# Carbon fibres with ordered graphitic-like aggregate structures from a regenerated cellulose fibre precursor

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## ABSTRACT

The production and characterisation of low modulus carbon fibres is reported from a commercially available regenerated cellulose fibre (Cordenka™). The fibres were heat treated before graphitisation at a temperature of 200 °C. Fibres were then further heat treated and graphitised at a temperature of 2000 °C. Polarised Raman spectra of carbonised/graphitised fibres were recorded. The ratio of two Raman peaks located at ~1350 cm$^{-1}$ (D-band) and at ~1600 cm$^{-1}$ (2D band) – the $I_D/I_G$ ratio – was used to follow the onset and development of the carbon/graphitic structure. It is shown, using tensile testing, that single carbon fibres processed at 2000 °C have a modulus of ~70 GPa and strain at break >2%. A Raman spectroscopic method that follows the shift in the position of the 2D band suggests a modulus of ~77 GPa. Transmission Electron Microscope imaging of the fibres reveals a sub-structure containing aggregates of oriented concentric turbostratic carbon domains, some of which are reminiscent of carbon nanotubes. These relatively high strength fibres (1.5 GPa) could be possible alternatives to E-glass fibres in low weight (~30% lighter than E-glass), high volume automotive and marine applications. It is also shown that these fibres can be converted in a woven precursor form to a carbon fibre fabric without the need to weave brittle filaments.

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## 1. Introduction

Carbon fibres are entirely based on the element carbon and represent some of the lightest inorganic materials available for industrial application. Their use has dominated the recent surge in the development of lightweight composite materials, particularly for use in aerospace applications e.g. Boeing's 787 Dreamliner [1]. The use of carbon fibres for composite materials is set to grow dramatically over the next 5–10 years, with high volume market applications in the automotive sector being predicted to be one such growth area. Polyacrylonitrile (PAN) has been traditionally used as a precursor for high modulus/strength carbon fibres [2]. Before the development of PAN based carbon fibres, cellulose was used by Union Carbide in the 1950s to make mid-range modulus materials [3,4]. Production of carbon fibres using PAN is known to produce toxic gases e.g. hydrogen cyanide, whose extraction during the process increases costs [5]; this is not an issue for cellulose precursors. There has recently been a resurgence of interest in the use of more sustainable and environmentally friendly precursor materials for the production of carbon fibres, particularly

for medium stiffness and strength. Cellulose fibres lend themselves very well for this purpose [6], with continuous filaments being produced in an established industrial process and in large volumes for applications in the textile and tyre cord industries. Much progress has been made in the intervening years from the 1950s to develop highly oriented cellulose fibres, which could serve as much better precursors for carbon fibres. One such example are Cordenka fibres, the use of which for this purpose, is the topic of the present work.

Cordenka fibres are produced using a viscose process, with the addition of formaldehyde, forming a derivative of cellulose in sodium hydroxide, which is subsequently dissolved in carbon disulphide and converted back to cellulose using dilute sulphuric acid [7]. High stiffness fibres are produced, whose properties have been reported by a number of authors [8,9]. Their conversion to carbon fibres has not been previously reported, and neither their conversion from a woven form. Recent work has shown that both a liquid crystalline cellulose precursor and lyocell fibres can be converted to carbon filaments with moduli >100 GPa [10]. In the present work, the microstructure and micromechanics of graphitised Cordenka fibres and woven fabrics using Raman spectroscopy are reported.

The technique of Raman spectroscopy has been used to identify and characterise various forms of graphitic structures [11,12] and

to better understand the structure–mechanical properties of carbon fibres [13–17]. Typically the Raman spectrum of carbon fibres contains three main features; the G band (located at $\sim$1600 cm$^{-1}$), the D-band (at $\sim$1350 cm$^{-1}$) and the 2D (or G′) band (at $\sim$2660 cm$^{-1}$) [12,17]. The ratio of the intensities ($I_D/I_G$) can be used to give an indication of the level of graphitization of the material. It has been shown that both the G and 2D bands shift in position under the application of external tensile deformation [18]. Most notably it has been shown that the magnitude of the 2D band shift rate with respect to strain is directly proportional to the fibre modulus [15]; the same is true for the G band shift rate [19]. This approach allows one to predict the modulus of a carbon fibre based on a simple measurement of the shift rate with respect to strain of a single filament in air. The approach has previously been reported for Bocell fibres (a liquid crystalline spun cellulose fibre), and here now for Cordenka, a commercially available cellulose fibre that is widely used as a tyre cord yarn, and which can be woven in a fabric form, has also been reported as a potential composite reinforcement [20–23].

## 2. Experimental

### 2.1. Materials

The precursor fibre used for the preparation of carbon filaments was Cordenka-700. This is a commercial regenerated cellulose fibre with a linear density of 2440 dtex. The specified mechanical properties for this fibre are: breaking force 96.1–184.6 N, breaking tenacity 510–483 mN tex$^{-1}$. In addition a plane weave fabric using the same fibres was supplied by Cordenka GmbH. The fabric type was MA1 with a weight of 295 g m$^{-2}$.

### 2.2. Pretreatment of cellulose fibres

The pre-treatment (or stabilisation) process of the fibres was carried out in an Elite 2216CC tube furnace (Elite Thermal System Limited). The fibres were first cut into short bundles and placed in a ceramic boat. Prior to the heating, the tube was purged with nitrogen for 30 min to remove air and to stabilise the nitrogen flow. Fibres and fabrics were initially pre-treated by heating to 200 °C in nitrogen at a rate of 2 °C min$^{-1}$, followed by a 30-min isotherm at the final maximum temperature.

### 2.3. Carbonisation and graphitisation of cellulose fibres and fabrics

Cordenka-700 fibres and woven fabrics were first cut into 50 mm bundles (50 × 50 mm fabrics) and placed in a graphitic furnace insert separated by graphite sheets. Prior to the heating, the chamber was pressurised under vacuum for 5 min to remove air, which was maintained up to 900 °C. The process of carbonisation and graphitisation of the fibres was performed according to the following procedure: Fibres were initially pre-treated by heating to 240 °C in a vacuum at a rate of 5 °C min$^{-1}$, followed by a 30 min isotherm at the final maximum temperature. The sample was carbonised by heating up to 900 °C in a vacuum, then up to 1500 °C in an argon atmosphere at a rate of 10 °C min$^{-1}$, again followed by a 30-min isotherm at the final maximum temperature. In the case of the carbonisation process at 2000 °C, the heating rate amounted to 10 °C min$^{-1}$ up to 1700 °C and subsequently to 2000 °C at a rate of 5 °C min$^{-1}$, followed by a 30-min isotherm at the final maximum temperature. The processes were carried out in a HPW25 hot press furnace (FCT System GmbH). Cordenka-700 fibres carbonised at 400, 600, 800, 1000, 1500 and 2000 °C are labelled as Cordenka 700–400, Cordenka 700–600, Cordenka 700–800, Cordenka 700–1000, Cordenka 700–1500 and Cordenka 700–2000, respectively.

Woven fabrics were placed in a graphite 'box/coffin' and were initially stabilised by heating in a coke dust environment. The material was stabilised by heating to 200 °C at a rate of 2 °C min$^{-1}$, followed by a 90-min isotherm at the final maximum temperature. Graphitisation of the stabilised textile was performed in a resistance heated furnace (called a "Holman Tube"). The long sidewalls of the furnace were connected to the electrodes and act as the resistance heating elements. The furnace was at set 2950 °C at the start of the hold and by the end of the 1.5–2.0 h hold the temp was 3060–3085 °C.

### 2.4. Electron microscopy of fibres

The morphology of pure and carbonised Cordenka-700 fibres were studied using a HITACHI S3200N SEM-EDS scanning electron microscope operated at an acceleration voltage of 5 kV. Prior to imaging, the fibres were fixed on metal stubs using carbon tape and sputter-coated at $\sim$20 mA with a thin layer of gold. To perform Transmission Electron Microscopy (TEM) of carbonised fibre samples were embedded in a low-viscosity epoxy resin (Spurr™). The embedded bundles were cut using a diamond knife into slices of $\sim$100 nm thickness. The fibre bundle axis was oriented perpendicular to the cutting plane. The slices were deposited onto 400 mesh TEM copper grids (holey carbon films) and imaged using a JEM-2100 LaB6 TEM operated at 200 kV in a bright field mode. The magnifications used for the collection of SEM images were 1000× and 2000×, while for TEM images 400,000× was used.

### 2.5. Polarised Raman spectroscopy

Orientation of the cellulose chains and graphite planes along the fibre axis were studied using Raman spectroscopy. The measurements were performed using a Renishaw RM-1000 System equipped with a thermoelectrically cooled CCD detector. The laser was focused on the samples using a Leica microscope with a 50× objective lens. For the cellulose fibres, a 785 nm wavelength laser was used to record spectra using an exposure time of 10 s and three accumulations. The power of the laser was reduced to 50% of the source power. The incident and scattered laser light were polarised parallel to the principal axis of the spectrometer. This polarisation configuration is denoted "VV". The Cordenka 700 fibres' axes were oriented parallel to the polarisation configuration of the laser light used to excite and record the Raman scattering. A half-wave plate was used to rotate the polarisation direction for incident light, while a polariser/analyser was used to maintain the polarisation direction of scattered light parallel to the principal axis of the spectrometer. The incident laser light was rotated from 0° to 180° and each Raman spectrum was recorded at 4° increments. The intensity of a Raman band located at $\sim$1090 cm$^{-1}$ was used for the orientation studies of the cellulose. This band was fitted using a Lorentzian function. Intensities outputted from this fitting procedure were normalised to a Raman band localised at $\sim$1262 cm$^{-1}$ (which does not change in intensity with rotation of the sample). This approach allowed two polarisation arrangements; first where the incident and scattered light are parallel to the principal axis of the spectrometer ("VV" configuration) and second where the polarisation of incident light is rotated by 90° by the half-wave plate ("HV" configuration).

For the carbon fibres, a 532 nm wavelength laser was used to record Raman spectra using an exposure time of 10 s and five accumulations. The power of the laser was reduced to 1% of the source power to avoid heating effects. The fibres' axes were oriented parallel to the polarisation configuration of the laser light. The incident laser light was rotated from 0° to 180° using a half-wave plate and each Raman spectrum was recorded at 5° increments. The D, G and 2D Raman bands were used for the carbon fibre