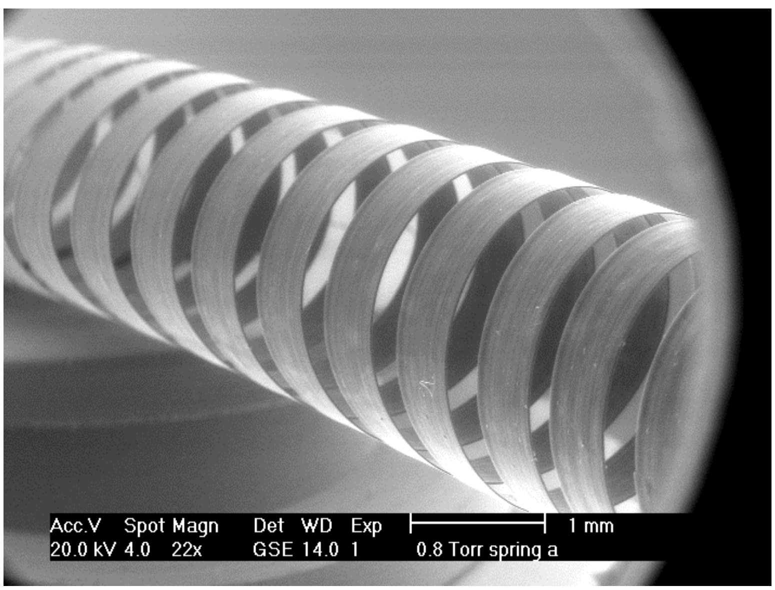


Figure 5. Scanning electron micrograph of continuous carbon tape spring

Following carbonisation to 1000°C the springs were highly extensible, *e.g.* with elastic extension to >2000% in the case of a 10mm diameter spring (figure 6).

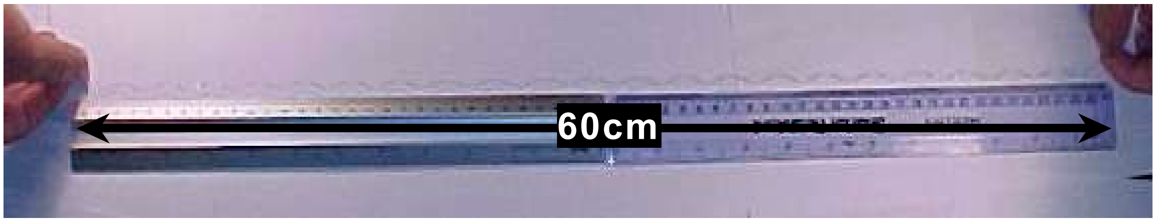


Figure 6. Demonstration of the elastic extensibility of the tape springs

The tape springs were also shown to possess a high degree of flexibility (figure 7).

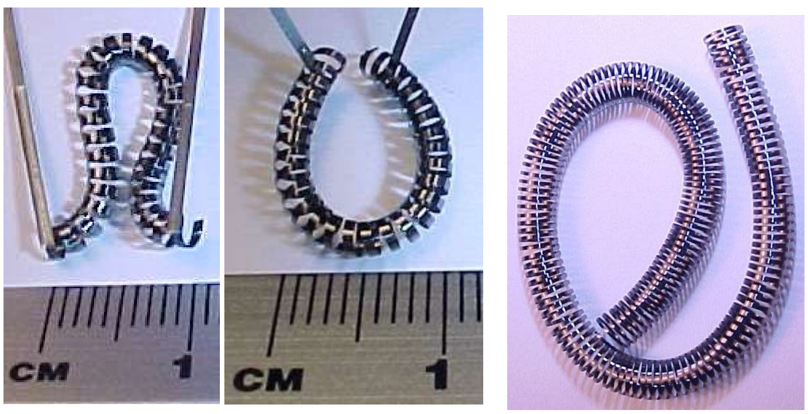


Figure 7. Demonstration of flexibility exhibited by carbon tape springs

Longitudinal spring stiffness was measured for 0.70mm and 0.32mm-wide springs as shown below in Figures 8 and 9, respectively:

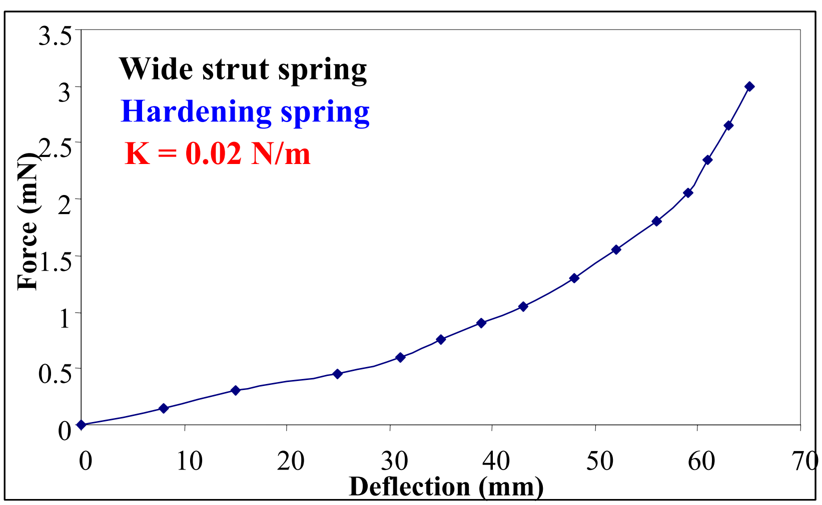


Figure 8. Longitudinal extension *vs* deflection of 0.70mm wide carbon tape spring

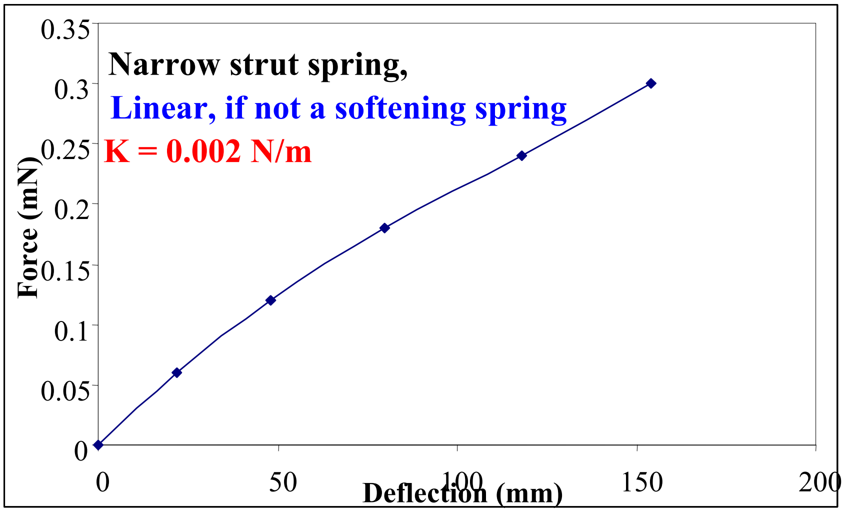


Figure 9. Longitudinal extension *vs* deflection of 0.32mm wide carbon tape spring

The spring formed from wider tape shows "hardening" behaviour whereas the spring formed from narrower tape tends toward "softening" behaviour in its extension.

The radial compressibility and strength of the springs have been measured. A spring of 0.70mm wide tape shows a compressibility of over 40% (reduction in diameter) and a radial strength of 0.04N/mm as calculated from the results shown below in Figure 10:

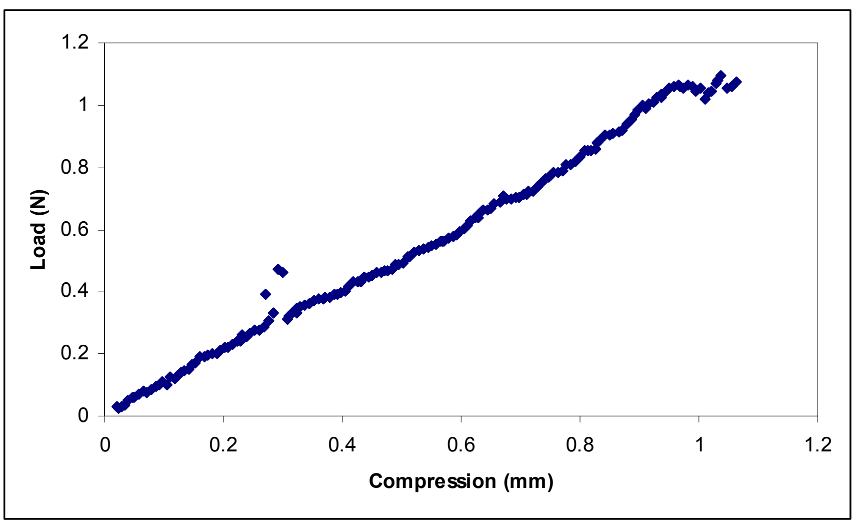


Figure 10. Radial compression *vs.* load for 0.70 mm wide spring

Resilience to torsional forces / twisting has also been assessed. A spring of 0.7 mm width tape can be twisted through over 1000°, in both clockwise and anticlockwise directions without breakage.

3.4 Sources of defects in carbon tapes and resulting springs

The successful forming of springs and their subsequent mechanical performance can be greatly affected by the presence of defects in the tape. The defects found are shown in the following SEM images (figures 11-13).

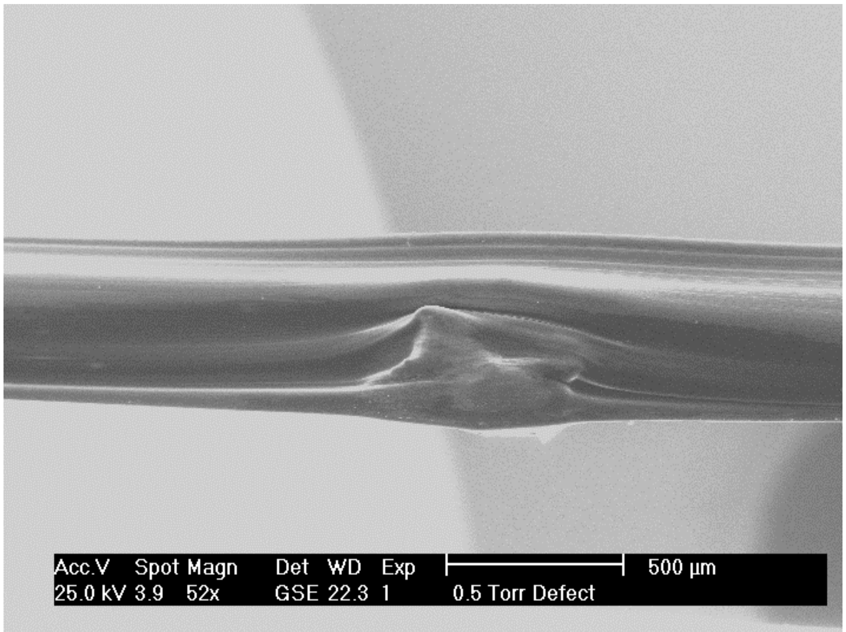


Figure 11. Nodes on the tape surface

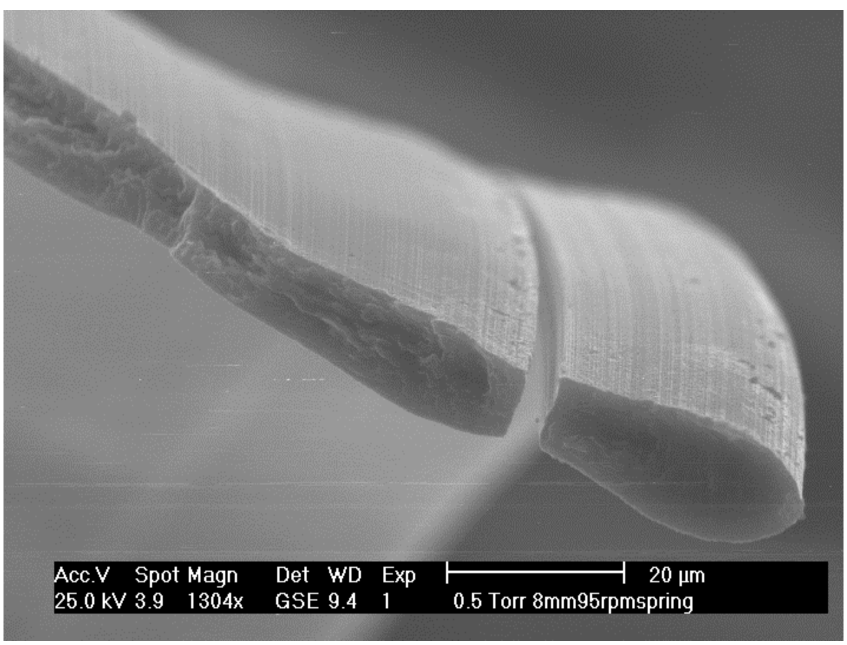


Figure 12. Striation lines on the face of tape cause the tape or spring split along its length

(Interestingly, the split continues along the length and does not cross along its width)

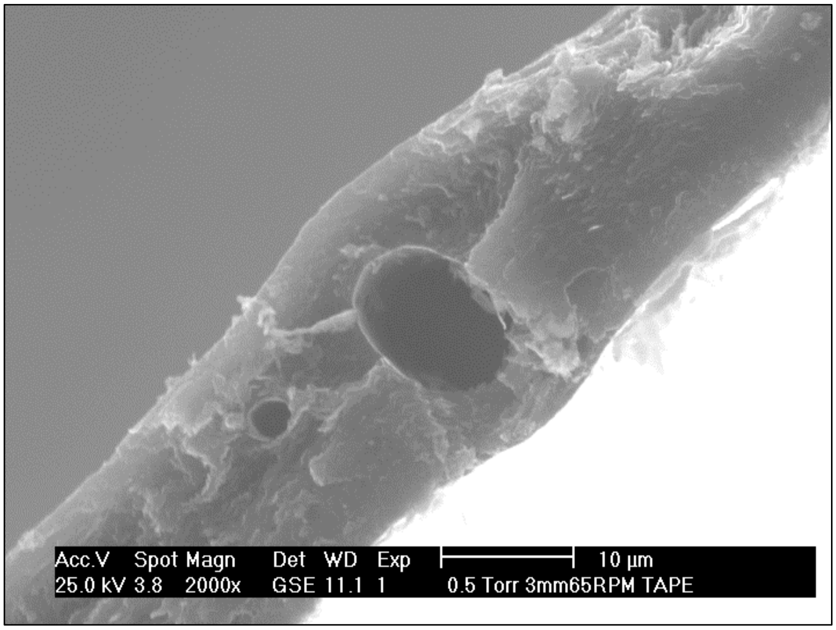


Figure 13. Pore within carbon tape resulting from air / gas entrapped during "melting" of the pitch precursor

CONCLUSIONS

Highly oriented carbon tapes have been produced from mesophase pitch which show thickness shrinkage of 36% but only small width reductions of around 2% upon carbonisation. Increasing the heat treatment temperature resulted in an increase in the apparent density of the tapes. X-ray texture analysis for the transverse area of tape heat treated to 1600°C indicate that the predominant molecular arrangement is parallel to the tape's main surface although there is evidence of some tilting of the molecular planes in relation to the surface of the tape. The tapes were highly flexible after carbonisation at 1000°C despite the fact that their transverse areas were comparable to that of ca. 150 conventional carbon fibres. The strength and Young's modulus of these tapes compare favourably with those of commercial high performance carbon fibres of much lower transverse cross-sectional area. Continuous springs with diameters as low as 1-2mm were successfully formed from the carbon tapes. Following carbonisation to 1000°C, the springs were highly extensible and flexible, *e.g.* with elastic extension to >2000% for a 10mm diameter spring. Longitudinal spring stiffness measurements show "hardening" and "softening" behaviour upon extension for 0.70mm and 0.32mm-wide springs, respectively. Springs of 0.70mm wide tape show a radial compressibility of over40 % (reduction in diameter) and a radial strength of 0.04N/mm. These springs also remain intact upon twisting through over 1000° in both clockwise and anticlockwise directions. The successful forming of springs and their subsequent mechanical performance can be greatly affected by the presence of defects in the tape. SEM studies reveal nodes, striation lines on the face of tape and pores within the tape, all of which can lead to weaknesses in the tapes and springs, if not controlled *via* careful processing.

REFERENCES

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