

Potential stiffness of carbon fibres produced from highly crystalline cellulose

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For some time, the use of cellulosic fibres as precursors for medium strength and stiffness carbon filaments has been industrially and experimentally investigated [1]. In recent times this research area has regained interest [2], due to the development of new fibre spinning processes [3] and the potential for bio-templating the cellular structures, such as wood, that cellulose can form [4]. Carbon structures from cellulose and derivative materials have also been topics of recent studies, of which particular highlights have been the manufacture of nanospheres [5] and a hierarchical porous structure formed from an acetate derivative [6].

The properties of the graphite produced by pyrolysis of cellulose largely depends on the nature of the precursor. The pyrolysis of natural, yet highly crystalline sources of cellulose, such as bacterial, where when the resultant material is intercalated with dopants has shown that increased conductivity, similar to soft carbon, can be achieved [7]. The structure of a number of other carbon materials produced from highly crystalline cellulose precursors (bacterial, algal, and tunicate) has also been reported [8]. The potential benefits of incorporating highly crystalline cellulose materials from bacterial [9] and animal [10] sources into composite materials are also well-known.

Raman spectroscopy has been used to determine the stiffness of a number of materials, particularly polymeric fibres [11]. The technique relies on the determination of the rate of shift of a particular spectral band, which is typically representative of a moiety along the backbone of the poly-

mer or main axis of the structure, as a function of applied tensile or compressive deformation [11]. This technique has been used to determine the stiffness of carbon nanotubes based on model of compressive deformation under cooling data obtained using Raman spectroscopy [12] and by 4-point bending dispersed material on a resin beam [13]. In the present paper we report the use of the resin beam technique to determine the relative stiffness, compared to published data on carbon, of a pyrolysed tunicate cellulose, and show that it could be a potential reinforcement in composite materials. This is an important result, as it shows for the first time the potential mechanical benefit of carbonising cellulose nanowhiskers for this purpose.

Tunicate cellulose samples were obtained in sheet form and pyrolysed at 800 °C in an oven using a method that has been previously described [8]. Higher temperatures were attempted, but the handling of the material was found to be difficult, and therefore this temperature was deemed suitable for these initial studies. It is however acknowledged that higher temperature values may induce enhanced mechanical properties. Raman spectra were recorded from non-pyrolysed and pyrolysed material using a Renishaw System 1000 spectrometer (633 nm laser) using a $\times 50$ objective lens which focussed the laser spot to a 2 μm spot size on the surface of the samples. Tunicate material, from non-pyrolysed and pyrolysed sources was dispersed into a cold-curing two-part epoxy resin (LY5052/HY5052) and then smeared onto a pre-prepared beam of the same material. Using a strain gauge attached to the surface of the beam, and a customised 4-point bending rig, samples were deformed in tension and spectra recorded at increasing increments of tensile strain. An exposure time of 10 s, using 10 accumulations was used, to obtain the spectra, and the polarisation of the laser was set parallel to the sample with the analysing polariser also positioned in the same configuration. Each

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spectrum was curve fitted using a mixed Gaussian/Lorentzian function to obtain the peak positions. A more detailed description of this experimental set-up and methodology can be found in a previous publication [14].

Typical Raman spectra, obtained from the pure tunicate (non-pyrolysed) and the pyrolysed material are shown in Fig. 1. The spectra obtained from pure tunicate (non-pyrolysed) material were found to be typical for cellulose-I, with a clear and intense peak located at 1095 cm^{-1} , which is thought to represent the C–O ring stretch vibration [15]. The pyrolysed sample spectrum indicates the presence of a broad and low intensity D-band (at about 1357 cm^{-1} , A_{1g} -mode) and a more intense G-band (1580 cm^{-1} , E_{2g} -mode), the structural source of which have been known for some time [16]. The Raman spectrum from this sample also shows the complete extinction of the cellulose peaks present for the precursor, which is an indication of the extent of graphitization. It has also been known for some time [16] that the magnitude of the intensity ratio of the D-band to the G-band is inversely proportional to the crystallite size (L_a). A decrease in the lateral dimensions (L_a) of graphite crystals has been observed for pyrolysed wood (cellulose-I) with increased temperatures [4], and it is thought that this may occur at higher temperatures for the tunicate samples (also cellulose-I), although this requires further work to confirm this.

The positions of the 1095 cm^{-1} band in the non-pyrolysed tunicate and the 1580 cm^{-1} G-band in the pyrolysed samples were found to shift towards a lower wavenumber (Fig. 2). This shift is thought to be due to the direct stress-transfer and deformation of the C–O bonds within the tunicate cellulose structure [14] and the C–C bonds in the graphitic structure of the pyrolysed material [13]. It is immediately evident that both bands have very

different band shift rates with respect to the applied tensile strain. The shift rate with respect to strain, in polymeric materials such as cellulose, has been shown to be proportional to the fibre modulus [17]. This effect has also been shown to hold true for both PAN- and pitch-based carbon fibres [18]. A previous report on the band shift rates in tunicate samples [14], under similar experimental conditions, yielded a value of $-2.5\text{ cm}^{-1}/\%$. The value reported here is clearly much higher than this ($-10.3\text{ cm}^{-1}/\%$), although we have used parallel–parallel polarisation in this instance, and therefore we expect that only fibres orientated in the same orientation as the strain applied are being recorded, rather than the effect of a network of fibres previously reported [14]. However, the 1580 cm^{-1} G-band in the Raman spectra for the carbon material formed by pyrolysis shifts at a rate of $-20.9\text{ cm}^{-1}/\%$. This indicates a much stiffer material than the cellulosic precursor, and

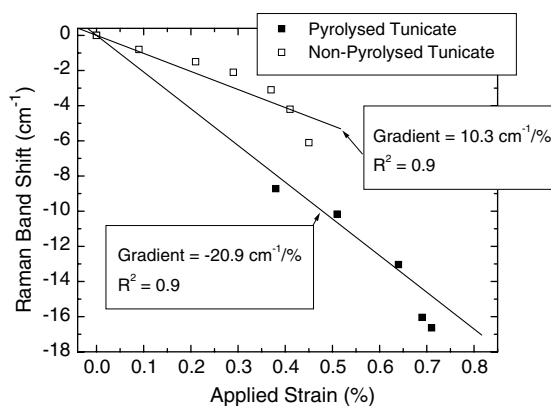
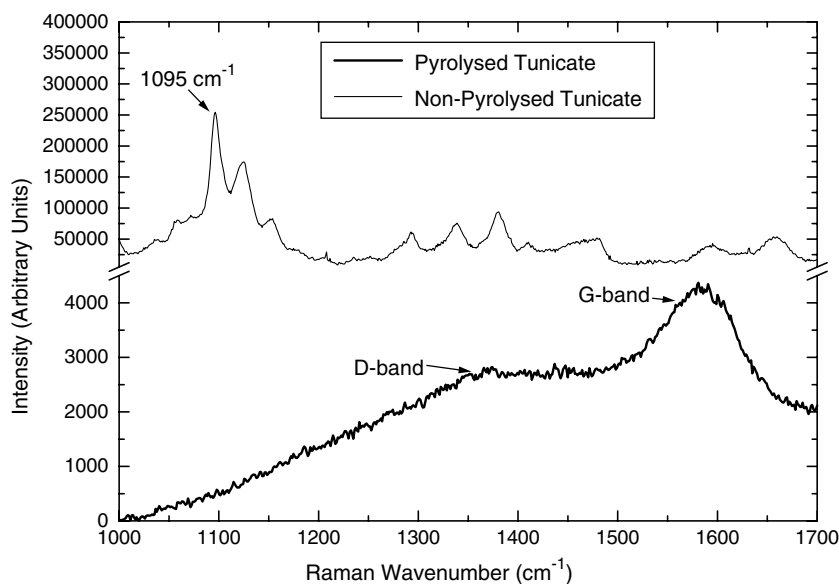


Fig. 2 Relative Raman band shifts for the 1580 cm^{-1} G-band from pyrolysed tunicate cellulose and for the 1095 cm^{-1} C–O band from non-pyrolysed cellulose

Fig. 1 Typical Raman spectra obtained from non-pyrolysed and pyrolysed tunicate samples indicating the positions of the 1095 cm^{-1} C–O stretch, a broad D-band (1357 cm^{-1}) and a G-band (1580 cm^{-1})



therefore its potential as a reinforcing phase is demonstrated. Huang and Young [18] have reported values for PAN and pitch based carbon fibre band shift rates for the 1580 cm^{-1} band in the range $-4\text{ cm}^{-1}/\%$ to $-12\text{ cm}^{-1}/\%$, with moduli ranging, in proportion to these, from 150 GPa to 700 GPa. However, the data reported [18] were obtained using different polarisation conditions to those used here. It is therefore clear that high stiffnesses can be obtained from pyrolysed cellulose whiskers, such as tunicate, but more work is required to determine the exact mechanical properties of this potential reinforcing phase.

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