What are the ranges and basis of auxeticity in the phases of cellulose microfibrils?

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ABSTRACT

The 1D bundles of cellulose microfibrils (lignified flax fibre) and 2D networks of cellulose microfibrils from tunicate, bacterial and microfibrillated cellulosues were strained in tension, and their molecular deformation followed by Raman spectroscopy in order to fully understand the ranges and basis of in-plane auxeticity for informing innovation in material processing and application. Cellulose is found to exhibit four distinct yielding points. Both crystalline and amorphous cellulose are found to be auxetic so long as interchain hydrogen bonding remains intact. Auxeticity of crystalline cellulose is found to be around unity (-1) while that of cellulose amorphous is found to be around twice (-2) that of crystalline cellulose with the possibility of auxeticity higher than -7 in 1D bundles of cellulose microfibrils in the absence of lignin. Though the network structure enhances strain to failure, they also significantly limit auxeticity in single 1D cellulose microfibrils in networks. Amorphous must exhibit higher auxeticity than crystals because amorphous has less interchain hydrogen bonding than crystals linking the chiral cellulose molecules together. The chirality of cellulose molecules must be responsible for auxeticity of cellulose microfibrils. Auxeticity must be directly correlated with the number of interchain hydrogen bonding. The similarity of the pattern of in-plane auxeticity of cellulose microfibrils to the off-axis auxeticity of zeolites (especially thomsonite zeolites) indicates the possibility of combining both phase change, semi-crystalline materials in nanosized composites with photo-electromechanical properties.

Keywords: Axial, lateral, expansion, Poissons, ratio and unusual.

1. INTRODUCTION

For many years, materials and structures have been unknowingly applied for their auxeticity (Evans and Alderson, 2000). Increasing understanding of auxeticity points to the fact that where auxeticity exists, it often exists with other desired properties such as increased indentation resistance, shear stiffness, break resistance, acoustic response, negative linear compressibility, and negative thermal expansion. Increasing knowledge of auxeticity in several substances increasing points to the fact that auxeticity is due to geometry than chemistry at a particular length scale which may translate to higher length scales (Yao, et al., 2012; Peura et al., 2006; Nakamura et al., 2004; Franke et al., 2011; Tanpichai et al., 2012; Yao et al., 2008; Coluci et al., 2008; Hall et al., 2008; Chen et al., 2009; Ma et al., 2010; Scarpa et al. 2010). Cellulose microfibril networks (Tanpichai et al., 2012) and fibre networks (Verma et al., 2014) are reported to exhibit different ranges of auxeticity in and out of plane but the origins of auxeticity in networks are not known.
Cellulose being the most plenteous natural polymer on earth shows potential to be better than steel. The desire for auxeticity and associated properties, and the opportunities that Raman spectroscopy presents for measuring atomic and molecular effects of cellulose, makes it overly needful to attempt to fully ascertain the ranges and basis of auxeticity in cellulose microfibrils, and how auxeticity may translate from the molecular (nano level) to higher lengths scales. A sample each of non-native 1D bundle and 2D networks of cellulose microfibrils from tunicate, bacterial and microfibrillated sources were strained in tension in a Deben micro-tester, and their molecular deformation followed with Raman spectroscopy.

2. FINDINGS

A model arrangement of cellulose and its accompanying Poisson’s ratio; the yield points of the bonds within cellulose microfibrils; the in-plane intensity map of cellulose microfibrils; the stress-strain behaviour of cellulose microfibrils; the ranges of in-plane Poisson’s ratios are described.

2.1 Arrangement of Cellulose Crystals and Amorphous

To fully appreciate the ranges of auxetics in the plane, the physical boundaries in which auxeticity operates in cellulose microfibrils must be appreciated. Non-native (processed) cellulose microfibrils whether in network or bundle crystals could be considered to be in a continuum with amorphous phases in alternating pattern throughout the nanoscale. A Raman light, whether on a 1D bundle of cellulose microfibrils or a 2D network of cellulose microfibrils could be considered to be covering a spot within which there is an alternate arrangement of crystal and amorphous phases (fig. 1).
C-O-C bonds of amorphous phases, whether in predominant tension or compression, vibrate somewhat confined by the long sides of crystal phases in the lateral direction or by the cross-sections of crystal phases in the axial direction or unconfined in the acute (45°) direction (fig. 2).

Figure 1: A schematic of the alternate arrangement of cellulose crystals and amorphous phases in cellulose microfibrils and its accompanying Poisson’s ratios.
Before any energy in the form of irradiation or strain is applied to cellulose microfibrils, the C-O-C bonds are in the ground (undisturbed) state. When energy is initially applied, cellulose is plunged into an excited completely reversible energy state in which the mean interatomic distances of C-O-C bonds in the amorphous phase are reset in the respective directions in-plane based on inherent confinements in spot imposed by the size of spot crystals. These two variants pre-determine the limits of mean vibrational frequencies of C-O-C bonds in the amorphous phase and those immediately in continuum with the crystal phase within spot as a direct function of spectral intensity (mean frequency of vibration). In generality, when initial mean interatomic distances of C-O-C bonds are relatively too wide or too narrow, mean vibrational frequency of the C-O-C bonds (1095 cm⁻¹ band intensity) would be seen to be lower. However, when initial mean interatomic distances of C-O-C bonds are not too far apart or too close together, then initial mean vibrational frequency of the C-O-C bonds are optimal and characteristic in the different directions in-plane. Hence, why C-O-C bonds in the amorphous phase lying solely in the acute (45°) directions in the plane with limited compressibility but unlimited extensibility register the

Figure 2: A schematic of a random network of cellulose microfibrils under uniaxial tensile strain showing instances of the majority of spot cellulose microfibrils in predominant tension or compression.
lowest mean vibrational frequency (1095 cm\(^{-1}\) band intensity). In the lateral directions, the long sides of crystal phases confine the extensibility of the C-O-C bonds of the amorphous and make them register relatively higher vibrational frequency (1095 cm\(^{-1}\) band intensity) in this direction. In the axial directions, crystals and amorphous form an immediate continuum and C-O-C bonds herein are fairly unconfined, thus registering relatively higher vibrational frequency (1095 cm\(^{-1}\) band intensity).

2.2 Yield Points of the Bonds in Cellulose Microfibrils

In generality, crystals phases are known to be stiff while amorphous phases are known to be fluid (somewhat colloidal). The stiffness of crystal phases and the fluidity of amorphous phases form the basis of the ‘varying strain-uniform stress’ assumption (Young and Eichhorn, 2007), on which material indices including Poisson’s ratios are sometimes calculated. Being more sorptive or hygroscopic, compliant, shear resistant, incompressible and limitlessly extensible, amorphous phase eventually receive a significant proportion of the stress from crystal phases and act as a cushion or shock absorber for crystals phases. Being stiffer, non-fluid and sorptive, crystal phases receive stress first and transfer it to the amorphous phases. Crystals are stiffer because their C-O-C bonds are stiff and well reinforced laterally by possibly re-entrant intermolecular hydrogen bonds, which must rupture before the C-O-C bonds themselves directly bear strain (fig. 3); the reason the limits of mechanical properties (determined by extents of molecular vibrations) of all cellulose bundles and networks are mainly determined by the dimensions of crystal phases as dictated by the packing (influenced by the relative amounts of rotamers) of cellulose chains from source (species and tissue).
Dimensions of crystal phases play a crucial role in defining the limits of the mean vibrational frequency of the C-O-C bonds (spectral intensity) in the respective directions in-plane (figs. 4 and 5).

Figure 3: Raman band shift with strain for a 2D random network of bacterial cellulose under polarisation inclination $\phi=45^\circ$ parallel to the principal spectrometer axis.
Crystals have been described as cubic to cuboid shapes through which light is polarisable to produce splendid colours which could change in the presence of certain stimuli to serve as sensors.

Figure 4: Intensity of Raman band located at 1095 cm$^{-1}$ as a function of rotation angle ($\phi$) for straight a 1D lignified flax fibre, a 2D random network of microfibrillated cellulose, a 2D bacterial cellulose and a 2D tunicate cellulose at 0.00% strain.
2.3 Intensity Map of Cellulose

Unlike the horizontally lying dumbbell-like intensity (of 1095 cm$^{-1}$ band) plots shown in Tanpichai et al. (2012) for 1D bundles of cellulose microfibrils without strains, intensity plots for both 1D bundle of cellulose microfibrils and 2D networks of cellulose microfibrils without strain rather showed as two orthogonally intersecting dumbbells using both half and quarter wave plates (figs. 4 and 5) just as is depicted in the off-axis auxetics plots for thomsonite zeolites (Grima et al., 2000). From the intensity and auxeticity plots, auxetics is highest in the acute (45°) direction (all amorphous) where the 1095 cm$^{-1}$ intensity is lowest. Hence, band intensity and auxeticity must be inversely related.

Figure 5: Intensity of Raman band located at 1095 cm$^{-1}$ as a function of rotation angle (Ø) for a 1D lignified flax fibre, a 2D random network of microfibrillated cellulose, bacterial cellulose and tunicate cellulose at 0.00% strain.
Intensity plots of both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils with strain showed the same orthogonally intersecting dumbbell-like shapes as those without strain (figs. 6 and 7), unlike the disfigured or unpreserved orientational plots Tanpichai et al. (2012) presented for the 2D networks of cellulose microfibrils. Unlike the intensity plots of both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils without strain by Tanpichai et al. (2012) which clearly dip in the lateral direction, intensity plots of both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils with and without strain rather clearly dipped in the acute direction (figs. 4; 5 and 6; 7). Intensity points stay relatively closer to each other while the entire plot negatively slopes, diminishes (from damping: the building of residual atomic vibrations) and shapes roughly for both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils without strain. The cellulose microfibril angle of $9.6 \pm 2.5^\circ$ for 1D bundles of cellulose microfibrils (flax fibre) is attainable only when intensity plots are presented as Tanpichai et al. (2012) did. Intensity plots for both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils prove to have the same shape in this work because cellulose molecules of both 1D bundles of cellulose microfibrils and 2D networks of cellulose microfibrils from any source have the same orientation about their long axis within the light spot. This can be very useful material forensics in easily identifying cellulose in composites and mixtures. Though intensity plots by Tanpichai et al. (2012) are not consistent with plots in this work, it is still possible to determine cellulose microfibril angle by the biggest angle on the horizontal dumb bell of the intensity plots. Consequently, the relations:
\[ I = a + b \cos^4(\varnothing + \theta) \]

\[ S_{\nu} (\varnothing) = \frac{S_0}{2} (1 - v) + \frac{S_2}{3} (1 + v) \cos(2\varnothing) \]

\[ S_{VH} (\varnothing) = \frac{S_0'}{2} (1 - v) \]

(Where \( v = 0.11, \nu = 0.89 \) and \( \nu' = 5.7 \); \( S_{VV} \) and \( S_{VH}(\varnothing) \) = the band shift rate at an angle \( \varnothing \) in the axial and lateral directions respectively; \( \theta = \) band shift rate for fibre aligned parallel to strain direction, and \( \nu = \) Poisson’s ratio of the matrix of the composite), put forward by Tanpichai \textit{et al.} (2012) does not hold wholly true for both 1D bundle and 2D networks of cellulose microfibrils. Discrepancies must arise out of misrepresentation and misinterpretation.

Figure 7: Intensity of Raman band located at 1095 cm\(^{-1}\) as a function of rotation angle (\( \varnothing \)) for a 1D lignified flax fibre, a 2D random network of microfibrillated cellulose, bacterial cellulose and tunicate cellulose.
Under significant strain, shape of intensity plots stays the same as for samples without strain, only the intensity points for samples with strain stay relatively further apart from each other while the entire plot also loses negative slope and wanes less for both 1D bundles and 2D networks of cellulose microfibrils (figs. 4; 5 and 6; 7). Plots stay further apart under strain because C-O-C bonds possess higher mean interatomic distances (vibrational frequency) under strain within the optimal range. Under significant strain, cellulose chains with C-O-C bonds stretch and straighten (lose kinks), thereby becoming more homogenous (figs. 6 and 7). Straightening and homogenization of cellulose chains under strain also cause C-O-C bonds to lose residual vibrations (damping) whose frequencies otherwise build and interfere destructively with whole vibrational frequencies of the C-O-C bonds. Hence, cellulose microfibrils without strain would be preferred for vibration damping applications than cellulose microfibrils with some strain. Gaps are seen in the intensity plots after the first few irradiations or halts in irradiation in the 2D networks of cellulose microfibrils without strain (fig. 5). These reveal that cellulose changes energy state after the first few completely reversible irradiations in the absence of any further irradiation. Evidence yet to be published, shows that different states and/or limits of energy of cellulose are characterised by different relative amounts of gg (gauche-gauche), gt (gauche-trans) and tg (trans-gauche) rotamers which in turn influence the level of disorder between chains (degree of crystallinity) and the tendencies of interconversion of allomorph and possibly of polymorph in non-native (processed) cellulose I (Jarvis, 2000). Raman band intensities are generally higher in the different directions of the 2D networks than the 1D bundle of cellulose microfibrils because in 2D networks of cellulose microfibrils, mean vibrational frequencies of C-O-C bonds in the different directions are recorded from a lot more cellulose microfibrils in the light spot.

2.4 Stress-Strain Behaviour of Cellulose
Stress-strain curves reveal stress and strain values typical of those measured for all cellulose bundles and networks (Eichhorn et al., 2001; Eichhorn and Young, 2001) (fig. 8).
Figure 8: Stress-strain curve of a 1D lignified flax fibre ($E = 9.88e-01 \pm 5.1e-02$ GPa; $R^2 = 0.99$); a 2D random network of microfibrillated cellulose ($E = 0.05602 \pm 0.00417$ GPa; $R^2 = 0.98$); bacterial cellulose ($E = 0.02454 \pm 0.00149$ GPa; $R = 0.99$); and tunicate cellulose ($E = \ldots$

Under axial strain, the 1095 cm$^{-1}$ Raman band continually shifts to lower wavenumber (towards 0) as depicted by Tanpichai et al. (2012) (fig. 9).
As was not found in work by Tanpichai et al. (2012), band shifts per stress (fig. 10) and band shift per strain (band shift rate) (fig. 11) in-plane reveal clear differences between those measured in the axial and lateral directions and those measured in the acute directions.

Figure 10: Raman band shift per stress with waveplate rotation angle ($\varnothing$) for a 1D lignified flax fibre, a 2D random network of microfibrillated cellulose, bacterial cellulose and tunicate cellulose.
Band shift rates show a better correlation with strain than with stress (Tanpichai et al., 2012). Here too, the absence of band shifts per stress and band shift rates in Tanpichai et al. (2012) for the acute directions must arise out of misinterpretation. Shift rates are found to be between -0.94 and -2.00 cm\(^{-1}\) %\(^{-1}\) in the axial direction, and between -1.20 and -1.70 cm\(^{-1}\) %\(^{-1}\) in the lateral direction, and between -4.7 and -5.0 cm\(^{-1}\) %\(^{-1}\) in the acute direction of the 1D bundle of cellulose microfibrils (flax fibre). Axial shift rate is higher than that by Eichhorn and Young (2001) of -0.72 cm\(^{-1}\) %\(^{-1}\) for crystals of flax fibre deformed in bending. Variations that come with different species and tissue or even processing must account for this. Shift rates are found to be between -0.31 and -0.64 cm\(^{-1}\) %\(^{-1}\) in the axial direction, and between -0.30 and -0.44 cm\(^{-1}\) %\(^{-1}\) in the lateral direction, and between -0.62 and -0.65 cm\(^{-1}\) %\(^{-1}\) in the acute direction of bacterial cellulose. Axial shift rate is lower than what was reported by Hsieh et al. (2008) of -1.77 cm\(^{-1}\) %\(^{-1}\) for bacterial cellulose deformed in tension for the same reasons as for flax fibre. Shift rates are between -2.60 and -3.00 cm\(^{-1}\) %\(^{-1}\) in the axial direction, and between -2.4 and -2.75 cm\(^{-1}\) %\(^{-1}\) in the lateral direction, and between -1.6 and -1.9 cm\(^{-1}\) %\(^{-1}\) in the acute direction of tunicate cellulose. Axial shift rate is in the order of what was reported by Sturcova et al. (2005) of -2.4 cm\(^{-1}\) %\(^{-1}\) for tunicate cellulose embedded in epoxy resin and deformed in tension.

Figure 11: Raman band shift rate with waveplate rotation angle (Ø) for 1D lignified flax fibre, 2D random network of microfibrillated cellulose, bacterial cellulose and tunicate cellulose.
Whether majority of cellulose microfibrils within light spot are predominantly in tension or compression, there is not much of a difference in shift rates between the axial direction and the lateral directions of both 1D bundles and 2D network of cellulose microfibrils, thus why shift rates in these two directions show themselves typical of crystals under any deformation regime. When majority of spot cellulose microfibrils are predominantly in tension or compression, shift rates in the acute (all amorphous) directions are either seen away from zero or towards zero respectively with a clear difference in shift rates in the axial and lateral directions but not much of a difference between those of any two orthogonal acute directions (fig. 11). The acute directions of only bacterial cellulose appeared to have shifted onto the axial and lateral directions with strain over time (fig. 12). This must be due to possible reorientation (through 45°) of the spot cellulose microfibrils from desorption (moisture loss) with repeated irradiation over time from the highly sorptive (hygroscopic) bacterial cellulose chains and/or tighter aggregation (crystallization) of the longer cellulose chains of bacterial cellulose with increasing temperature (to around 60°C) within light spot (Atalla and Isogai, 2010).

Figure 12: Poisson’s ratio as a function of waveplate rotation angle (Ø) for a 1D lignified flax fibre, a 2D random network of microfibrillated cellulose, bacterial cellulose and tunicate cellulose.
2.5 Range of Poisson’s Ratio in Cellulose
All cellulose bundle or network of microfibrils, clearly exhibit a four-point yielding, and each point characterises the rupturing of a specific nano-level bonding either between or within cellulose microfibrils. During deformation of all-cellulose composites, weak microfibril-microfibril van der Waals interactions stress and break first, followed by dominating microfibril-microfibril hydrogen bonding, and then by possibly re-entrant chain-chain hydrogen bonds which constantly receive stress from molecular glycosidic (C-O-C) bonds until rupture (fig. 3). Hence, molecular glycosidic (C-O-C) are the very last to break and the transfer of stress from C-O-C bonds to interchain hydrogen bonding is instantaneous. Hence, auxetics can be calculated before the yielding of any one of these bonds. In this work, auxetics is calculated before the yielding of interchain hydrogen bonding.

The 1D bundle of cellulose microfibrils shows the highest E. Both 1D bundle and 2D network of cellulose microfibril show clear differences in E (fig. 13) and Poisson’s ratio (fig. 12) in the axial and the acute directions. This depicts the dependence of Poisson’s ratios of cellulose on its E when the ‘uniform stress (cross-section) but variable strain’ assumption (Eichhorn and Young, 2001) is made. The 2D network of cellulose microfibrils show a more uniform but lower E than the 1D bundle of cellulose microfibrils (fig. 13).

Even though the 1D bundle of cellulose microfibrils is highly lignified, it still showed higher auxeticity (~-7) in the acute (all amorphous) directions than the axial and lateral directions, given that lignin would limit or impede expansibility in the lateral direction (Cao et al., 2006). Auxeticity in the acute (amorphous) direction of the 1D bundle of cellulose microfibrils (flax fibre) would be expected to be much higher than -7. Both the crystals and amorphous of the 2D networks of cellulose microfibrils are auxetic, but the amorphous phase is a lot more auxetic (~-2.2) than crystal phase (~-1) (fig. 12). Straight aggregates of unlignified 1D bundles of cellulose microfibrils offer the opportunity to create composites of higher auxeticity. Auxeticity (before the yielding of interchain hydrogen bonding) of both crystal phase and amorphous phase are in the order of what has been reported by Peura et al. (2006) (-0.26 to -1.17) and Yao et al. (2012) (-0.20 to -1.60) for crystalline cellulose using x-ray diffractometry and molecular mechanics simulations respectively. Networking of cellulose microfibrils along with tangling and bifurcations are seen to confer higher strain to failure but limit expansions in the different directions in-plane. Even under multi-axial tension, varying moisture conditions and decreasing lignin from pith to bark as pertains in real-life, the amorphous phase would still be expected to be a lot more auxetic. Cellulose chains of cellulose from all sources are inherently chiral (twist) due to
the intrinsic chirality of glucose units which makes cellulose from all sources spiral (helix) in a uniform pitch parallel to the imaginary long axis passing through the centre of cellulose microfibrils (Atalla and Isogai, 2010). Chirality (4 chiral centres around which glucose twists) must then be the basis of the auxeticity of cellulose chain (Dionne et al., 1991) with the number of interchain hydrogen bonds in each phase regulating the degree of auxeticity. That is, the higher the number of interchain hydrogen bonds as it pertains to the crystal phase and the amount of lignin and pectin if there are, the lower the auxeticity; and the lower the number of interchain hydrogen bonds as it pertains to the amorphous phase, the higher the auxeticity. Zeolites, particularly thomsonite zeolites, appear to show similar auxetic trends as non-native 1D bundles and 2D networks of cellulose microfibrils (Grima et al., 2000). Zeolites must be structurally ordered in a similar way to cellulose microfibrils at the nano length scale. Cellulose must have a cubic unit cell as thombosite zeolites do as a twelve or its multiples chain base offers. This offers the opportunity to explore functional nanocomposites from both cellulose and zeolites (or like phase-change materials which exhibit changes in refractive index with changes in electric current and stress). This offers combined photo-electro-mechanical functionalities as is seen in hyper-sensitive nano-sized thick foldable display screens and batteries.
3. CONCLUSION

Cellulose is found to exhibit four distinct yielding points. Both crystalline and amorphous cellulose are found to be auxetic so long as intermolecular hydrogen bonding remains intact. Auxeticity of crystalline cellulose is found to be around unity (-1) while that of cellulose amorphous is found to be around twice (-2) that of crystalline cellulose with the possibility of auxeticity higher than -7 in 1D bundles of cellulose microfibrils in the absence of lignin. Though the network structure enhances strain to failure, they also significantly limit auxeticity in single 1D cellulose microfibrils in networks. Amorphous must exhibit higher auxeticity than crystals because amorphous has less intermolecular hydrogen bonding than crystals linking the chiral cellulose molecules together. The chirality of cellulose molecules must be responsible for auxeticity of cellulose microfibrils. Auxeticity must be directly correlated with the number of intermolecular hydrogen bonding. The similarity of the pattern of in-plane auxeticity of cellulose microfibrils to the off-axis auxeticity of zeolites (especially thomsonite zeolites) indicates the possibility of combining both phase change, semi-crystalline materials in nanosized composites with photo-electromechanical properties.

4. EXPERIMENTAL PLAN

The experiment was executed as follows.

4.1 A Processing of Samples
A bundle of cellulose microfibrils (lignified single flax fibre) was teased out of the bunch and processed by Steam explosion by FH, Reutlingen, Denmark. Whiskers were processed from Tunicates (Styela clava) collected (selection method unreported) from floating docks at Point View Marina (unreported location) and freeze-dried following protocols developed by Favier et al. (1995), Yuan et al. (2006) Shanmuganathan et al. (2010), and van der Berg et al. (2007). Cellulose microfibrils of bacterial cellulose and microfibrillated cellulose were processed following Seydibeyoğlu et al. (2012) and Sehaqui et al. (2012) respectively.

4.2 Raman Spectroscopy
The 50X objective lens of the Renishaw RM1000 Raman microscope (RENISHAW, Wootton-Under-Edge, UK) was used to focus light onto samples after calibration with the 520 cm\(^{-1}\) band of a silicon wafer using a 1200-line/mm grating (for a spectral resolution of 1 cm\(^{-1}\)), and a diode laser producing excitation at 785 nm up to 300 mW power. Spectral data was acquired using Renishaw v.1.2 WiRE software; analysed and plotted with Qtiplot and Origin.

4.3 Mapping of Samples
One sample of 1D bundle of cellulose microfibrils in the form of lignified flax fibre (0.10526 mm x 10 mm), and one 2D networks of cellulose microfibrils in the form of tunicate cellulose (0.07 mm x 5 mm x 10 mm), bacterial cellulose (0.135 mm x 5 mm x 10 mm) and microfibrillated cellulose (0.08 mm x 5 mm x 10 mm) were put on a glass slide parallel to the principal spectrometer axis. Raman spectra were measured all round in-plane under both half (in 5° steps) po-
larisation from 0° to 360° in extended mode between 100 cm\(^{-1}\) and 1150 cm\(^{-1}\) in 3 accumulations at 10s exposure and 100% laser power. The cursor was placed at the peak of the 1095 cm\(^{-1}\) band, and intensity read.

4.4 Deformation Experiments
The above samples were put under incremental tension in extension steps of 0.01 mm from zero 0.00 mm to failure in a Deben micro-tester (rig) (with a 200 N load cell at a rate of 0.1 mm min\(^{-1}\), 10.00 mm gauge length), and molecular deformation followed by Raman spectroscopy (pl. 1 and 2). Extended spectra were taken in 3 accumulations (and the averages of which plotted) between 100 cm\(^{-1}\) and 1550 cm\(^{-1}\) at 10s exposure and 100% laser power under both half and quarter wave plates (polarisation from 0° to 90°) in 5° steps respectively. Band shift per stress and band shift per strain (band shift rate) were calculated following Tanpichai et al. (2012).
Plate 1: a. Cellulose sample mounted in Deben rig on Raman spectroscope stage under the 50 x lens, b. the inside of Raman spectroscope showing polarizer in, half wave plate out of the path of emitted Raman light, and c. half wave plate in place at the bottom of Raman spectroscope for rotating emitted Raman light.
4.5 Calculation of Poisson’s Ratio

The stretching and vibration of the C-O-C bonds correspond with changes in the position and intensity of the 1095 cm\(^{-1}\) Raman band respectively. Under axial strain, the 1095 cm\(^{-1}\) Raman band continually shifts to lower wavenumber whereas, under compressive strain, the 1095 cm\(^{-1}\) Raman band continually shifts to higher wavenumber.

An auxetic material expands in at least one orthogonal direction to stretch.

\[
Poisson's\ ratio\ (\nu) = \frac{lateral\ deformation\ (\varepsilon_y)}{axial\ deformation\ (\varepsilon_x)}
\]

Raman band shift rate or Raman band shift with strain (So) in a bundle or network of cellulose microfils,
\[ S_{\text{born}} = \frac{d(\Delta v_R)}{d\varepsilon} \] (in cm\(^{-1}\%^{-1}\))

is related to Young’s Modulus, where \((\Delta V_R)_{\text{b or n}} = \) Raman band shift in a bundle or network of cellulose microfils; \((\varepsilon)_{\text{b or n}} = \) strain in a bundle or network of cellulose microfils and \((\sigma)_{\text{b or n}} = \) stress in a bundle or network of cellulose microfils.

Young's modulus of a bundle or network of cellulose microfils,

\[
E_{\text{b or n}} = \frac{\text{tensile stress} \ (\sigma_{\text{b or n}})}{\text{tensile strain} \ (\varepsilon_{\text{b or n}})}
\]

and,

\[
E_{\text{b or n}} \times \frac{d(\Delta v_R)_{\text{b or n}}}{d\sigma_{\text{b or n}}} = S_0
\]

and,

\[
E_{\text{b or n}} = n_o \times E_f
\]

where \(n_o\) is the efficiency factor and \(E_f\) is Young’s modulus of a single microfibril in a bundle or network of cellulose microfils.

\[
E_{\text{x or y}} \times \frac{d(\Delta v_R)_{\text{x or y}}}{d\sigma_{\text{x or y}}} = S_{0 \text{x or y}}
\]
where \( x \) and \( y \) symbols denote properties or equations for the axial and lateral directions respectively.

\[
E_{(b \ or \ n)x \ or \ y} \cdot \frac{d(\Delta v_R)_{x \ or \ y}}{d\varepsilon_{x \ or \ y}} = \frac{d\sigma_{x \ or \ y}}{d\varepsilon_{x \ or \ y}}
\]

where \( x \) and \( y \) symbols denote properties or equations for the axial and lateral directions respectively.

Assuming each cellulose microfibril in a bundle or network of cellulose microfils has a uniform cross-section and stress at each strain (\%) increment, stress in the axial and lateral directions are equal, that is,

\[
d\sigma_x = d\sigma_y, \quad \frac{E_{(b \ or \ n)x}}{E_{(b \ or \ n)y}} = \frac{d\varepsilon_y}{d\varepsilon_x} = v_{b \ or \ n}
\]
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