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TOWARDS A BETTER UNDERSTANDING OF THE FIBRE/MATRIX ADHESION IN FLAX/EPOXY COMPOSITES

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Abstract

The fibre/matrix interface is a critical feature of plant fibre-reinforced composites, governing load transfer and damage initiation. However, although this interface has a direct impact on the global mechanical performance of the composite, the nature of the interactions between the fibres and the matrix components remains poorly understood to this day. In the case of plant fibres combined with thermosetting polymer matrices, potential covalent/hydrogen bonding might occur at the interfacial level, given the organic nature of both components. However, due to the insufficient spatial resolution and inability to perform localised measurements using conventional infrared (IR) spectroscopy techniques, no experimental data directly probing covalent bond formation for fibre-reinforced composites has been reported to this day. In this study, a novel photothermal IR technique, namely O-PTIR sub-micron spectroscopy, was employed to investigate the chemical nature of the fibre/matrix interface in a flax/epoxy composite. IR chemical mappings and localised spectra were acquired, providing distinct signatures for the flax fibres and the chosen epoxy system. A gradient in the 1511 cm^{-1} band intensity was evidenced across the fibre/matrix interface, suggesting resin penetration into the flax fibre cell wall over a depth of approximately 1.6 µm. Further analyses focusing on the fibre/matrix interface are required to help unveil the possibility of covalent bonding formation at this level.

Keywords: *Flax fibres; O-PTIR spectroscopy; Chemical bonds; Sub-micron IR mappings; Localised IR spectra*

1 Introduction

Composite performance is governed not only by the intrinsic properties of the fibre reinforcement and the polymer matrix, but also critically by the quality and stability of the fibre/matrix interface [1]. In conventional systems, reinforcement fibres such as glass and carbon are typically characterised by inorganic chemistries. As a consequence, the direct interfacial adhesion to organic matrices is often insufficient to ensure effective stress transfer, thereby limiting load transfer efficiency and compromising long-term durability [2]. To address this limitation, inorganic fibres are commonly surface functionalised through a coating step using an organic coupling agent commonly referred to as sizing. This thin layer (typically a few tens to hundreds of nanometres) modifies the chemical molecular features of the fibre/matrix interface and promotes chemical bonding with the matrix, which will improve the overall mechanical properties of the composite such as strength and interlaminar shear strength [3, 4].

In contrast, plant-derived reinforcements such as flax fibres are inherently organic and exhibit surface functionality associated with lignocellulosic constituents. This fundamental difference in surface chemistry can significantly reduce the need for additional compatibilising agents, since the native fibre polarity and functional groups may provide a more favourable basis for interfacial interaction with organic matrix systems. Accordingly, when flax fibres are employed, adhesion enhancement may be achieved through the intrinsic fibre/matrix compatibility, rather than relying on exogenous coupling agents.

Flax fibres and amine/epoxy-based matrices are known to exhibit relatively high interfacial shear strength with reported values ranging from 13.2 to 22.5 MPa [5–7]. High shear strength may arise from a combination of mechanisms and physicochemical phenomena such as mechanical interlocking due to fibre surface roughness, chemical affinity between flax functional groups and the epoxy network, and potential contributions from interdiffusion and/or covalent or hydrogen-bonding interactions in the vicinity of the interface [8, 9]. Another possible phenomenon is reaction-induced phase separation of the epoxy matrix during curing, which could result in a compositional gradient near the interface. This may involve preferential migration of one of the resin components (either the amine hardener or the epoxy prepolymer) towards the fibre surface, leading to the formation of a resin-rich or hardener-rich interphase region [10]. Previous AFM PF-QNM (Atomic Force Microscopy – PeakForce Quantitative Nanomechanical Mapping) measurements evidenced an ultra-thin interfacial layer of only a few tens of nanometres [11].

To this day, and to the authors' best knowledge, there are no existing studies that propose comprehensive experimental investigations into the existence and nature of the above-described physicochemical phenomena at the fibre/matrix interface in flax/epoxy composites, mainly due to the lack of techniques enabling highly localised measurements at high spatial resolution.

Novel infrared spectroscopy techniques, namely Optical Photothermal Infrared (O-PTIR) spectroscopy, enable high-spatial-resolution chemical imaging (down to 416 nm) of intrinsic molecular bonds within a system. By combining infrared spectroscopic selectivity with sub-micrometric spatial resolution, this technique might help provide detailed insight into the local chemical environment at the fibre/matrix interface level.

Thus, the objective of this study is to investigate the chemical nature of the fibre/matrix interface in a flax/epoxy composite and its contribution to interfacial adhesion. O-PTIR measurements, precisely IR spectra and chemical mappings were performed to probe the chemical specific features at the fibre/matrix interface. The resulting information could contribute to a more comprehensive understanding of the physicochemical mechanisms governing interfacial adhesion between flax fibres and a thermosetting epoxy matrix.

2 Methodology

2.1 Sample preparation

A unidirectional (UD) composite plate with in-plane dimensions of 100 × 100 mm² and a thickness of 4 mm was manufactured for this study. UD flax fibre plies (FlaxTape™, Ecotechnilin, France) were employed as reinforcement. The matrix consisted of an epoxy system (Sicomin, France), obtained by mixing a partially biobased epoxy resin (SR GreenPoxy 56) with an amine hardener (SD 7561) at a mass ratio of 100:37. The composite was processed following the protocol optimised by Cadu et al. [12]. Curing was performed by thermocompression for 1 h at 60°C under a pressure of 3 bar. A subsequent post-curing step was performed at 130°C for 1 h in an oven without applied pressure. The volumetric composition of the UD plate was determined by weighing method [12], yielding a void content of 2.4% and a fibre volume fraction

of 52.7%.
A specimen with dimensions of 6 × 8 × 4 mm³ was then extracted by laser cutting. Surface preparation for analysis was performed using an ultramicrotome Leica Ultracut E (Leica Microsystems, Austria) equipped with diamond knives (DiATOME, Switzerland) to prepare the surface to be studied by block face polishing: a DiATOME Histo knife was first used to remove semi-thin layers (500 nm), followed by a DiATOME ultra knife to remove ultra-thin layers (50 nm). Cutting was performed in dry conditions at a speed of 1 mm/s. All subsequent analyses were conducted on the ultramicrotomed surface of the bulk specimen.

2.2 O-PTIR spectroscopy measurements

O-PTIR is a non-contact, non-destructive technique that combines infrared spectroscopic selectivity with sub-micrometric spatial resolution [13]. O-PTIR spectroscopy measurements, namely IR spectra and chemical mapping, were carried out using the mIRage® microscope (Photothermal Spectroscopy Corp., Santa Barbara, United States of America).
A Quantum Cascade Laser (QCL) IR laser beam and a visible probe beam (532 nm wavelength), simultaneously irradiate the sample, both focused through a 40× Cassegrain Objective. The IR laser is swept across the infrared range with four QCL modules, enabling spectral coverage across the 950-1800 and 2700–3000 cm^{-1} ranges.
As the specimen is irradiated by the IR laser beam, its constituent molecules undergo vibrational excitations at specific wavelengths, thereby absorbing the laser energy. This absorption induces a photothermal effect, resulting in localised thermal expansion of the material as well as a change in its refractive index. This photothermal response is detected by the visible probe beam (416 nm in diameter).
In co-propagating mode, both laser beams scan the sample from the top through the same objective, making this configuration suitable for opaque or bulk samples.
Thus, owing to the tunability of the IR laser in wavenumber and the localised submicrometric probing capability of the visible beam, both point spectra and spatially resolved IR absorption maps (416 nm spatial resolution) at selected wavenumbers can be acquired over a region of interest.

3 Results and discussion

O-PTIR distinctive mapping requires clear discrimination between fibre and matrix signals. This is achieved by selecting an absorption band that is specific to one constituent, which requires prior knowledge of the IR spectra of flax fibres and the used amine-epoxy system. Therefore, preliminary measurements were performed on the studied sample: point spectra were acquired at 8 cm^{-1} spectral resolution, at different locations within the fibre and matrix regions, carefully avoiding interfaces, lumens, and other microstructural features that could compromise the spectral purity of each constituent.
Figures 1-a and 1-b present the spectra of the fibre and the matrix respectively, each resulting from the averaging of five point-spectra acquired over their respective regions. Each measurement point corresponds to the size of the visible probe. The baseline of each individual spectrum was first corrected, then each spectrum was normalised by its maximum absorption value to account for the difference in IR absorption intensity between the fibre and the matrix. The resulting spectra were subsequently averaged. All post-processing was carried out using the PTIR studio v4.6.9130 software. Some characteristic bands for both materials are displayed on Figure 1. Peak assignations were performed based on literature data [14–18] for flax fibres and [18, 19] for amine-epoxy system.

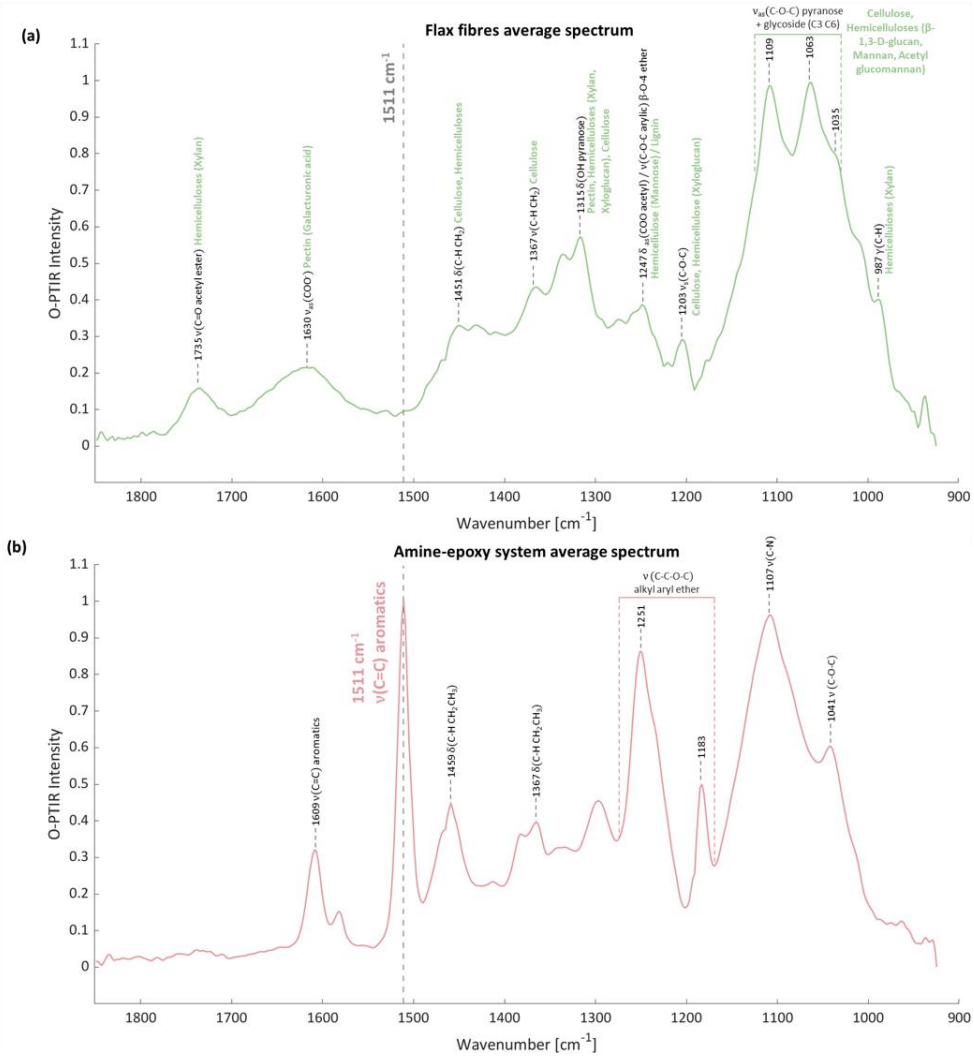

Figure 1. Average IR spectra of (a) flax fibres and (b) used amine-epoxy matrix

Only the infrared range between 950 and 1800 cm^{-1} is displayed, as this region contains the most relevant chemical information. The higher wavenumber range (2700-3000 cm^{-1}) is dominated by C–H stretching vibrations and does not provide significant additional insight for the present analysis.

As can be seen in Figures 1a and b, the IR spectra of the flax fibres and the epoxy matrix exhibit distinct features, although some band overlap is present in certain spectral regions.

In addition to the bands shown in Figure 1b, the band at 915 cm^{-1}, characteristic of epoxy ring (oxirane) vibrations, falls outside the O-PTIR scanning range defined in Section 2.2 and hence cannot be used as a discriminant band. The band at 1109 cm^{-1} could be attributed to C–N stretching vibrations of either the amine hardener or the polymerised matrix, however, the disappearance of the 1593 cm^{-1} band assigned to NH_2 vibrations confirms full consumption of the amine hardener during curing, allowing this band to be attributed to the polymerised matrix. Nevertheless, it overlaps with C–O–C vibrations of glycosidic bridges and pyranose rings from the cellulose and hemicellulose content of flax fibres. More broadly, the 1000–1300 cm^{-1} region is shared by both the epoxy matrix and the fibre constituents due to overlapping C–O–C stretching vibrations. The band at 1511 cm^{-1}, attributed to C=C stretching of phenyl rings in the epoxy resin, is expected to be absent from the flax fibre IR spectrum, as lignin, which contains

polyphenolic structures absorbing in this region, is barely present in extraxylematic fibres such as flax. Therefore, the 1511 cm^{-1} band was selected to generate O-PTIR distinctive chemical mappings and will serve as the polymerised epoxy matrix marker throughout this study.
Hence, Figure 2a shows the optical micrograph of the region of interest, in which a fibre bundle can be distinguished. Figure 2b shows the O-PTIR chemical map acquired at 1511 cm^{-1}, corresponding to the region highlighted by a white rectangle in Figure 2a. The mapping in Figure 2b was acquired at a rate of 1 line per second, with a spatial sampling of 0.1 µm (i.e., the distance between two pixels). The effective spatial resolution is governed by the probe beam diameter, corresponding to a pixel size of 416 nm, as detailed in Section 2.2.

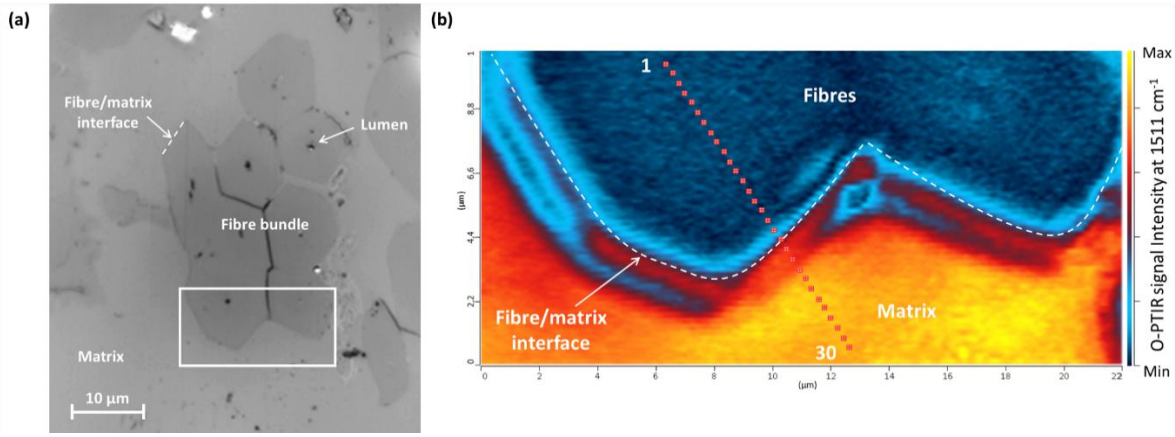

Figure 2. (a) Optical micrograph of the region of interest in a flax/epoxy composite. (b) O-PTIR chemical map acquired at 1511 cm^{-1}, corresponding to the region highlighted by the white rectangle in (a) and highlighting the spatial distribution of the epoxy matrix.

As observed in Figure 2b, the matrix region shows the highest absorption of the IR signal at 1511 cm^{-1}, with very little absorption in the flax fibres' region. Moreover, regions of intermediate IR absorption are observed at the fibre/matrix interface, which may reflect localised physicochemical phenomena such as reaction-induced phase separation of the epoxy matrix during curing. Such phase separation could result in a gradient in the chemical composition of the matrix near the interface, potentially involving preferential migration of one of the resin components (amine hardener or epoxy prepolymer) towards the fibre surface, or the formation of a resin-rich or hardener-rich interphase region. Additionally, chemical interactions between the fibre surface and the matrix such as hydrogen bonding or covalent bonding between hydroxyl groups of the cellulose and the epoxy or amine functions could further contribute to a chemically distinct interfacial zone.
However, provided that the physicochemical interfacial phenomena extend over an ultra-thin spatial range (a few tens of nanometres), comparable to that of the elastic properties variations reported in a previous study employing AFM quantitative nanomechanical mappings [11], the maximum achievable spatial resolution (416 nm) may still be insufficient to accurately determine the thickness of the interphase characterized by chemical bonding variations. Thus, to avoid possible misinterpretations arising from the potential pixel overlapping, a more detailed analysis focusing on the fibre/matrix interface region is required. An array of 30 consecutive point-spectra was acquired along a line crossing the fibre/matrix interface, with a spacing of 400 nm between consecutive points to prevent measurement overlap. The points were selected on the map shown in Figure 2b so as to cover all distinct regions: pure fibre, near-interface fibre, fibre/matrix interface, near-interface matrix, and pure matrix. The corresponding IR spectra in

the 950–1800 cm^{-1} range are displayed in Figure 3a.

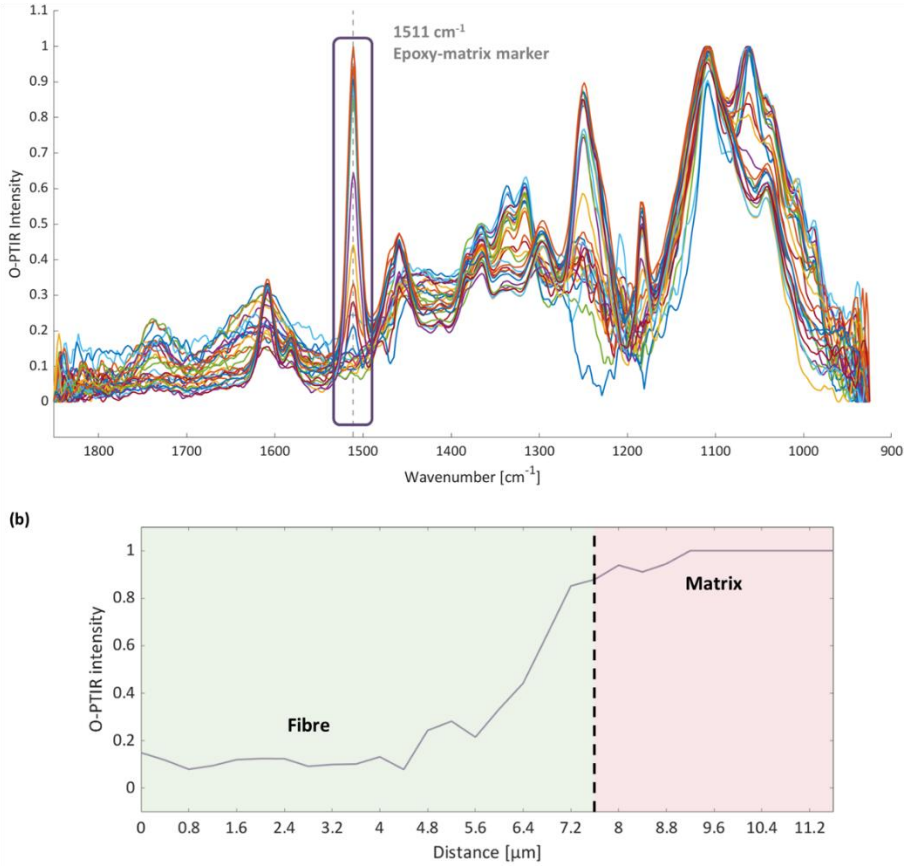

Figure 3. (a) IR spectra of the 30 measurement points displayed in Figure 2b. (b) Evolution of the absorption intensity of the IR signal at 1511 cm^{-1}, previously chosen as the epoxy-matrix marker.

By displaying the IR spectra of distinct measurement points crossing the fibre/matrix interface on a single graph, subtle spectral variations can be probed and identified, such as peak shifts, abrupt or gradual changes in intensity, or the emergence of additional bands.

In the present work, focus was made on the evolution of the absorption intensity of the band located at 1511 cm^{-1}, previously identified as a marker of the polymerised epoxy-matrix. As can be seen on Figure 3a, several spectra within the flax fibre exhibit non-negligible absorption at this wavenumber, suggesting the presence of epoxy-related species within the fibre itself.

Hence, for deeper investigations, Figure 3b displays the evolution of the absorption intensity of the 1511 cm^{-1} band across the 30 measurement points. A gradient of intensity can be observed between 4.4 µm (pure fibre), and up to 7.4 µm (near-interface matrix). This transition involves 6 points within the pure fibre cell wall, corresponding to an approximate total thickness of 2 µm. The observed gradient might reflect the penetration of the polymerised matrix into the flax fibre's cell wall. These findings are coherent with literature findings suggesting a penetration range of 1.7 – 2.2 µm of epoxy resin in the flax fibre cell wall [7].

The present study aims to investigate the possible existence of specific physicochemical interactions occurring at the fibre/matrix interface for the studied flax/epoxy system, including the possible formation of covalent bonds, interpenetration of the matrix into the fibres' cell walls, or reaction-induced phase separation of the epoxy matrix components. While a more detailed investigation of this interfacial region would be required to draw definitive conclusions,

preliminary observations suggest that O-PTIR spectroscopy might be a promising tool for probing such phenomena in this region at the sub-micrometric scale. A more in-depth analysis of these interfacial signatures will therefore be necessary to better understand the nature of adhesion mechanisms in flax/epoxy composites and to assess the contribution of interfacial chemistry to their macroscopic properties.

4 Conclusions

This study focuses on the applicability of O-PTIR micro-spectroscopy for the investigation of flax/epoxy composites with sub-micrometric spatial resolution, combining chemical mappings and localised IR spectra. The selected diagnostic band at 1511 cm^{-1} allowed for a distinctive chemical mapping of the region of interest. A spectral array was acquired, revealing potential penetration of the epoxy-resin in the flax fibre's cell wall. A deeper analysis in the visible changes on the different constituents' spectra (new bands, band shifts or intensity variations) is needed to probe the chemical phenomena that might be occurring at the fibre/matrix interface.
Overall, this work provides a first step towards a more detailed understanding of the chemical nature of the fibre/matrix interface for the studied flax/epoxy system. In the long term, combining O-PTIR chemical information with AFM nanomechanical mappings through a correlative spectro-mechanical microscopic approach is required to achieve a more comprehensive description of the fibre/matrix interface, by elucidating the relationship between local chemical signatures and local nanomechanical properties. Such an approach, further integrated with macroscopic experimental characterizations, would enable the establishment of structure–property relationships, linking interfacial phenomena to the overall performance of the composite at the structural scale.

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References

[1] Plonka R, Mäder E, Gao SL, et al. Adhesion of epoxy/glass fibre composites influenced by aging effects on sizings. *Compos Part Appl Sci Manuf* 2004; 35: 1207–1216.

[2] Sharma M, Gao S, Mäder E, et al. Carbon fiber surfaces and composite interphases. *Compos Sci Technol* 2014; 102: 35–50.

[3] Ishida H. A review of recent progress in the studies of molecular and microstructure of coupling agents and their functions in composites, coatings and adhesive joints. *Polym Compos* 1984; 5: 101–123.

[4] Thomason JL. Glass fibre sizing: A review. *Compos Part Appl Sci Manuf* 2019; 127: 105619.

[5] Le Duigou A, Davies P, Baley C. Interfacial bonding of Flax fibre/Poly(l-lactide) bio-composites. *Compos Sci Technol* 2010; 70: 231–239.

[6] Le Duigou A, Davies P, Baley C. Exploring durability of interfaces in flax fibre/epoxy micro-composites. *Compos Part Appl Sci Manuf* 2013; 48: 121–128.

[7] Le Duigou A, Kervoelen A, Le Grand A, et al. Interfacial properties of flax fibre–epoxy resin systems: Existence of a complex interphase. *Compos Sci Technol* 2014; 100: 152–157.

[8] Huang S, Fu Q, Yan L, et al. Characterization of interfacial properties between fibre and polymer matrix in composite materials – A critical review. *J Mater Res Technol* 2021; 13: 1441–1484.

[9] Leveziel A, Boutenel F, Gabrion X, et al. Engineering the flax/epoxy interface: Impact of iron oxide fibre functionalization revealed by microbond testing. *Compos Part Appl Sci Manuf* 2026; 206: 109766.

[10] Canavy N, Rouilly A, Drouet C, et al. Influence of flax fibers on epoxide-amine composites: Energetics of interphase formation. *Polymer* 2022; 254: 125047.

[11] Arafat I, Colas G, Gaillard Y, et al. Ultra-Thin interphase in Flax/Epoxy composites revealed by AFM PF-QNM nanomechanics. *Compos Part Appl Sci Manuf* 2026; 204: 109602.

[12] Cadu T, Berges M, Sicot O, et al. What are the key parameters to produce a high-grade bio-based composite? Application to flax/epoxy UD laminates produced by thermocompression. *Compos Part B Eng* 2018; 150: 36–46.

[13] Prater CB, Kansiz M, Cheng J-X. A tutorial on optical photothermal infrared (O-PTIR) microscopy. *APL Photonics* 2024; 9: 091101.

[14] Mukherjee S, Goulas E, De Waele I, et al. Tracking flax dew retting by infrared vibrational spectroscopy combined with a powerful multivariate statistical analysis. *Ind Crops Prod* 2025; 227: 120798.

[15] Himmelsbach DS, Khalili S, Akin DE. The use of FT-IR microspectroscopic mapping to study the effects of enzymatic retting of flax (*Linum usitatissimum* L) stems. *J Sci Food Agric* 2002; 82: 685–696.

[16] Garside P, Wyeth P. Identification of Cellulosic Fibres by FTIR Spectroscopy DIFFERENTIATION OF FLAX AND HEMP BY POLARIZED ATR FTIR. *Stud Conserv* 2006; 51: 205–211.

[17] Faix O. Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy. *Holzforschung* 1991; 45: 21–28.

[18] Infrared Spectroscopy Absorption Table [Internet]. 2025 [cited 2026 Apr 29]. Available from: https://chem.libretexts.org/@go/page/22645.

[19] Nikolic G, Zlatkovic S, Cakic M, et al. Fast Fourier Transform IR Characterization of Epoxy GY Systems Crosslinked with Aliphatic and Cycloaliphatic EH Polyamine Adducts. *Sensors* 2010; 10: 684–696.