What conformational isomerism and auxetics typify crystalline cellulose?

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Summary

Almost all matter including viscoelastic cellulose respond to energy changes which almost invariably influence its atomic and molecular bond characteristics (length, orientation, and geometry). Changes in bond characteristics and quantised energy states/levels of conformationally isomeric cellulose is characterised by variations in the relative amounts of rotamers which has implications on the molecular organization and physical properties/integrity of cellulose that informs the processing and material application of cellulose. Cellulose is also reported to be auxetic. To fully establish how variations in the relative amounts of rotamers impact molecular organization and physical properties/integrity of cellulose and auxetics typical of crystalline cellulose as is usually found in non-native sources, a 1D bundle of cellulose microfibrils and 2D networks of cellulose microfibrils were stretched in a Deben microtester, and their molecular straining followed with Raman spectroscopy. In generality, the amounts of rotamers was found to decrease with stress or strain, which influences the level of molecular order or disorder (degree of crystallinity), and in turn changes (inter-conversions) of cellulose conformations/allomorphs or even polymorphs. The auxetics of crystalline cellulose was also found to be around unity (-1.00).

Expanded background

Almost all matter respond to quantised energy changes as occurs in chemical reactions or physical loading, which almost invariably influence atomic and molecular organisation, bond characteristics (orientation and geometry) which in turn results in changes in energy states of matter. This change in atomic and or molecular bond characteristics is even more dramatic and crucial in in viscoelastic polymers (polymers with side chains). Cellulose as a plentiful, renewable, tuneable, affordable, non-toxic, semi-crystalline, lightweight, thermally stable, stiff and green viscoelastic polymer, exhibits conformational isomerism under quantised energy change (be it endothermic or exothermic) in which its isomers (low energy side chains) are found to solely rotate about at least one characteristic sigma bond as occurs in the CH₂ (C-6) scissor mode of –CH₂OH (hydroxymethyl/methylene bridge) functional group/moiety on (C-6) of cellulose (Jarvis; Agarwal and Ralph). Three kinds of rotamers, namely: gg (gauche-gauche), gt (trans-gauche) and tg (gauche-trans) characterize this scissor mode, and according to Argawal and Ralph (2014), the relative amounts of these three rotamers, are found to influence the intensity, shape and frequency of spectra located at 1460 cm⁻¹, 1470 cm⁻¹ and 1480 cm⁻¹ Raman bands corresponding to each kind of rotamer respectively. The relative amounts of the three ratamers varies within and between native (unprocessed) cellulose I and non-native (processed) cellulose I (i.e cellulose I, II, III, IV), with relative amounts of rotamers being significantly higher and more complex in native cellulose than non-native cellulose (Argawal and Ralph, 2014). Nevertheless, the implications of the variations in the
relative amounts of rotamers on the molecular organization and physical properties/integrity of native and non-native cellulose are yet to be fully established. Adequate knowledge of such implications would not only inform of suitable processing but optimal material application of cellulose.

Cellulose (in both crystalline and amorphous phases) also enlarge in at least one direction at right-angles to the direction of strain (i.e auxetic or with negative Poisson’s ratio) (Asamoah (2017), Yao et al. (2012), Peura et al. (2006), Nakamura et al. (2004), and Franke and Magerle (2011)). Auxetics may be present with increased indentation resistance, increased shear stiffness, increased break resistance, increased acoustic response, negative linear compressibility, and negative thermal expansion in some cellulose functionalities. Raman band initially located at 1095 cm$^{-1}$ corresponds to the C-O-C (glycosidic bond/linkage) stretching mode (Tanpichai et al., 2012).

Thus, the need to establish auxetics typical of crystalline cellulose as is usually found in non-native sources along with the opportunity that Raman spectroscopy presents for following specific molecular occurrences, makes it exciting to attempt to fully establish how variations in the relative amounts of rotamers impact molecular organization and physical properties/integrity of cellulose, and the in-plane auxetics typical of crystalline cellulose by stretching non-native 1D bundles of microfibrils (lignified flax fibre) and 2D networks of microfibrils (tunicate, bacterial and microfibrillated celluloses) as models in a Deben micro-tester and following molecular deformations with Raman spectroscopy (plate 1) in order to fully inform future innovation of functionalized crystalline cellulose materials.
Plate 1: a. Cellulose samples mounted in Deben rig on Raman spectroscopy stage under the 50 x lens, b. the inside of Raman spectroscopy 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 spectroscopy for rotating emitted Raman light.
Findings

Intensities of Raman band initially located at 1095 cm$^{-1}$ was highest in the first axial (0°) direction, lower in the first lateral (90°) direction, and much lower in the second axial (180°) direction, and much lowest in the second lateral (270°) direction for 1D bundle of cellulose microfibrils (flax fibre) (fig. 1).

![Figure 1: Typical spectra from flax fibre in the region of the Raman band located at 1095 cm$^{-1}$ in the parallel (0° or 180°) and perpendicular (90° or 270°).](image)

Intensities of Raman band initially located at 1095 cm$^{-1}$ was highest in the first axial (0°) direction, lower in the first lateral (90°) direction, and slightly increased in the second axial (180°) direction, and decreased to the lowest in the second lateral (270°) direction for bacterial cellulose (fig. 2).
Figure 2: Typical spectra from bacterial cellulose in the region of the Raman band located at 1095 cm\(^{-1}\) in the parallel (0\(^{\circ}\)).

Intensities of Raman band initially located at 1095 cm\(^{-1}\) was highest in the first axial (0\(^{\circ}\)) direction, lower in the first lateral (90\(^{\circ}\)) direction, and much lower in both the second axial direction (180\(^{\circ}\)) and the second lateral (270\(^{\circ}\)) direction for tunicate cellulose (fig. 3).
Figure 3: Typical spectra from tunicate cellulose in the region of the Raman band located at 1095 cm$^{-1}$ in the parallel (0° or 180°) and perpendicular (90° or 270°).

Apart from bacterial cellulose whose intensity increased from the first lateral (90°) direction to the second axial (180°) direction, flax fibre and tunicate cellulose showed decreased intensity all the way from the first axial (0°) direction to the second lateral (270°) direction. The superior sorptive (moisture exchange) properties of bacterial cellulose may have caused the re-orientation of cellulose molecules (decrease in relative amounts of rotamers) or microfibrils slightly towards the axial direction in which crystals and amorphous forms a continuum of fairly proximal unconfined C-O-C bonds with most optimal starting mean interatomic distances and subsequent highest vibrational frequency (spectral intensity) in agreement with Asamoah, (2017). Bacterial cellulose and tunicate cellulose registers relatively higher intensities than flax fibre (fig. 4 and 5).
Figure 4: Intensity of Raman bands as a function of rotation angle (Θ) for flax fibre at 0.00% strain using 1095 cm\(^{-1}\), for bacterial cellulose pre-strained to fracture using 1095 cm\(^{-1}\) and 1120 cm\(^{-1}\), and for tunicate cellulose pre-strained to fracture using 1095 cm\(^{-1}\) and 1120 cm\(^{-1}\).

This is because the average number of spot cellulose microfibrils in 2D networks of cellulose microfibrils is higher than that in 1D bundle of cellulose microfibrils in agreement with Asamoah, (2017). Shapes and trends of 1095 cm\(^{-1}\) and 1120 cm\(^{-1}\) intensity plots are consistent with those reported by Asamoah, (2017) unlike those reported by Tanpichai \textit{et al.}\(^5\) (fig. 4 and 5). Intensities of Raman band initially located at 1095 cm\(^{-1}\) and 1120 cm\(^{-1}\) are lowest in the acute (45°) direction (fig. 4 and 5) because of the lowest mean vibrational frequency of the atoms of C-O-C bonds (spectral intensity) in the acute (45°) in agreement with Asamoah, 2017. Gaps are seen in the intensity plots after the first few incidences or a long halt in incidence respectively (fig. 5) because of the reversibility of cellulose energy states/levels (relative amounts of rotamers) within allowable limits in agreement with Asamoah, (2017).
The 1095 cm\(^{-1}\) Raman band consistently shifts vertically to lower wavenumbers at 0.00\% strain before starting to shift in a slope to lower wavenumbers with strain from 0.00\% to 1.40\% for bacterial cellulose, tunicate cellulose and microfibrillated cellulose (figs. 6a, 7a, 8a and 8b). This was most likely due to the purely quantum conformational isomerism (conformation interconversions) occurring under the slightest initial stress even before any strain was sustained as was reported of cellulose under bending by Jarvis, (2000), thus the need to investigate this possible phenomenon further. Meanwhile, Umesh and Ralph (2014) indicate that the relative amounts of \(gg\), \(gt\) and \(tg\) rotamers (corresponding to the 1460 cm\(^{-1}\), 1470 cm\(^{-1}\) and 1480 cm\(^{-1}\) Raman bands respectively) vary significantly within and between native (unprocessed) cellulose and non-native (processed) cellulose. On close examination of intensity
plots within the region 1450 cm\(^{-1}\) and 1480 cm\(^{-1}\) to fully appreciate how changes in relative amounts of \(gg\), \(gt\) and \(tg\) rotamers (conformational isomers) with stress and strain impact the physical properties/integrity of cellulose (i.e. ordinary paper, bacterial cellulose, microfibrillated cellulose and tunicate cellulose). In ordinary paper (predominantly \(\beta\) cellulose), there is no much of a difference between the relative amounts of \(gg\) (1460) rotamer and \(gt\) (1470) rotamer, but a clear difference exists between the relative amounts of \(gg\) (1460) rotamer and the \(tg\) (1480) rotamer (being lowest) with both stress and strain (fig. 9). In generality, amounts of rotamers of bacterial cellulose decrease with stress or strain (fig. 9).

In bacterial cellulose as occurs in algae (predominantly \(\alpha\) cellulose), there is a clear steady difference between the relative amounts of both the \(gg\) (1460) and \(gt\) (1470) rotamers and the \(tg\) (1480) rotamer. The \(tg\) (1480) rotamer is lowest without stress or strain but evens out with both the \(gg\) (1460) and \(gt\) (1470) rotamers with stress or strain (fig. 10). Differences between relative amounts of rotamers in bacterial cellulose narrow significantly to uniformity under stress and strain due to its high sorptive property which results in re-orientation and tighter chain packing. In generality, amounts of rotamers of bacterial cellulose decrease with stress or strain (fig. 10).

Figure 9: Relative amounts of \(gg\) (1460), \(gt\) (1470) and \(tg\) (1480) rotamers (conformational isomerism) with stress and strain in a. ordinary paper at 0.0MPa, 0.0%, b. ordinary paper at 12.5 MPa, 0.0%, c. ordinary paper at 37.50MPa, 2.0% and d. ordinary paper at 25.0MPa, 0.3%. 
Figure 10: Relative amounts of gg (1460), gt (1470) and tg (1480) rotamers (conformational isomerism) with stress and strain in a. bacterial cellulose at 0.0MPa, 0.0%, b. bacterial cellulose at 8.0MPa, 0.04%, c. bacterial cellulose at 17.0MPa, 0.18% and d. bacterial cellulose at 25.0MPa, 0.38%.

Besides high degree of polymerization (long chain length), the uniformity of relative amounts of rotamers (evening of degree of crystallization) of bacterial cellulose may jointly explain why it has high modulus of elasticity. In microfibrillated cellulose as sourced from plant fibres (predominantly β cellulose), there is a clear steady difference between the relative amounts of both gg (1460) and gt (1470) rotamers and tg (1480) rotamer. The tg (1480) rotamer is lowest with both stress and strain (fig. 11). In generality, amounts of rotamers of microfibrilated cellulose decrease with stress or strain (fig. 11).
In tunicate cellulose (completely β cellulose), there is no much of a difference between the relative amounts of the $gg$ (1460) rotamer and the $gt$ (1470) rotamer, but a clear difference exists between the relative amounts of both the $gg$ (1460) and $gt$ (1470) rotamers and the $tg$ (1480) rotamer. The $tg$ (1480) rotamer is highest and most prominent with both stress or strain (fig. 12). In generality, amounts of rotamers decrease with stress or strain (fig. 12).
Figure 12: Relative amounts of gg (1460), gt (1470) and tg (1480) rotamers (conformational isomerism) with stress and strain in a. tunicate cellulose at 0.0MPa, 0.0%, b tunicate cellulose at 14.0%, 0.00%, c. tunicate cellulose at 27.0MPa, 0.01% and d. tunicate cellulose at 42.0MPa, 0.43%.

Slight increases in relative amounts following a stress or strain increments, constitute a recovery of the relative amounts of rotamers as is most likely to occur at relaxation points in stress-strain curves of viscoelastic cellulose. This indicates that stress and strain (as with rigorousness and lengthiness of processing) reduces the relative amounts of rotamers which tend to reduce the degree of molecular disorder and in turn, increase the degree of crystallinity in non-native cellulose (processed) as suggested by Agarwal and Ralph (2014). The level of molecular order or disorder (degree of crystallinity) as a result of changes in relative amounts of rotamers causes different chains to take on different conformations (allomorphs), or even different polymorphs (cellulose I, II, III, IV).
Figure 13: a. Raman band shift with strain with wave-plate rotation angles, $\phi$ (direction in-plane) for bacteria cellulose; b. Raman band shift with strain with wave-plate rotation angle, $\phi$ (direction in-plane) for bacteria cellulose.
Raman band shift rate is highest (highest negative value: -1.010 cm\(^{-1}\) \%\(^{-1}\)) for tunicate cellulose, while that for microfibrillated cellulose (45% pre-strained) shifts moderately (medium negative value: -0.943 cm\(^{-1}\) \%\(^{-1}\)) and that for bacterial cellulose shifts least to lower wavenumber (least negative value: -0.076 cm\(^{-1}\) \%\(^{-1}\)) axially (0° or 180° to strain axis) in plane (figs. 6a, 7a, 8a and tab. 1). These axial Raman band shift rates are in the order of those measured by Sturcova et al., (2005) of -2.4 cm\(^{-1}\) \%\(^{-1}\) for tunicate cellulose embedded in epoxy resin and deformed in tension, and by Rusli and Eichhorn (2008) of -0.87 cm\(^{-1}\) \%\(^{-1}\) for microfibrillated cellulose (not pre-strained to alignment) embedded in epoxy resin and deformed in tension, and by Hsieh et al., (2005) of -1.77 cm\(^{-1}\) \%\(^{-1}\) for bacterial cellulose. Rusli et al. (2009) quantified the stress-transfer mechanisms of tunicate whiskers and found tunicate whiskers to have efficient stress transfer which may explain its highest axial Raman band shift rates. Raman band shift rate is higher (higher negative value: -0.307 cm\(^{-1}\) \%\(^{-1}\)) for tunicate cellulose, while that for bacterial cellulose shifts moderately (medium negative value: -0.229 cm\(^{-1}\) \%\(^{-1}\)) to lower wavenumber laterally (90° to strain axis) in plane. These lateral Raman band shift rates are somewhat lower than those measured by Asamoah, (2017) of -2.70 cm\(^{-1}\) \%\(^{-1}\) for tunicate cellulose, and of -0.70 cm\(^{-1}\) \%\(^{-1}\) for microfibrillated cellulose, and of -0.40 cm\(^{-1}\) \%\(^{-1}\) for bacterial cellulose deformed in tension. This may be as a result of inherent variations in samples from processing regimes. Raman band shift rate in the acute (45°) direction is lower than Raman band shift rate in the lateral direction, which in turn is slightly lower than Raman band shift rate in the axial direction for both tunicate cellulose and bacterial cellulose (fig. 13 and 14).
Thus, Raman band shifts at a lowest rate (lowest negative values) in the acute (45°) direction of tunicate cellulose and bacterial cellulose. Coincidentally, it is in the acute (45°) direction that Raman band intensity is minimal (signifying minimal mean vibrational frequency of atoms of C-O-C bonds) relative to Raman band intensity in the axial and lateral of both tunicate cellulose and bacterial cellulose as explained by Asamoah (2017). Raman band shift rate of -0.104 cm⁻¹ %⁻¹ in the first acute (45°) direction [which is orthogonal to the second acute (45°) direction] and Raman band shift rates of -0.106 cm⁻¹ %⁻¹ for the second acute (45°) direction of bacterial cellulose (fig. 9b) works into an acute shift rate proportion of 0.98 which is higher than the non-acute shift rate proportion of 0.690 [lateral shift rate to axial shift rate] for bacterial cellulose. Thus, as orthogonal Raman shift rates decreases (approaches zero) shift rate proportion increase, and in turn negative Poisson’s ratio increases as confirmed by Asamoah (2017). Tunicate cellulose and bacterial cellulose showed a Poisson’s ratio of around unity (-1.00) based on the ratio of lateral strain to axial strain, $-\frac{\varepsilon_y}{\varepsilon_x}$ (tab. 1). This value is proven to be consistent with those of -1.17 (by x-ray defractometry) reported by Peura et. al. (2005) and -1.00 (by Raman spectrometry) reported by Asamoah (2017) for crystalline cellulose. Regardless of source (size/dimension), crystalline cellulose maintains auxet-
ics around unity, which makes cellulose nanocrystals from any source equally useful for uniform high-precision auxetic applications. Crystalline size would only matter where packing and adhesion are of prior consideration to material application.

Microfibrils of bacterial cellulose (a ‘spaghetti’ of cellulose microfibrils) pack, meander and tangle together most (highest packing density), while microfibrils of microfibrillated cellulose (bigger bundle of microfibrils) pack, meander and tangle together less (medium packing density), and microfibrils of tunicate cellulose (smaller, shorter and straighter bundle of pre-strained microfibrils) pack and tangle together least (lowest packing density). Cellulose microfibril packing density and degree of tangling influence axial and lateral Raman band shift rates and strain to failure (figs. 6a, 7a, 8a, 12, 13 and tab.1).

Table 1: In-plane Poisson's ratio for tunicate (TC), bacterial cellulose (BC) and microfibrillated celluloses (MFC) calculated from axial and lateral molecular deformation

<table>
<thead>
<tr>
<th>Type of cellulose</th>
<th>Unpolarised Axial Measurements</th>
<th>Polarized Axial and Lateral Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Axial Raman shift with strain ((S_{0x}))</td>
<td>Lateral Raman shift with strain ((S_{0y}))</td>
</tr>
<tr>
<td>tunicate cellulose</td>
<td>-1.0100</td>
<td>0.0580</td>
</tr>
<tr>
<td>bacterial cellulose</td>
<td>-0.0760</td>
<td>0.0045</td>
</tr>
<tr>
<td>microfibrilated cellulose</td>
<td>-0.9430</td>
<td>0.1900</td>
</tr>
</tbody>
</table>

This would explain why tunicate cellulose would shift most axially but show lowest strain to failure, and why microfibrillated cellulose would shift medium axially but show medium strain to failure and why bacterial cellulose would shift least axially but show highest strain to failure. Bacterial cellulose shift least axially but shows highest strain to failure because the packing density, degree of meandering and tangling of its microfibrils limits axial and lateral Raman band shift rates but improves axial and lateral strain to failure as indicated by
(Asamoah, 2017). Besides microfibril-microfibril interactions (which is predominated by hydrogen bonding), Tanpichai et al. (2012) indicate that heterogeneities such as bifurcations that are formed in microfibrils of bacterial cellulose during cell division make microfibrils stiffer, thus why axial and lateral strain to failure would be improved. That tunicate cellulose expands highest axially but registers lowest strain to failure (figs. 6a, 7a, 8a, 13, 14 and tab.1) shows that strain to failure and Raman band shift rates are two indirectly related properties while strain to failure and the degree of packing (packing density) which also depends on degree of tangling of microfibrils are two directly related properties.

Experimental Plan

Processing of samples

A bundle of cellulose microfibrils (lignified single flax fibre) was teased out of the bunch processed by Steam explosion by FH, Reutlingen, Denmark. Whiskers were processed from Tunicates (Styela clava) collected (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 was processed following Seydibeyoğlu et al. (2012) and Sehaqui et al. (2012) respectively.

Raman spectroscopy

The 50 x objective lens of the Renishaw RM1000 Raman microscope (RENISHAW, Wooton-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.

Mapping of samples

One sample of 1D bundle of cellulose microfibrils (lignified flax fibre) (0.10526 mm x 10 mm), and 2D networks of tunicate cellulose microfibrils (0.07 mm x 5 mm x 10 mm), bacterial cellulose microfibrils (0.135 mm x 5 mm x 10 mm) and microfibrillated cellulose microfibrils (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 half wave plate (polarization from 0° to 360°) in 5° steps in extended mode between 100 cm\(^{-1}\) and 1150 cm\(^{-1}\) in 3 accumulations at 10s exposure and 100% laser power.

Deformation experiments

Same 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. Extended spectra were recorded in 3 accumulations between 100 cm\(^{-1}\) and 1550 cm\(^{-1}\) at 10s exposure and 100% laser power under both half and quarter wave plates (polarization from 0° to 90°) in 5° or 4° steps respectively.
Calculation of Poisson’s ratio

According to Tanpichai et al., Raman band shift rate (Raman band shift with strain), \((S_0)\) defined as \(d(\Delta v_R) / d \in\) within bundle or 2D network of cellulose microfibril is related to Young’s modulus of 1D bundle of cellulose microfibrils (\(E_{\text{bundle}}\)) or 2D network of cellulose microfibril (\(E_{\text{network}}\)), and Raman band shift (\(\Delta v_R\)) with stress (\(d\sigma\)) [defined as \(d(\Delta v_R) / d\sigma\)] of 1D bundle of cellulose microfibril or 2D network of cellulose microfibril by:

\[
E_{\text{networkorbundle}} \times \frac{d(\Delta v_R)}{d\sigma} = S_0 \quad \text{Eq. 1}
\]

Hsieh et al. (2008), Sturcova et al. (2005) and Rusli and Eichhorn (2008) determined the value of \(d(\Delta v_R) / d\sigma\) to be \(-4.3 \text{ cm}^{-1} \text{ GPa}^{-1}\) from micromechanical deformation of a number of natural and regenerated cellulose microfibrils or fibres using Raman spectrometry, and assumed it to be valid for all other cellulose networks, though this assumption is not made in this paper.

Young’s modulus of 1D bundle of cellulose microfibrils (\(E_{\text{bundle}}\)) or 2D network of cellulose microfibril (\(E_{\text{network}}\)) is related to Young’s modulus of a single, bundle (of) or network (of) cellulose microfibril (\(E_{\text{fibrilorbundleornetwork}}\)) by the equation (Krenchel, 1964):

\[
E_{\text{fibrilorbundleornetwork}} = \eta_0 E_{\text{fibrilorbundleornetwork}} \quad \text{Eq. 2}
\]

Where \(\eta_0\) is an efficiency factor.

In the axial direction of a single fibril, a bundle of microfibrils, and 2D network of microfibrils, the band shift with stress equation below holds.
In the lateral direction of a single fibril, a bundle of microfibrils, and 2D network of microfibrils, the band shift with stress equation below holds.

\[ E_{\text{fibrilbundle network}} \times \frac{d(\Delta v_{Rx})}{d\sigma_x} = S_{0x} \]  \hspace{1cm} \text{Eq. 3}

In the axial direction of a single fibril, a bundle of microfibrils, and 2D network of microfibrils, the band shift with strain (shift rate) equation below holds.

\[ E_{\text{fibrilbundle network}} \times \frac{d(\Delta v_{Ry})}{d\sigma_y} = S_{0y} \]  \hspace{1cm} \text{Eq. 4}

In the axial direction of a single fibril, a bundle of microfibrils, and 2D network of microfibrils, the band shift with strain (shift rate) equation below holds.

\[ E_{\text{fibrilbundle network}} \propto \frac{d(\Delta v_{Rx})}{d\varepsilon_x} = \frac{d\sigma_x}{d\varepsilon_x} \]  \hspace{1cm} \text{Eq. 5}

In the lateral direction of a single fibril, a bundle of microfibrils, and 2D network of microfibrils, the equation below holds.

\[ E_{\text{fibrilbundle network}} \propto \frac{d(\Delta v_{Ry})}{d\varepsilon_y} = \frac{d\sigma_y}{d\varepsilon_y} \]  \hspace{1cm} \text{Eq. 6}
Assuming each test microfibrils has uniform cross-section along whole length and in turn uniform stress along whole length at each strain increment (Young and Eichhorn, 2007), then

\[ d\sigma_x = d\sigma_y = \frac{E_{\text{fibrilbundlenetwork}x}}{E_{\text{fibrilbundlenetwork}y}} = -\frac{d\varepsilon_y}{d\varepsilon_x} \]

\[ \text{Eq. 7} \]

\[ \text{and } -\frac{d\varepsilon_y}{d\varepsilon_x} = v_{\text{fibrilbundlenetwork}} \]

References


