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Raman Spectroscopy as a Tool for Natural Fiber Characterization: A Mini-Review

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Abstract:

Plant-derived fibers, such as flax, hemp, jute, sisal, coir, and bamboo, are being incorporated into polymer matrices at an increasing rate. This trend has revealed a gap in the analytical toolbox: very few techniques provide molecular specificity together with sub-micrometer spatial resolution at the level of an individual fiber, and even fewer can do so without destroying the sample. Raman spectroscopy offers both requirements in one non-destructive measurement. However, there is still no literature review that explicitly deals with its application in natural fiber reinforced composites (NFRCs); the corresponding results are scattered over studies addressing other questions. In this work, we bring together this scattered body of work and critically evaluate it. Five thematic strands are discussed: the spectral fingerprints of cellulose, lignin and hemicellulose; molecular tracking of surface treatments (mercerization, silane grafting, acetylation); confocal Raman imaging of fiber/matrix microstructure; micromechanical analysis based on stress-induced band shifts; and assessment of degradation and durability under ultraviolet, hydrothermal and oxidative ageing. The glycosidic C–O–C stretching band at about 1095 cm^{-1} is a recurring motif: it behaves as a molecular strain gauge with a shift rate $\Delta\nu/\Delta\varepsilon$ between -0.5 and $-4.3\text{ cm}^{-1}/\%$ strain depending on fiber type and crystallinity, which opens the way to spatially resolved measurements of interfacial shear stress that bulk pull-out testing cannot provide. We also compile published band-shift data from across fiber species into one comparison and benchmark Raman directly against FTIR, XRD and SEM. When used in mapping mode, the technique can resolve degradation in its component processes, cellulose amorphization, lignin photo-oxidation and matrix chemi-crystallization phase by phase. As far as we are aware, no competing method combines chemical specificity, sub-micrometer resolution and mechanical sensitivity in a single non-destructive measurement. The limitations are set out with equal candour: an intrinsically weak effect, fluorescence from lignin-rich fibers, a mapping throughput still far below industrial requirements, and a sampling depth governed by excitation wavelength and objective numerical aperture. Further into the future, nanoscale tip-enhanced Raman spectroscopy, MCR-ALS chemometric decomposition and convolutional neural networks (already exceeding 95% classification accuracy) should help to bring the technique out of specialist laboratories and into routine industrial quality assurance, provided that an open-access, curated spectral database of natural fibers is assembled in parallel to these advances.

Keywords: Raman spectroscopy; natural fibers; bio-composites; cellulose; fiber–matrix interface; Raman mapping; micromechanics; surface treatment; machine learning; degradation monitoring

1. Introduction

The composites industry has used glass and carbon fibers for almost 40 years because of their well-understood mechanical behavior and because supply chains have had time to develop. When it comes to the environment, the picture is considerably less rosy: production is still very energy-intensive, the fibers are, for all practical purposes, not biodegradable, and recycling routes have not yet become economically convincing (Mohanty *et al.*, 2005; Faruk *et al.*, 2012; Pickering *et al.*, 2016). Such concerns have slowly focused attention on lignocellulosic substitutes such as flax, hemp, jute, sisal, kenaf and ramie. Their behavior is very different from synthetic reinforcements. Their densities lie in the $1.2\text{--}1.5\text{ g cm}^{-3}$ range, against 2.5 g cm^{-3} for E-glass; combined with competitive specific stiffness, full compostability and feedstock costs that

are a fraction of the synthetic equivalent, the case for their use becomes compelling wherever performance per unit weight matters more than ultimate strength (Bledzki & Gassan, 1999; Saheb & Jog, 1999). Significantly, the automotive industry was quick to respond: door panels, parcel shelves and underbody shields molded from natural-fiber blends based on polypropylene or polyester have been coming off production lines since the early 2000s (Holbery & Houston, 2006; Yan *et al.*, 2014).

The field has advanced well beyond the classic bast fibers more recently. Coir, the fiber of the coconut husk, contains an unusually high lignin portion (~45 wt%) and is relatively resistant to moisture, which has gained it usage in geotextiles and packaging composites (Verma *et al.*, 2013; Hasan *et al.*, 2020). Bamboo, botanically a grass and not a true bast fiber, can attain tensile moduli of some 30 GPa for the better grades, comparable to low-end glass fiber (Osorio *et al.*, 2011). Bagasse, the residue of sugarcane after the sugar has been pressed out, is of particular importance in tropical economies where it accumulates as an agro-industrial residue in the order of hundreds of millions of tonnes per year (Candido *et al.*, 2017). The matrices have changed, too: in the quest for fully bio-based composites, petroleum-derived polypropylene is increasingly replaced by polylactic acid (PLA) and polybutylene adipate-co-terephthalate (PBAT) (Graupner *et al.*, 2009; Jian *et al.*, 2020). Each new fiber/matrix combination presents new analytical challenges, and the characterization toolbox must stay abreast of them.

An engineer used to glass fiber rarely faces the difficulties in describing these materials. A plant fiber is not a uniform cylinder but a hierarchically built multi-walled tube in which cellulose microfibrils are spirally arranged in a hemicellulose/lignin matrix, with the helix pitch and the wall thickness varying from one cell-wall layer to the next and from one botanical species to another (Bismarck *et al.*, 2005). This structural complexity is further enhanced by the well-known hydrophilic/hydrophobic incompatibility between the cellulose surfaces and most polymer matrices, which results in interfaces that are poor at transmitting load unless they are specifically designed (Li *et al.*, 2007; Kabir *et al.*, 2012). The variety of surface modifications is admittedly wide: mercerization, silane coupling, acetylation, plasma treatment, but verifying how deep each treatment penetrates, and how uniformly it is distributed, requires analysis that combines chemical specificity with fine spatial resolution. Bulk-averaged spectra are not up to the task (Kalia *et al.*, 2009; Xie *et al.*, 2010).

This is where Raman spectroscopy comes into play. In an inelastic scattering event, a photon exchanges energy with a molecular vibration, gaining or losing exactly one vibrational quantum of the bond involved, and the resulting spectrum is effectively a chemical fingerprint of the point being probed (Ferraro *et al.*, 2003; Smith & Dent, 2019). A sample, a focused laser and a dispersive spectrometer are enough: no vacuum, no contact, no elaborate preparation. Add this laser to a confocal microscope objective and the volume being interrogated shrinks to a fraction of a cubic micrometer, small enough to address single fibers and even the interphase region. Each of the competing approaches leaves something out. FTIR is water-sensitive and limited by a diffraction-limited lateral resolution that rarely exceeds 5–10 μm in attenuated-total-reflectance mode (Stuart *et al.*, 2004), despite its status in functional-group analysis. XRD gives the crystallographic structure, but tells us nothing about the chemical identity of the interphase. SEM resolves morphology beautifully but is blind to chemistry unless combined with energy-dispersive spectroscopy, which itself has no molecular specificity. Raman is not without weaknesses of its own, and they are better stated at the outset than discovered at the bench. The effect is intrinsically weak, on the order of one

inelastically scattered photon in 10^6 to 10^8 , so acquisition times are long and minor constituents are easily missed. Fluorescence from lignin and phenolic extractives can bury the signal outright under visible excitation. The tightly focused beam can heat or photodegrade the very cell wall it is meant to probe. Confocal mapping remains slow by any industrial standard, and

Raman is a poor absolute quantifier: without a matched calibration set, band intensities report relative rather than absolute composition. The complementary techniques carry restrictions of their own. ATR-FTIR is confined to a few micrometers of lateral resolution and is defeated by adsorbed water; XRD averages over large sample volumes and speaks only to the crystalline fraction; SEM needs a conductive coating and, in conventional instruments, a vacuum. These trade-offs are set out criterion by criterion in Table 4, which is discussed in Section 7.1; the essential point at this stage is that Raman is complementary to all three, and that its stress-dependent band shifts add a micromechanical dimension which FTIR, XRD and SEM cannot reach (Young *et al.*, 1995).

Somewhat surprisingly, what one does not find in a survey of the literature is a review specifically dedicated to Raman spectroscopy in NFRCs. Individual case studies appear here and there in larger expositions on natural-fiber characterization, but no one has followed the thread continuously from spectral fundamentals through surface-treatment monitoring, confocal imaging, and micromechanical band-shift analysis to degradation tracking. Thus, the present mini-review aims to fill that gap. The thematic sections that follow are ordered so that each build on the previous one, and a closing section considers the current limitations and looks at emerging Raman methodologies that could, as they mature, substantially reshape the field.

2. Principles of Raman Spectroscopy Applied to Natural Fibers

Stripped of its botanical hierarchy, the Raman spectrum of any lignocellulosic fiber reduces to a weighted sum of three macromolecular voices: cellulose, hemicellulose, and lignin (Agarwal *et al.*, 2008, 2019). Cellulose is the loudest. It makes up 60–80 wt% of most bast fibers (the fraction falls to about 40% in coir and exceeds 70% in good flax), and its vibrations dominate the fingerprint region in proportion. The dominant feature is the glycosidic C–O–C stretch at around 1095 cm^{-1} and, as developed in Section 5, it responds measurably to mechanical strain (Eichhorn *et al.*, 2001; Gierlinger & Schwanninger, 2006). More subtle information is carried by its neighbour at $\sim 1120\text{ cm}^{-1}$, due to coupled C–O stretching and C–C ring motion. The intensity of this band relative to the 1095 cm^{-1} band is sensitive to the orientation of the cellulose chains with respect to the laser polarization. This enables a polarization-resolved acquisition to read out the microfibril orientation across a fiber cross-section (Wiley & Atalla, 1987). The engineering payoff is significant; microfibril angle determines axial stiffness, and one measurement that captures chemistry and orientation simultaneously removes the need for a separate X-ray diffraction experiment. Completing the picture are a ring-breathing mode at about 898 cm^{-1} , CH_2 bending vibrations at 1380 and 1460 cm^{-1} , a C–H stretching envelope covering 2890 – 2940 cm^{-1} and a broad O–H stretching region above 3200 cm^{-1} (Edwards *et al.*, 1997). Particular attention has been given to the skeletal deformation near 380

cm⁻¹. (Agarwal *et al.*, 2010) proposed the intensity ratio I_{380}/I_{1096} as a rapid Raman crystallinity index (%CI) that tracks XRD peak-height measurements reasonably well (Park *et al.*, 2010). That qualifier is important: excitation wavelength, residual fluorescence, and even the choice of baseline-correction routine all introduce scatter, so it is unwise to rely on a single calibration curve. (Queiroz *et al.*, 2021) applied the same univariate model to thirty commercial batches of microcrystalline cellulose and had to re-fit it for each probe geometry, a reminder that the calibration is instrument-specific rather than universal. (Agarwal *et al.*, 2021a) went further and showed that crystalline and non-crystalline cellulose contribute in the same spectral regions, which places an intrinsic ceiling on the accuracy of any band-ratio crystallinity index. The pragmatic approach is to treat the Raman %CI as a screening number and to benchmark any quantitative statement against solid-state ¹³C NMR or carefully performed XRD.

The distinction between cellulose I (native, parallel chains) and cellulose II (antiparallel, mercerized) is directly relevant to NFRC design because the allomorphic change affects crystallinity, moisture uptake, and resets the population of surface hydroxyls available for covalent or hydrogen bonding to the matrix. (Agarwal *et al.*, 2021b) showed that the band at 577 cm⁻¹ is unique to cellulose II; it appears in the spectrum of neither cellulose I nor amorphous cellulose, and they used the intensity ratio I_{577}/I_{1096} to build a linear calibration ($R^2 = 0.994$) for the polymorph content. Their Raman method still detected 5 wt% cellulose II, whereas the corresponding XRD reflections became indiscernible below roughly 20 wt%. In other words, for the composite case, a single confocal Raman measurement on a single fiber can tell whether an alkali treatment has gone over the allomorphic threshold, which bulk XRD can only report as an average over many thousands of fibers. The payoff is real: mercerization batch-to-batch drift, a stubborn quality-control headache in industrial NFRC manufacture, can be seen fiber-by-fiber.

Lignin speaks a different spectral language. The aromatic skeleton gives a strong, cleanly isolated signal near 1600 cm⁻¹ from ring C=C stretching (Agarwal *et al.*, 2011), with a shoulder around 1650 cm⁻¹ (conjugated olefinic stretches) and a band near 1730 cm⁻¹ (acetyl and carboxyl carbonyls). The 1600 cm⁻¹ feature is in a region virtually free from cellulose interference and is thus the marker of choice for mapping lignin, for example, to differentiate the lignin-rich compound middle lamella from the cellulose-rich secondary wall in confocal Raman images of wood and fiber cross-sections (Gierlinger *et al.*, 2014, 2018). This selectivity carries over cleanly to NFRC work. The 1600 cm⁻¹ band, recorded before and after alkali treatment, offers a molecularly resolved gauge of delignification depth that no gravimetric weight-loss figure can match. The point bites hardest for high-lignin fibers, coir at about 45 wt% lignin and bamboo at about 25 wt%, where lignin left behind at the interface can behave as a weak boundary layer if not adequately stripped (Osorio *et al.*, 2011; Verma *et al.*, 2013).

Hemicellulose is the more difficult analytical case. Most of the vibrational modes of its xylose- and mannose-based sugars coincide with those of cellulose, and the overlap is broad enough to frustrate any simple univariate reading. However, Agarwal (2024) noticed differences subtle enough to be missed but

significant enough to be exploited. In the presence of xylan, the CH₂ scissoring band near 1460 cm⁻¹ shifts downward by a few wavenumbers, while the C–H feature at 2937 cm⁻¹ increases in relative intensity. These shifts are small, but multivariate chemometric tools such as PCA and MCR-ALS amplify them into component-distribution maps of publication quality (Sun *et al.*, 2011). Whether these particular assignments have been corroborated elsewhere is a fair question, and the answer is a qualified yes. The underlying spectroscopy is not new: (Kačuráková *et al.*, 1999) recorded FT-Raman spectra of isolated xylan-type polysaccharides and located their characteristic contributions in the CH₂ region near 1460 cm⁻¹ and in the C–H stretching envelope around 2940 cm⁻¹, while the normal-coordinate analysis of Wiley and Atalla had already established that most cellulose modes below 1500 cm⁻¹ are strongly coupled, so that an added xylan chain perturbs existing band positions rather than creating wholly new features. Agarwal and Ralph reached the same conclusion from the opposite direction when they separated carbohydrate from lignin contributions in the FT-Raman spectrum of black spruce, and the MCR-ALS decompositions of wood cross-sections reported by Gierlinger recover a hemicellulose end-member whose profile is consistent with those assignments. What has not yet been done, and what would settle the matter, is a systematic study on isolated hemicelluloses of controlled composition reconstituted with cellulose at known ratios. Until then the hemicellulose entries in **Table 1** are best treated as well-supported but not independently validated. The major band assignments used throughout this review are listed in **Table 1**.

Table 1. Raman band assignments of the major natural fiber constituents and polymer matrices commonly used with the fibers.

Wavenumber (cm ⁻¹)	Assignment	Component	Diagnostic Use
380	Skeletal deformation	Cellulose	Crystallinity index (I_{380}/I_{1095})
577	Ring deformation	Cellulose II	Allomorph I → II conversion
898	Ring breathing (β-glycosidic)	Cellulose	Amorphous content marker
1095	C–O–C glycosidic stretch	Cellulose	Strain gauge (band shift)
1120	C–O stretch + C–C ring	Cellulose	Microfibril orientation (polarization)
1375	CH ₃ symmetric deformation	Acetyl group	Acetylation monitoring
1380–1460	CH ₂ bending	Cellulose / Hemicellulose	Composition; xylan shift at 1460
1600	Aromatic C=C stretch	Lignin	Lignin mapping; delignification depth
1650	Conjugated C=C olefinic	Lignin	Lignin substructure
1713	C=O (carboxylic acid)	PP oxidation products	Matrix degradation marker

1725–1735	C=O ester stretch	PCL / PLA / Acetylated fiber	Matrix ID; acetylation degree
809 / 841	CH ₂ rocking doublet	iPP (crystalline / amorphous)	PP crystallinity changes
2890–2940	C–H stretching envelope	Cellulose / Hemicellulose	General organic; xylan weight at 2937
>3200	O–H stretching (broad)	Cellulose / Water	H-bonding network; moisture uptake

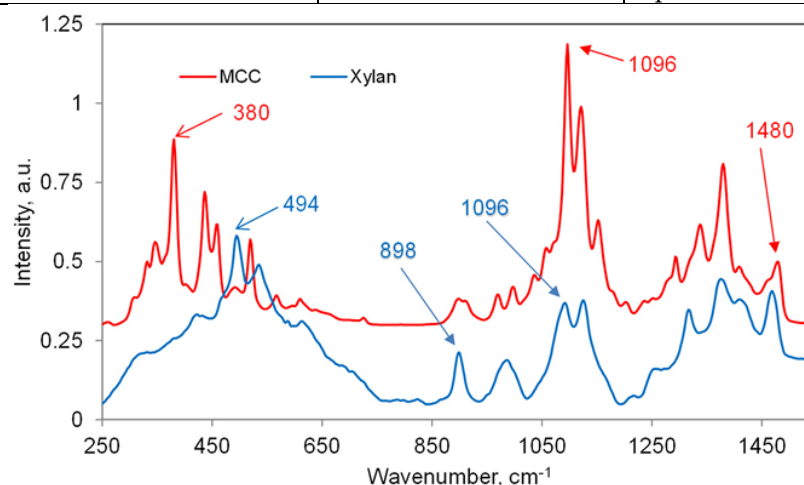


Figure 1. Schematic of the characteristic Raman bands of cellulose, hemicellulose and lignin as they appear in a typical natural-fiber spectrum; the most diagnostically useful features are annotated with their approximate wavenumber positions (Agarwal *et al.*, 2024).

3. Monitoring of surface treatments and chemical modifications

In NFRC engineering, few points have been more widely agreed upon than the importance of the fiber/matrix interface among design variables (Kim & Mai, 1998; Akter *et al.*, 2022). Poor interface bonding sheds load, invites premature debonding and pins mechanical properties well below what a rule-of-mixtures estimate would promise. Chemical surface treatments attack the problem from many angles at once by removing non-structural elements, roughening the surface, and attaching reactive functional groups to the cellulose backbone (Siroky *et al.*, 2010; Kabir *et al.*, 2012). The unique contribution of Raman here is the molecular audit trail that it leaves behind. Every treatment leaves a characteristic spectral signature that can be read directly off the fiber surface, with no destructive step such as dissolution or extraction intervening.

Mercerization is an obvious place to start. A soak of plant fibers in 5–10% NaOH at 60–80 °C removes most of the hemicellulose and a good part of the surface lignin, and the Raman spectrum leaves little doubt: the aromatic ring band at 1600 cm⁻¹ decreases sharply against the cellulose envelope and, as the alkali concentration or the soak time is increased, a new band at 577 cm⁻¹ signals the partial conversion of cellulose

I to cellulose II (Siroky *et al.*, 2010; Agarwal *et al.*, 2021b). (Ramamoorthy *et al.*, 2015) followed precisely this sequence in Lyocell fibers subjected to a stepwise alkali-then-silane protocol. A spectrum taken after each stage gave a molecular chronology of the two-step modification, the kind of time resolution that a single post-treatment FTIR scan would level into one undifferentiated average. One caveat should be emphasized: the sampling depth is governed by the excitation wavelength, the confocal pinhole, and the numerical aperture of the objective. At 532 nm, through a 50 μm pinhole and a high-aperture objective, the effective sampling depth in cellulose is around 2–5 μm , sufficient for surface-localized treatments but likely to mislead anyone who takes the spectrum to represent the whole fiber cross-section. This subtlety, rarely discussed in the NFRC literature, is well documented among wood scientists (Everall *et al.*, 2009; Gierlinger *et al.*, 2018).

Silane grafting is a different chemistry. After hydrolysis, the organosilane molecules condense with the surface hydroxyls of the cellulose, knitting Si–O–C bridges with vibrational bands in the 400–600 cm^{-1} window. The sticking point is sensitivity: the amount of silane deposited is tiny compared to the volume of bulk cellulose under the beam, and the signal is lost in the cellulose background in a normal FT-Raman geometry. (Freire *et al.*, 2017) avoided this problem by using high-numerical-aperture confocal Raman microscopy, in which the excitation volume is small enough to separate the silane-related bands from the noise. Their depth profiles were equally revealing: the silane signal remained confined to the outermost 2–3 μm of the fiber wall, confirming that the coupling agent had never penetrated the lumen spatial information that no bulk technique could have provided. That same depth-profiling has not yet been applied to the newer coupling chemistries, maleated-anhydride grafting and isocyanate treatments among them, now gaining ground for PLA-based biocomposites (Bax & Müssig, 2008); the gap is an obvious target for future Raman work.

Acetylation, the esterification of surface hydroxyls with acetic anhydride, leaves the most self-evident signature of the three. Success of the reaction is announced by the appearance or intensification of a band near 1735 cm^{-1} (ester C=O stretch) together with increased intensity at 1375 cm^{-1} (CH_3 deformation of the grafted acetyl group) (Hill *et al.*, 1998; Tserki *et al.*, 2005). (Ramalingam *et al.*, 2023) compared Raman and FTIR side by side and reached a measured verdict: FTIR was more sensitive for quantifying the bulk degree of substitution, while confocal Raman, taken through a tight pinhole, added a reading of how the modification was distributed radially across the fiber cross-section, something FTIR could not do. The operative fact for the production floor is that the three dominant treatments, alkali, silane, and acetylation, leave fingerprints separable enough to be told apart unambiguously in a single Raman acquisition (**Figure 2**), which makes rapid at-line quality control on full-scale biocomposite lines a realistic prospect.

One treatment class that is just emerging is worth mentioning: enzymatic surface modification, where cellulases and hemicellulases selectively consume amorphous polysaccharides and leave crystalline cellulose intact (George *et al.*, 2014). This selectivity leads to the expected Raman fingerprint: sharpening of the cellulose bands as apparent crystallinity rises, and loss of the hemicellulose-related shifts around 1460 cm^{-1} . However, so far dedicated Raman studies of enzymatically treated NFRC fibers are very sparse, which is mildly surprising considering the momentum gained by green surface-modification routes for PLA and PBAT bio-composites (Jian *et al.*, 2020).

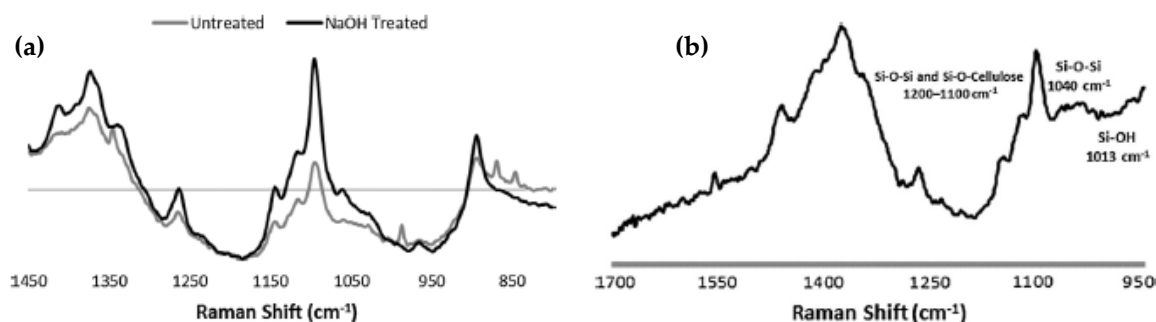


Figure 2. Comparison of vibrational spectra of untreated, NaOH- and silane-treated fibers: (a) Raman shift region 850–1450 cm^{-1} ; (b) silane-treated fiber, 950–1700 cm^{-1} (Ramamoorthy *et al.*, 2015).

4. Raman Imaging of Biocomposite Microstructure

The bulk behavior of the composite is determined by the arrangement of fibers in the matrix, their spacing, their tendency to cluster, and the direction they prefer, to an extent that coupon testing tends to underplay, since it samples only a few representative volumes (Thomason *et al.*, 2002). Confocal Raman imaging (CRI) was developed to fill this gap. A tightly focused laser is rastered across the specimen surface, a full Raman spectrum is acquired at each pixel, and the resulting hyperspectral data cube is sliced along chemically diagnostic wavenumber windows to provide spatial maps in which fiber and matrix are differentiated by molecular identity and not merely by morphology (Schaeberle *et al.*, 1995; Dieing *et al.*, 2011). Two instrument parameters set what such a map can actually resolve, and they deserve to be stated explicitly because they are so often left implicit in the NFRC literature. Lateral resolution is diffraction-limited and follows $d \approx 0.61\lambda/\text{NA}$: a 532 nm laser through a 0.90 NA objective reaches about 0.36 μm , the same objective at 785 nm gives roughly 0.53 μm , and a modest 0.25 NA objective at 785 nm barely reaches 1.9 μm , coarser than many of the interphase features one wishes to see. Axial resolution degrades faster still, scaling approximately as $1.4n\lambda/\text{NA}^2$, which is why depth profiles taken with low-aperture optics smear structure over several micrometers and, through refraction at the air/sample interface, report depths that are systematically distorted (Everall *et al.*, 2000, 2009). High numerical aperture is not free: working distance shortens, and for a given laser power the power density at the focus rises steeply, so photodegradation of lignin-rich walls becomes a genuine risk. Signal quality then pulls in the opposite direction from resolution, since the Raman cross-section scales as λ^{-4} while fluorescence from lignin falls as the excitation moves to the red. The practical consequence is that the best-resolved map and the cleanest spectrum are rarely obtained under the same conditions, a tension revisited in Section 7.4.

A particularly instructive example is the work of (Graupner *et al.*, 2017), who used CRI at about 1.3 μm lateral resolution to image hemp fiber-reinforced polycaprolactone composites at a range of loading fractions. By integrating the cellulose band near 1095 cm^{-1} relative to the polyester C=O band near 1725 cm^{-1} , they constructed binary maps from which they derived quantitative fiber-specific surface area, aggregate size, and orientation statistics. Of significant note was that fiber aggregation was statistically

significant for loadings > 20 wt% and the degree of alignment was vastly different for injection molded versus compression molded samples. SEM images of these same cross-sections showed the fibers well enough but no chemical contrast was obtained, the resin-filled lumens were indistinguishable from empty ones, and the lignin left at the interface was not visible. The authors did not shy away from the weakness of the study: the field of view was narrow. Each $100 \times 100 \mu\text{m}^2$ map captured no more than a handful of fibers, which quite justifiably raises the question of how representative such statistics can be. That concern could be relieved by stitching many high-resolution tiles into a millimeter-scale panoramic chemical map, an approach well within reach of today's motorized-stage microscopes but, as far as we are aware, not yet attempted on NFRC specimens.

The third spatial dimension is added to create a three-dimensional chemical reconstruction of the fiber architecture without the need for physical microtomy and hence preserving the interphase, the region most easily corrupted by preparation artifacts (Graupner *et al.*, 2017). This is done by moving the confocal plane in 1–2 μm steps through the specimen. Gierlinger and co-workers first applied this approach to native wood, combining Raman depth scans with MCR-ALS in order to disentangle the cellulose, lignin and hemicellulose contributions within single cross-sectional images. It is not conceptually difficult to extend the method to NFRCs. For example, one can visualize how far resin has penetrated the fiber cell wall, or map pockets of residual lignin strung along the fiber/matrix boundary, each of which feeds directly into adhesion modeling and failure prediction.

The real sticking point must be named: throughput. The cost of an image scales as the square of the inverse step size, and the arithmetic is unforgiving. A $100 \times 100 \mu\text{m}^2$ area sampled at a 1 μm step is 10^4 spectra; at a 2 s dwell time per pixel, that is 5.6 h of instrument time, acceptable for academic research but not for production-line quality control. Halving the step to 0.5 μm quadruples the number of spectra and pushes the same map beyond 22 h. Table 2 makes the trade-off explicit for a fixed field of view. Shortening the dwell time is the obvious remedy, but signal-to-noise improves only as the square root of integration time, so the fourfold speed-up obtained by moving from 2 s to 0.5 s per pixel is paid for by halving the signal-to-noise ratio tolerable when mapping a strong, isolated band such as the cellulose feature at 1095 cm^{-1} against a polyester carbonyl, but not when the target is a weak silane or residual-lignin signal. The figures in Table 2 are dwell times only; stage settling and detector readout typically add a further 10–30%, and the practical parameter sets reported for plant cell walls (0.3–0.5 μm steps, 0.5–2 s per pixel, maps of a few thousand square micrometers) sit squarely in the upper half of the table (Gierlinger *et al.*, 2012). Faster schemes exist line-focus illumination, compressed-sensing spectral recovery, and hierarchical scans that zoom from a coarse overview into regions flagged as anomalous (Zhang *et al.*, 2013) but all of them buy throughput by surrendering spatial or spectral resolution. The most promising way to accelerate bio-composite inspection is probably stimulated Raman scattering (SRS) microscopy, which is capable of video-rate imaging by interrogating one vibrational frequency at a time, although its adoption in the NFRC community is still at an early stage (Cheng & Xie, 2015). Detector quantum efficiency and real-time data-processing algorithms are steadily improving this trade-off, and it should become less restrictive in time; for the moment, however, the throughput ceiling is a real barrier.

Table 2. Dwell-time cost of a confocal Raman map over a fixed $100 \times 100 \mu\text{m}^2$ field of view, as a function of pixel step size and integration time per pixel. Values are pure acquisition times; stage settling and detector readout

Step size (μm)	Spectra per map	0.1 s per pixel	0.5 s per pixel	2 s per pixel
2.0	2 500	4 min	21 min	1.4 h
1.0	10 000	17 min	1.4 h	5.6 h
0.5	40 000	1.1 h	5.6 h	22.2 h
0.25	160 000	4.4 h	22.2 h	88.9 h

typically add a further 10–30%. Lateral resolution is in any case diffraction-limited ($\approx 0.4 \mu\text{m}$ at 532 nm with a 0.9 NA objective), so step sizes below $\sim 0.25 \mu\text{m}$ oversample rather than resolve.

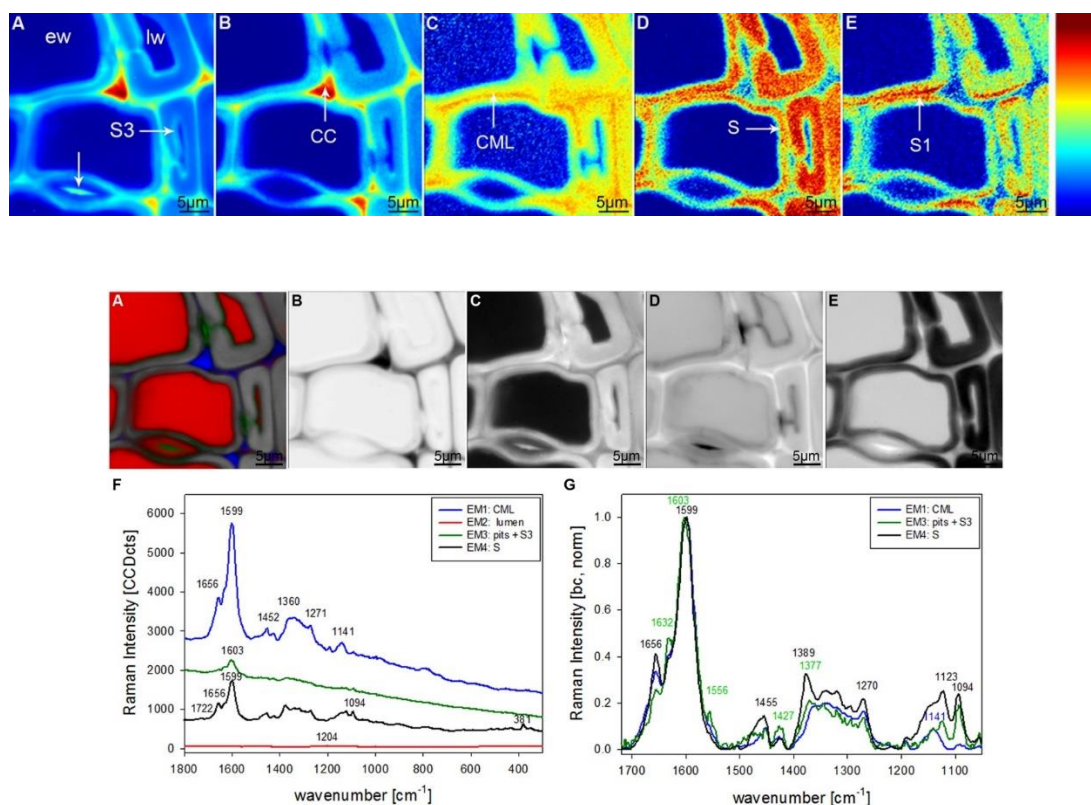


Figure 3. Confocal Raman imaging applied to natural fiber-reinforced composites: univariate chemical maps (fluorescence, lignification, cellulose content and microfibril orientation) together with a VCA composite map whose endmembers correspond to the individual cell-wall layers (Gierlinger *et al.*, 2014).

5. Micromechanical analysis by Raman Band Shift

Among Raman's contributions to composite science, its role as a molecular-scale strain gauge is arguably the most distinctive. The mechanism is simple. Place a cellulose backbone under tension and the C–O–C stretching mode at $\sim 1095\text{ cm}^{-1}$ shifts to lower wavenumber, a direct consequence of bond anharmonicity and of the increase in interatomic distances under stress (Hamad & Eichhorn, 1997; Štuncová *et al.*, 2005). The shift rate $\Delta\nu/\Delta\epsilon$ is typically between -0.5 and $-4.3\text{ cm}^{-1}/\%$ strain set by fiber origin, cellulose crystallinity and microfibril angle and has proved to be reproducible enough to serve as a calibrated local strain readout (Eichhorn *et al.*, 2001; Gierlinger *et al.*, 2006). No foil gauge, no resistance grid, no lead wires – a laser spot smaller than the fiber itself does the job.

This was first convincingly shown by embedding hemp fibers partially in epoxy microdroplets by Eichhorn and Young. Raman spectra were recorded every $5\text{ }\mu\text{m}$ along the fiber axis. Strain profiles were reconstructed point by point, and the distribution of interfacial shear stress (ISS) was extracted from a simple force balance. The values they obtained of 4 to 8 MPa were in the range that conventional micro-bond pull-out testing returns for comparable hemp/epoxy systems, typically 5–12 MPa (Beckermann & Pickering, 2009). The shear stress was clearly non-uniform and reached a maximum near the points where the fiber entered and exited the matrix and decreased towards the center of the embedded length, as described by the classical Cox (1952) shear-lag model. Raman added what pull-out testing cannot: spatial resolution. A micro-bond test returns a single, spatially averaged ISS and says nothing about how stress is actually distributed along the embedded length. The systematic offset of the Raman values towards the low side has a straightforward explanation: Raman probes the elastic regime before debonding initiates, whereas pull-out registers the stress peak at the onset of interfacial failure. The distinction is rarely stated explicitly, yet it matters whenever the two data sets are compared.

The technique transplanted to other cellulosic reinforcements with no real change of method. (Tze *et al.*, 2007) worked on regenerated cellulose (Lyocell) fibers bonded to polystyrene micro-droplets, converting the shift of the stress-sensitive 895 cm^{-1} band into local axial stress through a calibration of 0.44 cm^{-1} per 100 MPa. The maximum interfacial shear stress rose from $9.3 \pm 1.2\text{ MPa}$ for untreated fibers to $13.8 \pm 1.8\text{ MPa}$ after amino-silane treatment and $12.1 \pm 1.6\text{ MPa}$ after grafting with a styrene–maleic anhydride copolymer, while a non-polar octadecyl silane depressed it to $8.0 \pm 1.4\text{ MPa}$. Read as a series, those figures amount to a molecular-scale ranking of coupling chemistries that no bulk mechanical test delivers so directly. (Štuncová *et al.*, 2005) obtained $-2.4 \pm 0.2\text{ cm}^{-1}/\%$ strain for tunicate whiskers dispersed in an epoxy beam deformed in four-point bending, (Štuncová *et al.*, 2005 and Rusli *et al.*, 2010) later followed the same band in tunicate whisker/poly(vinyl acetate) nanocomposites, where the response proved to depend on the local orientation of the nanocrystals as much as on the matrix; the steepest rates reported for any cellulosic reinforcement, and squarely consistent with the near-90% crystallinity of tunicate whiskers. (Gierlinger *et al.*, 2006) applied the method to single wood fibers deformed in controlled tension and mapped the strain field across the cell wall, showing that the S2 layer carries most of the mechanical load. The published values of $\Delta\nu/\Delta\epsilon$ for the fiber types and test conditions are compiled in **Table 3** to provide the first quantitative benchmark in a review against which future studies can be set.

Table 3. Reported Raman band-shift rates ($\Delta\nu/\Delta\varepsilon$) of the C–O–C stretching mode ($\sim 1095\text{ cm}^{-1}$) for different cellulosic fiber types.

Fiber type	Matrix	λ laser (nm)	$\Delta\nu/\Delta\varepsilon$ ($\text{cm}^{-1}/\%$)	ISS (MPa)	Ref.
Hemp (single fiber)	Epoxy microdroplet	633	–1.0 to –1.2	4–8	(Eichhorn & Young, 2004)
Regenerated cellulose (Lyocell), untreated	Polystyrene microdroplet	785	– †	9.3 ± 1.2	(Tze <i>et al.</i> , 2007)
Regenerated cellulose (Lyocell), amino-silane	Polystyrene microdroplet	785	– †	13.8 ± 1.8	(Tze <i>et al.</i> , 2007)
Regenerated cellulose	Free-standing	632.8	–0.5 to –0.9	–	(Hamad & Eichhorn, 1997)
Tunicate whiskers	PVAc film	785	–4.3	–	(Rusli <i>et al.</i> , 2010)
Wood (spruce, S2 layer)	Native cell wall	532	–1.5 to –2.0	–	(Gierlinger <i>et al.</i> , 2006)
Tunicate whiskers (dispersed)	Epoxy beam (4-point bending)	785	-2.4 ± 0.2	–	(Šturcová <i>et al.</i> , 2005)
Cotton	Free-standing	632.8	–0.7	–	(Eichhorn <i>et al.</i> , 2001)
Bamboo (extracted)	Free-standing	532	–1.3*	–	(Wang <i>et al.</i> , 2013)

* Estimated from the published spectra rather than stated explicitly by the authors. † (Tze *et al.*, 2007) calibrated the stress-sensitive 895 cm^{-1} band directly against tensile stress (0.44 cm^{-1} per 100 MPa) rather than against strain; the corresponding $\Delta\nu/\Delta\varepsilon$ is therefore not reported. PVAc = poly(vinyl acetate); ISS = interfacial shear stress; – = not measured or not applicable.

It is worth pausing to think about what the band shift actually encodes. (Eichhorn, 2005) demonstrated that the observed change in frequency arises from disruption of the inter- and intra-chain hydrogen bonds in conjunction with stretching of the backbone, predominantly at high strains where the first indications of a crystalline-to-amorphous transition appear. The measured $\Delta\nu/\Delta\varepsilon$ is therefore not a clean signal of mechanical strain: it folds together lattice strain and supramolecular rearrangement, and carries richer but more tangled information than a foil strain gauge would (**Figure 4**). The separation of the two contributions is still an open problem. Ab initio molecular-dynamics simulations have started to address this, but not yet with the full complement of cellulose polymorphs found in commercial NFRCS. The near order-of-

magnitude spread of $\Delta\nu/\Delta\varepsilon$ in Table 3 from $-0.5\text{ cm}^{-1}/\%$ for regenerated cellulose to $-4.3\text{ cm}^{-1}/\%$ for tunicate nano-whiskers is a measure in itself of how forcefully crystallinity, chain alignment and hydrogen-bond density govern the mechano-spectral response.

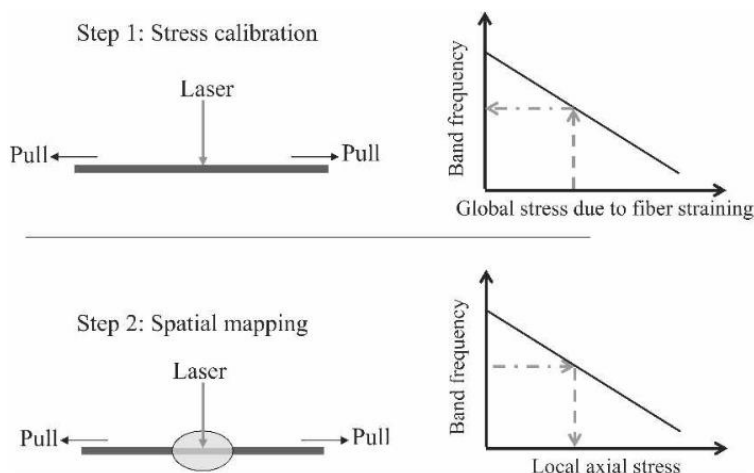


Figure 4. Schematic of the Raman micro-spectroscopy technique used for mapping the tensile stress at the fiber/polymer interphase (Tze *et al.*, 2007).

6. Degradation and Durability Assessment

The most obvious weakness of NFRC technology is durability, and its more enthusiastic proponents tend to downplay that fact. Outdoor service implies exposure to ultraviolet light, repeated wet/dry cycles and biological colonization, all acting on the fiber, on the matrix, and very often on the fiber/matrix interface, the most exposed region of the lot (Beg & Pickering, 2008; Azwa *et al.*, 2013). Predicting service life is more than just confirming degradation is taking place. One has to know what shifted at the molecular level, where in the composite architecture the damage gathers, and how those chemical changes feed through into lost mechanical performance. Raman is non-destructive and molecularly discriminating and can provide this kind of information.

Ultraviolet light attacks lignin first. Lignin, the major chromophore in lignocellulosic tissue, absorbs strongly in the near-ultraviolet and photo-oxidizes to break down its aromatic rings into quinones and ring-opened carbonyl species. The Raman trace is straightforward: the aromatic band at 1600 cm^{-1} decays stepwise while a broad feature between 1700 and 1730 cm^{-1} , the fingerprint of carbonyl photo-products, grows in (Pandey & Vuorinen, 2008; Guo *et al.*, 2018). The rate of this evolution is not the same for all fibers. High lignin content fibers such as coir ($\sim 45\text{ wt}\%$ lignin) and wood flour exhibit rapid and significant change in spectral response within 200–500 h of UV exposure, while low lignin bast fibers such as flax ($\sim 2\text{--}5\%$ lignin) show a much slower response (Sinha & Rout, 2009; Verma *et al.*, 2013). Such fiber-dependent kinetics has a practical consequence: Raman degradation-monitoring protocols cannot be calibrated once and for all, but must be referenced to the lignin content of the particular fiber under consideration. In a recent and

careful review (Nezafatkhah *et al.*, 2025) explicitly linked the magnitude of these spectral changes to the retention of tensile strength in weathered NFRCs, suggesting that Raman-derived lignin degradation indices could potentially provide a non-destructive proxy for residual load-bearing capacity. Confirmation is still needed over a wider spread of fiber/matrix combinations but if the correlation holds up it would be a genuinely useful tool for in-service health monitoring.

Matrix degradation tells a different spectral story. Polypropylene, the thermoplastic most often combined with natural fibers, presents the well-known Raman markers of oxidative ageing: a band appearing near 1713 cm^{-1} (the carboxylic-acid C=O stretch) and shifts in the crystallinity-sensitive 809/841 cm^{-1} doublet, which track the amorphous-to-crystalline rearrangements induced by chain scission and chemi-crystallization (Schoolenberg & Vink, 1991; Nielsen *et al.*, 2002). PLA-based biocomposites degrade along a different spectral signature (Meaurio *et al.*, 2006). Hydrolytic chain scission drains intensity from the ester C=O band near 1755 cm^{-1} and gives rise to new carboxylate features, while the steady loss of the helical band at 921 cm^{-1} registers amorphization of the PLA crystalline phase. Raman reads fiber and matrix markers in a single acquisition, providing a phase-resolved portrait of degradation that separates cellulose breakdown from polymer oxidation or hydrolysis, separations not possible with global indicators such as mass loss or colorimetric ΔE^* .

A third line of attack is moisture, systematically underestimated in accelerated-ageing protocols. The cellulose microfibrils swell and contract in cycles, breaking hydrogen bonds; the outermost cellulose layers become amorphous, and gradually the fiber is pried from the surrounding resin. Raman mapping of composite cross-sections after hygrothermal conditioning shows localized drops of the 1095 cm^{-1} cellulose band at the fiber periphery, a spatial fingerprint of incipient amorphization that typically precedes any macroscopic loss of properties by a wide margin (Dhakal *et al.*, 2007). Such maps provide the spatially resolved mechanistic basis for designing effective moisture-barrier treatments or for tuning fiber/matrix coupling chemistries for wet-environment service. A logical next step would be to combine in situ Raman mapping with controlled-humidity chambers and track the amorphization front as it advances in real time an experiment that, to our knowledge, has not yet been reported.

7. Challenges, Emerging Trends, and Prospects

7.1. Analytical Benchmarking: Raman in Perspective

Before tackling the frontiers, it is worthwhile to locate Raman right alongside the analytical platforms that are used on a day-to-day basis for NFRC characterization. **Table 4** compares Raman with FTIR, XRD and SEM across eleven performance criteria. The exercise is more than academic: referees and industrial users alike need a clear-eyed reckoning of where Raman pulls ahead and where the other techniques remain indispensable. The comparison confirms what makes Raman unique, the combination of chemical specificity, spatial resolution and mechanical sensitivity in a single non-destructive measurement, a combination no other single technique can match.

Table 4. Benchmarking of the main analytical methods used for NFRC characterization.

Standard	Raman	FTIR (ATR)	XRD	SEM (+ EDX)
Spatial resolution	<1 μm (confocal)	5–10 μm (IR-ATR)	~50–100 μm (micro-XRD)	<10 nm (imaging)
Chemical specificity	High (molecular fingerprint)	High (functional groups)	Low (crystal phases only)	Low (elemental, no molecular)
Crystallinity measurement	Semi-quantitative (I_{380}/I_{1095})	Semi-quantitative (TCI, LOI)	Quantitative (Segal, Rietveld)	Not applicable
Allomorph discrimination (I vs II)	Yes (577 cm^{-1} band)	Partial (O–H region)	Yes (diffraction peaks)	No
Mechanical strain sensing	Yes (band shift)	No	Limited (peak broadening)	No
Sample preparation	None (non-destructive)	Minimal (ATR contact)	Minimal (powder or film)	Coating + vacuum
Water/moisture compatibility	Excellent (weak Raman scatterer)	Poor (strong IR absorber)	Good	Poor (vacuum)
Mapping / imaging speed	Slow (hours per 100×100 μm^2)	Moderate (ATR imaging)	Very slow (synchrotron μ -XRD)	Fast (SE/BSE imaging)
Interface / interphase analysis	Excellent (chemical + mechanical)	Limited (surface only)	Not applicable	Morphological only
Cost / availability	Moderate–high	Low–moderate	Moderate	Moderate
Fluorescence interference	Yes (lignin-rich fibers)	No	No	No

TCI = total crystallinity index (FTIR); LOI = lateral order index (FTIR). The comparison assumes standard laboratory-grade instruments; synchrotron sources or specialized configurations may extend what XRD and FTIR can achieve.

7.2. Tip-Enhanced Raman Spectroscopy (TERS)

TERS is the most ambitious spatial frontier of them all. It pushes chemical imaging down to 10–20 nm, two orders of magnitude beyond the confocal diffraction limit, by squeezing the electromagnetic field into the apex of a metallic scanning-probe tip (Stadler *et al.*, 2012). (Stadler *et al.*, 2012) set out practical guidelines for the technique and are candid about its difficulties. Applied to cellulose surfaces, TERS should in principle resolve variations in band position on the scale of individual crystallite boundaries, a level of detail to which confocal Raman, blind to nanoscale heterogeneity in chain packing, has no access. Turning TERS on the fiber/matrix interphase of an NFRC would be transformative, since the molecular composition of that zone, rarely thicker than 50–200 nm, could in principle be imaged directly. The practical obstacles,

however, are formidable. Tip fabrication remains poorly reproducible and signal variations of 30–50% between batches are not unusual. Signal stability suffers during the long acquisitions required by mapping. The method requires smooth surfaces, which composite cross-sections rarely are. The progress is real but the rate is dispiriting to anyone hoping to image actual composite interphases.

7.3. Machine Learning and Chemometric Discrimination

The more immediate disruption will probably come from data science. Raman images of plant tissue with overlapping spectral contributions are routinely resolved by PCA and MCR-ALS (Sun *et al.*, 2011; Gierlinger, 2014). The more momentous development is the rise of supervised learning for Raman classification, roughly in the last five years. (Acquarelli *et al.*, 2017) trained a convolutional neural network (CNN) directly on raw vibrational spectra and reached classification accuracies above 95% without manual preprocessing, outperforming both support-vector machines and conventional peak fitting on the same data sets. (Lussier *et al.*, 2020) surveyed the extension of these methods to Raman and SERS data and documented reported accuracies above 97% for tasks as demanding as the identification of bacterial species from their spectral fingerprints. Neither study was designed for NFRC fibers, but the algorithmic machinery transfers without modification. In principle, a CNN trained on a labelled library of cellulose, hemp, flax, jute, coir and bamboo spectra could identify the fiber type, predict crystallinity and flag early-stage degradation in a single automated pass.

If such classifiers were embedded in the acquisition firmware of a commercial Raman microscope, the instrument would be transformed from a specialist research platform into an automated quality-assurance station, able to inspect, say, every tenth fiber bundle passing down a production line. Much of that algorithmic machinery is already there. What is conspicuously lacking, and the need is now pressing, is a curated, open-access spectral database of natural fibers and their composites against which models can be trained, validated, and benchmarked from one laboratory to the next. In our opinion, this is the single biggest bottleneck preventing routine implementation of ML-assisted Raman analysis in the biocomposite industry. A community effort such as the RRUFF database for minerals would be a suitable template (Lafuente *et al.*, 2015).

7.4. Fluorescence and the Practical Choice of Excitation Wavelength

No working account of Raman on natural fibers can avoid fluorescence. Lignin and its phenolic relatives fluoresce strongly under visible excitation (532 nm being the usual choice), and in lignin-rich fibers such as coir, wood flour, and unbleached hemp, that fluorescent background can drown the Raman signal outright. When the excitation is switched to the near-infrared (785 nm, 1064 nm), the fluorescence is quenched, but at a high price: because the Raman cross-section scales as λ^{-4} , the signal drops by a factor of ~5 between 532 and 785 nm, bringing down spatial resolution and acquisition speed with it (Agarwal, 1999). Three approaches time-gated detection, coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering (SRS) each provide some relief, and each carries its own trade-offs (Cheng & Xie, 2015; Schmid & Dariz, 2019). In everyday practice, the choice of excitation for a given fiber/matrix pair is still made empirically, but the accumulated experience of the wood- and fiber-spectroscopy communities supports a set of working rules, which are summarized in **Table 5**. As a first approximation, the excitation should be matched to the lignin content of the fiber. Bleached, delignified and regenerated cellulosic fibers (lyocell, viscose, cotton, bleached flax) fluoresce weakly and are best served by 532 nm, where the λ^{-4} advantage

and the finest spatial resolution are both obtained; this is the wavelength of choice for confocal mapping of fiber/matrix interfaces and for polarization-resolved measurements of microfibril orientation. Bast fibers of intermediate lignin content flax, hemp and ramie, roughly 2–13 wt% lignin usually gives usable spectra at 532 nm after moderate photobleaching, but 633 nm is the safer default, and it is also the wavelength at which most published band-shift calibrations were established, which is a strong argument for retaining it whenever $\Delta\nu/\Delta\varepsilon$ values are to be compared with the literature. For lignin-rich fibers jute, sisal, bamboo at about 25 wt% lignin, coir at about 45 wt%, and wood flour 785 nm should be the starting point: fluorescence is largely suppressed while a dispersive instrument with a CCD detector still delivers usable throughput and sub-micrometer imaging. Where even 785 nm fails, which is typically the case for unbleached, extractive-rich or weathered coir and for dark-pigmented composites, 1064 nm FT-Raman removes fluorescence almost completely and becomes the only practical option, at the cost of imaging: InGaAs detection and the diffraction limit at 1064 nm confine it to millimeter-scale sampling with acquisition times of minutes per spectrum (Agarwal, 1999, 2014). One caveat cut across all of these recommendations. The matrix fluoresces too, and pigmented or recycled polyolefins and some unsaturated polyester resins can dominate the background irrespective of the fiber; in such systems the wavelength should be selected on a cross-section of the actual composite rather than on the neat fiber. A systematic benchmarking study over the most industrially relevant fibers (flax, hemp, jute, coir, bamboo) at several excitation wavelengths (532, 633, 785, 1064 nm) is long overdue and would serve the community well.

Table 5. Practical guide to the selection of the Raman excitation wavelength for natural fibers and their composites. The dominant selection criterion is the lignin content of the fiber; where the matrix itself is pigmented or fluorescent, the choice should be validated on a cross-section of the actual composite rather than on the neat fiber.

λ (nm)	Best suited to	Main advantages	Main limitations
532	Bleached, delignified and regenerated fibers (lyocell, viscose, cotton, bleached flax); confocal mapping; polarization studies	Highest scattering efficiency (λ^{-4}); best lateral resolution ($\approx 0.4 \mu\text{m}$); shortest acquisition times	Strong fluorescence from lignin and extractives; risk of local heating and photodegradation
633	Bast fibers of intermediate lignin content (flax, hemp, ramie, $\approx 2\text{--}13$ wt% lignin); micromechanical band-shift measurements	Good compromise between signal and fluorescence; wavelength of most published $\Delta\nu/\Delta\varepsilon$ calibrations, hence directly comparable	Fluorescence still significant above ≈ 10 wt% lignin; lower throughput than 532 nm
785	Lignin-rich fibers (jute, sisal, bamboo ≈ 25 wt%),	Fluorescence largely suppressed; still	Signal $\approx 5\times$ weaker than at 532 nm; lateral

	coir $\approx$ 45 wt%); weathered and aged composites	compatible with confocal imaging on CCD instruments	resolution degraded to $\approx$ 0.5–1 μ m
1064	Coir, wood flour, unbleached or dark-pigmented samples where shorter wavelengths fail	Fluorescence essentially eliminated; robust for bulk crystallinity, allomorph and composition analysis	FT-Raman only; no practical imaging; minutes per spectrum; millimetre-scale sampling spot

7.5. In situ and Hyphenated Experimentation

One final frontier worth noting is hyphenated experimentation where the Raman microscope is coupled to an in situ tensile, fatigue or thermal stage. Real-time monitoring of the shift of the 1095 cm^{-1} band during a controlled strain ramp, or tracking the 1600 cm^{-1} lignin marker during an isothermal aging experiment, would provide kinetic and mechanistic information that is approximated only by post-mortem measurements (Thomas *et al.*, 2024). The hardware is not the bottleneck anymore. Linkam, Deben and others already sell tensile and heating stages that are compatible with most research-grade Raman microscopes. What is left is for the composites community to treat these configurations as routine, not the occasional proof-of-concept. The payoff for the extra experimental effort is in closing the loop between microstructural evolution and macroscopic performance prediction.

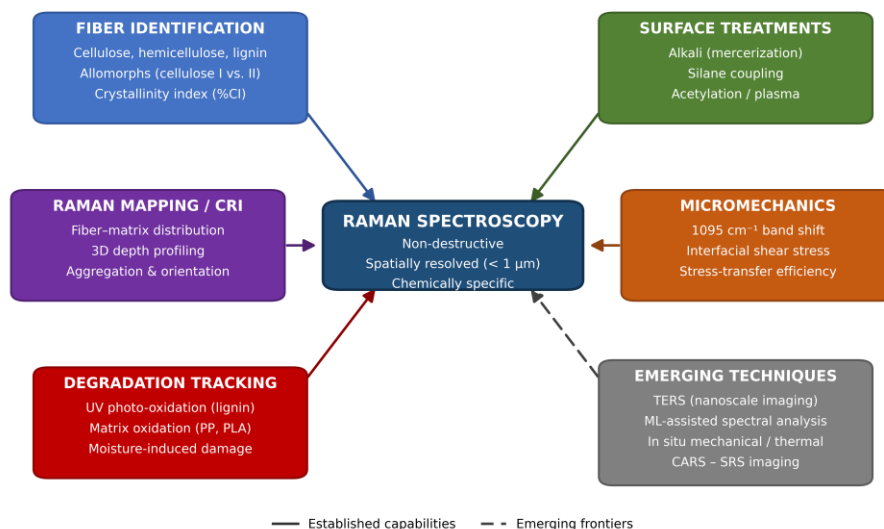


Figure 5. Overview of Raman spectroscopy applications for the characterization of natural fiber-reinforced composites. Solid arrows denote established capabilities; the dashed arrow denotes emerging frontiers (TERS, machine-learning-assisted spectral analysis, in situ hyphenated methods and CARS/SRS imaging).

8. Conclusions

In summary, the material collected here provides a coherent picture of the status of Raman spectroscopy in the characterization of NFRC. The technique combines molecular specificity, sub-micrometer spatial resolution, and sensitivity to mechanical loading in a way that no other single method can match (Table 4). Identification of fiber constituents and their allomorphic state, auditing molecular effects of surface treatments, three-dimensional mapping of fiber/matrix distributions, quantification of interfacial stress transfer at micrometer accuracy, and diagnosis of degradation pathways at the level of individual bonds are within reach of standard Raman instrumentation.

So far, three contributions have been the most influential in the field to date. The first is the use of the 1095 cm^{-1} C–O–C band shift as a molecular strain gauge, which for the first time enabled spatially resolved interfacial shear stress measurements on single fibers and revealed stress distributions systematically averaged out in bulk pull-out testing (Table 3). The second is confocal Raman imaging of composite cross sections, which adds chemical contrast to the morphological detail available with SEM, and has thus revealed resin-filled lumens, pockets of residual lignin at fiber/matrix interfaces, and the fiber-aggregation patterns that ultimately control macroscopic mechanical response. The third is the ability to follow degradation mechanisms UV photo-oxidation of lignin, chemi-crystallization of polypropylene, and moisture-driven amorphization of cellulose within one spectral acquisition, providing a phase-resolved degradation portrait with which no global measurement can compete.

There are still hurdles, and there is no point in playing them down. Fluorescence interference is a permanent problem for lignin-rich fibers such as coir and unbleached hemp. Confocal mapping is slow by any industrial standard. And the lack of standardized protocols for the measurement and reporting of Raman-derived crystallinity and strain data remains a limitation to comparability between laboratories. These are not footnotes, but practical limitations.

Moving forward, the creation of an open-access curated spectral database of natural fibers and their composites is considered the most important task for the community. Without it, the machine-learning classifiers, already above 95% accuracy on related spectral-identification problems (Acquarelli *et al.*, 2017; Lussier *et al.*, 2020), cannot be properly trained, validated, or benchmarked for NFRC-specific use, and the switch from specialist research tool to automated industrial quality-assurance station remains stuck. In addition to the data infrastructure question, the two technological advances we think most likely to transform the field in the next decade are the maturation of SRS microscopy for high-speed chemical imaging and the continued improvement of TERS tip fabrication for nanoscale interfacial analysis. Raman spectroscopy is adaptable and information-dense; it is improving at a rate that few rival analytical platforms can match, and it looks well placed to meet the increasingly exacting characterization demands of the biocomposite industry.

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F.D.: Conceptualization, literature review, writing — original draft, visualization. R.K.: Conceptualization, methodology, writing — review & editing, supervision. A.J.M. and N.B.: writing — review & editing. All authors have read and agreed to the published version of the manuscript.

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Declaration of Generative AI and AI-Assisted Technologies in the Writing Process

During the preparation of this manuscript, the authors used ChatGPT (OpenAI) to enhance readability and improve language clarity. After utilizing this tool, the authors thoroughly reviewed, edited, and validated all content to ensure scientific accuracy and integrity. The authors take full responsibility for the final version of the manuscript.

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