HIGH RESOLUTION CHARACTERISATION OF BIOFIBRE/RESIN INTERFACE BONDS OF THERMOSET COMPOSITES THROUGH SYNCHROTRON ILLUMINATION

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Abstract
In this study, a Canadian linseed flax variety and a Chinese linen flax variety of biofibres were combined with Hydropel® R037-YDF-40, an infusion vinyl ester resin provided by AOC, Hydropel R037-YDF-40 with a 1% additive of Acronal™ Acrylic, provided by BASF, and Soy-matrix, a polyurethane provided by Urethane Soy Systems. Both fibre types were tested with and without a sodium hydroxide treatment. The methodology of producing samples for analysis, the observations from the Mid Infrared Spectromicroscopy and Soft X-ray Spectromicroscopy beam lines at the Canadian Light Source Synchrotron, and the resultant findings are discussed. It is anticipated that when completed the results of this study will enable a rationally designed, rather than purely empirical, approach to product improvement in the biocomposites sector.

1 Introduction
1.1 Background
The use of natural bast fibres as a replacement to E-glass reinforcement in thermosetting resins has been limited in part by issues with poor bonding [1]. Coupling agents used for glass and resins, such as silanes, have been tested on fibres, but substantial improvements in comparison to their E-glass counterparts have not been realized. Some fibre treatments, such as NaOH exposure, have shown moderate success in improving bonding due to the suspected removal of most non-cellulose surface materials, such as lignin, in addition to creating a rough surface topography and transforming cellulose I to cellulose II [2][3]. A rational, mechanistic optimization of the bond requires a more direct understanding and mapping of the chemical and physical properties of the fibre-resin interface.

2 Materials and Preparation

2.1 Materials

Materials were selected based on their potential to provide a gradient of bond strengths, as determined from previous findings [4][5][6][7][8], in order to determine the mechanisms of bonding being utilized in each situation

2.1.1 Fibres

The fibres selected were both flax; a linseed flax originating from Canada and a linen flax originating from China. The unretted linseed flax was produced from 5-6 passes through a lab scale scutching machine to minimize the mechanical damage during decortication. The Chinese linen flax was water retted using minimal machine separation. Figure 1 shows the surface differences between the untreated Canadian and untreated Chinese fibres as captured by an inverted microscope (Axio Vert.A1). The linseed flax fibres were anticipated to have a larger percentage of noncellulose materials including waxes, hemicellulose, lignin, and pectin due to being unretted.

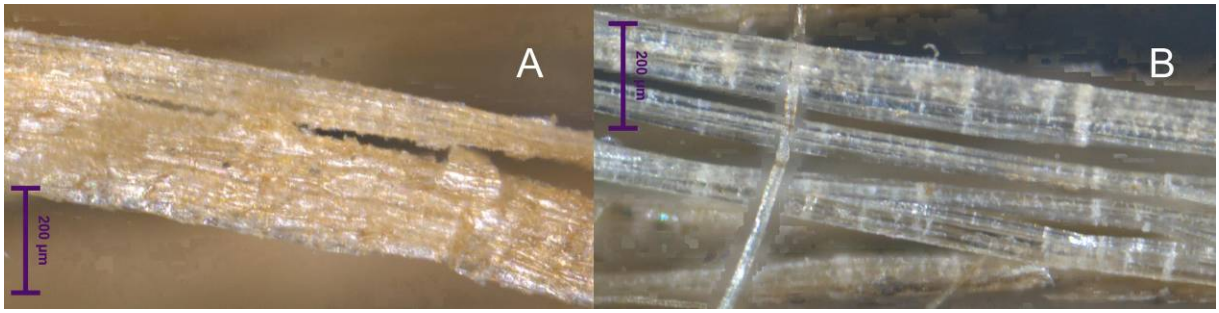

Figure 1. Untreated Canadian linseed fibres (A) and untreated Chinese linen fibres (B).

2.1.2 Treatments

While there are many treatments that have been tried in literature, the use of alkaline treatments, particularly NaOH, have been documented to provide improvements in the interfacial performance. A 95% ethanol concentration was used to make a 10g/L NaOH solution. The NaOH/ethanol solution was used instead of a NaOH /water solution because the ethanol solution reduces the curling of flax fibers during the treatment. Both alkaline treatments show similar effects on the flax fibers, but fibers treated with NaOH/ethanol solution are easier to process into composites. Images of the fibres after treatment, Figure 2, show a reduction of surface contamination and some reduction in fibre bundle size.

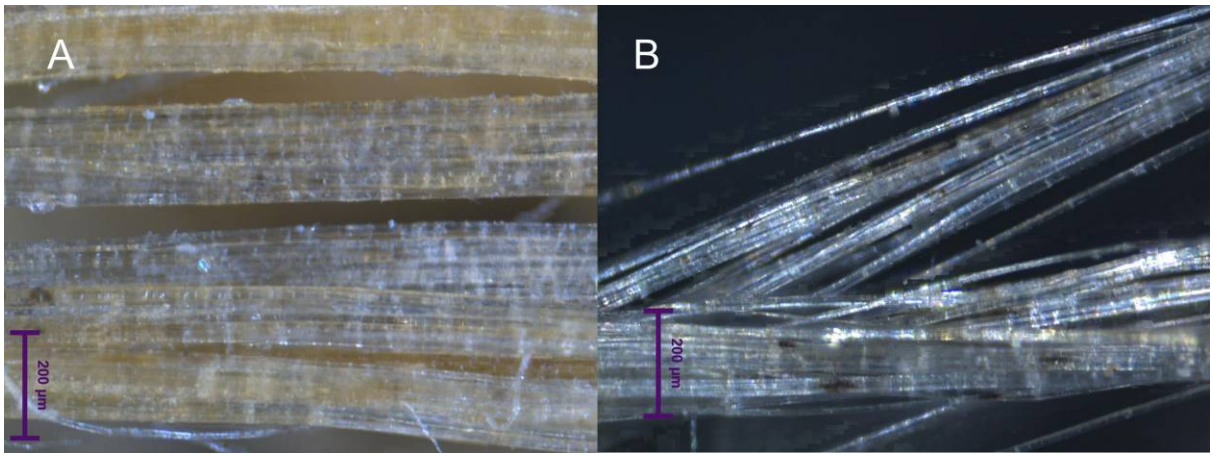

Figure 2. NaOH treated Canadian linseed fibres (A) and NaOH treated Chinese linen fibres (B).

2.1.3 Resins

The Composites Innovation Centre has an interest in utilizing natural fibres in vacuum assisted resin transfer moulding (VARTM) processes for the ground transportation industry. In these applications polyester and vinyl ester resins are predominantly used due to their low viscosity, room temperature cure, and economical cost. From previous research, Hydropel was found to have better natural fibre composite panel properties than other resins in its category [9]. Previous trials indicated that an addition of Acronal acrylic resin at 1% by weight to Hydropel resulted in improved properties suspected to be linked to improved bonding characteristics with the fibres [4][5]. A third resin, polyurethane, was selected due to the anticipated chemical bonding formed through the isocyanate component forming strong covalent bonds with the cellulose hydroxyl groups [6].

2.1.4 Sample Matrix

The samples that were produced are represented in Table 1.

	Fibres			
	Canadian Linseed		*Chinese Linen*	
Resins	Untreated	NaOH/Ethanol	Untreated	NaOH/Ethanol
Hydropel® R037-YDF-40	x	x	x	x
99% Hydropel and 1% (wt) Acronal™ Acrylic	x	x	x	x
Soy-matrix, polyurethane	x	x	x	x

Table 1. Matrix of samples produced

2.2 Sample Preparation

2.2.1 Composite Manufacture

In order to produce cross sections of individualized fibres surrounded by resin, 8 to 10 technical fibres were weighted to hang vertically into a pot of resin. The resin curing was done at room temperature and initiated using 2-Butanone peroxide (Luperox® DDM-9) solution from Sigma-Aldrich. The ratio of Hydropel to peroxide was 100:1.5 by weight. Once cured, the excess resin was trimmed using a small table saw with a diamond blade to produce smaller samples of approximately 1 cm^3.

2.2.2 Sectioning for Mid Infrared Spectromicroscopy

Samples for testing at the Mid Infrared Spectromicroscopy beamline were produced at the Biological Sciences Department of the University of Manitoba, Canada, using an Ultra Microtome (Leica Reichert Ultracut S).

To provide a surface to clamp the samples during sectioning, the samples, with the biofibers oriented in cross section, were mounted with crazy glue to a blank stub. The stubs were then cured in a 60°C oven (GCA/ Precision Scientific/ Model 19) overnight.

Samples were removed from the 60°C oven and allowed to sit at room temperature for a minimum of 2 hours prior to trimming. Preliminary trimming of the sample stubs was done with a steel file to removing excess resin and reducing the block face to 5mm in size.

Using a razor blade, the final blocks faces were trimmed into a 1-2 mm trapezoid shape. Blocks were washed briefly using Millipore filtered water then dried using filtered compressed air before sectioning.

Once the stub was secured in the chuck it was attached to the ultra-microtome in the appropriate orientation. Using a fresh glass knife (LKB 7801) material was removed from the block face to ensure the surface was polished and the sections would be scratch free. The chuck and sample was removed from the ultra-microtome and washed briefly using distilled water and then dried using compressed air before sectioning was resumed using a new glass knife or diamond knife (Dupont 3mm).

The 4 μm sections were floated in a water filled boat off of the knife. Sections were harvested using a glass rod and deposited on a small droplet of water located on the IR crystal discs (CaF^2 Polished Disc- 25mmx2mm). The transfer was repeated until 10-15 sections were mounted on the crystal. To insure the sections adhered properly, the IR crystal was placed on a 60°C slide warmer (Fisher) until the water droplets evaporated (approximately 10-15 min.). The knife was changed or cleaned between samples to avoid cross contamination.

2.2.3 Sectioning for Scanning Transmission X-ray Microscopy Analysis
The STXM sections were manufactured at McMaster University Faculty of Health Sciences Electron Microscopy Facility. Similar to the Mid-IR sectioning, a razor blade was used to trim away excess resin around the block of embedded flax fibres and a glass knife was used to smooth out the surface of the block face and expose the flax fibres at the surface.

Thin (100nm) sections were cut with a diamond knife (DiATOME 45 degree) on a Leica UCT Ultramicrotome, floated onto water and deposited onto Formvar-coated 100 mesh Cu grids, uncoated 200 mesh Cu grids and silicon-nitride windows.

Some 1 μm thick sections were sectioned for analysis of Na residuals using a diamond histoknife (Histo DiATOME 45 degree) on the Leica UCT Ultramicrotome. The histoknife has a bigger cutting surface making it better suited to cut thicker sections without damaging the knife edge.

3. Testing

Two beam lines at the Canadian Light Source were selected for studying the samples; Mid-Infrared Spectromicroscopy (Mid-IR) to map all of the specimens and a few samples were selected for further analysis using the narrower spot size of the Scanning Transmission X-ray Microscopy (STXM) in the soft X-ray Spectromicroscopy (SM) beamline. The Mid-IR beam line operates between 560-6000 cm^{-1}. The resolution (ΔE) is between 16.0 and 0.125 cm^{-1}. The SM beam line covers an energy range of 130 to 2500 eV and the spatial resolution of STXM is ~ 35 nm. The spectral power of the beamline ((ΔE) is between 3000 and 10,000.

3.1 Mid-IR

Following the sectioning process, the crystal IR windows contained 8 to 10 sections of approximately 4 μm thick. Sections that contained several fibres together with a consistent thickness were selected for mapping. Qualitatively it appeared that samples that had not been treated with NaOH displayed more empty spaces or cavities between the fibres and the resin.

Specific regions where a couple of fibres were in close proximity with each other and displayed good contact with the resin were targeted for the mapping. These regions were selected to provide insight into the resin to fibre interfaces as well as fibre to fibre interface regions.

The mapping process was done in 10 µm step sizes in both the X and Y directions with a complete IR spectrum collected at each step (400-4000 cm^{-1}). Vibrational bands that correspond to either the resin or the fibre were used to map the extent of resin integration in the fibre samples. The integrated area under the peak was used to map either resin or fibre modes. Integration of peaks in the second derivative of the absorbance spectrum was used to remove baseline interference.

3.2 STXM

The soft X-ray spectromicroscopy data was first collected on the untreated Canadian flax sample embedded in Hydropel and Acronol resin. The sample prior to beamtime was first pre-viewed using the optical microscope and intact fibre bundle with the resin block was selected for further analysis in STXM. Figure 3 shows an image of the sections mounted for STXM analysis and the fibre bundle that was analyzed using the STXM. All STXM data was collected in the transmission mode using the transmission detector at the at the C 1s region (280 to 320 eV).

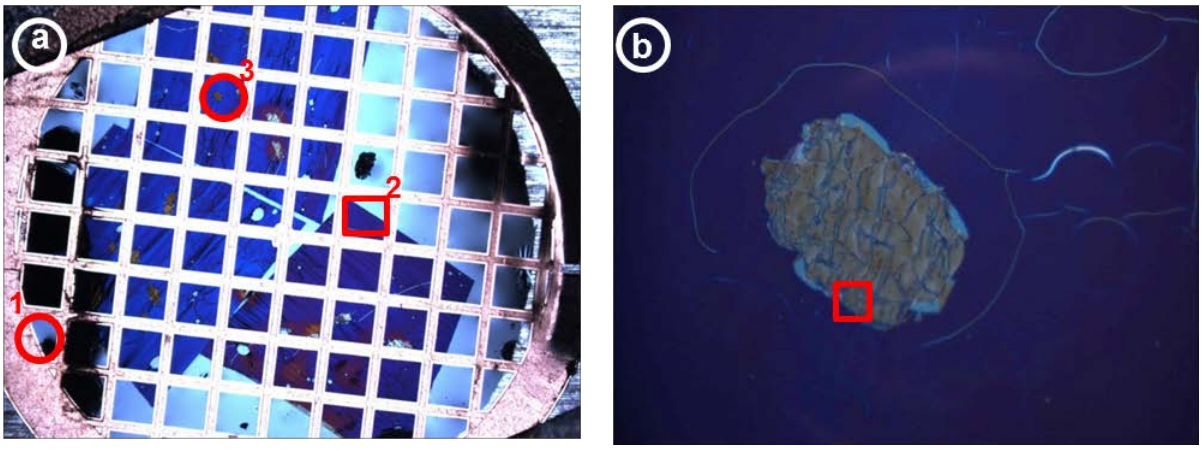

Figure 3. Optical microscopic images: a) Sample prepared for STXM (sections mounted on Formvar coated TEM grid, region marked 1,2 and 3 were used for X-ray analysis); b) fibre bundle from region 3

Image maps (at pre-edge and at peak absorption edges) were collected on the entire fibre bundle at nm spatial resolution to show the distribution of different components. A stack of images at a high spatial resolution was recorded in a region (marked in Figure b) to determine if the resin has impregnated into the fibre bundle.

As the sample was mounted on a Formvar coated grid, the Io signal required for normalizing the data was first acquired in a clean Formvar region where there was no sample.

All STXM data were analyzed using the aXis2000 software (http://unicorn.mcmaster.ca/aXis2000.html). The stack images were first aligned across the different energies and then the images (transmitted signals) were converted to optical densities. The stack image was analyzed using the principal component analysis procedure to determine the distribution of the resin and fibre polymer in the sample.

4. Results

4.1 Mid-IR

All of the samples indicated in Table 1 were mapped using Mid-IR. Figures 4, 5 and 6 illustrate the regions mapped (right image) and the 2600 to 3800 cm^{-1} portion of the spectra collected for the NaOH treated Chinese linen flax in each of the resins. The spectra were

analyzed to determine if there were peaks at wavelengths specific to the constituent materials in order to produce isometric maps representing the locations of the constituents based on the intensity of the measurements. Using existing knowledge of flax fibre and polymer chemistry, the C=O and C-O vibrational modes were selected for mapping. The flax fibres, being predominantly cellulose (crystalline, polymeric D -glucose) and hemicellulose (amorphous, polymers of several different sugars), were not anticipated to have strong C=O bonds, a feature expected in either the resin or treatments. This allowed the C=O bonds to be used as a potential marker for resin penetration.

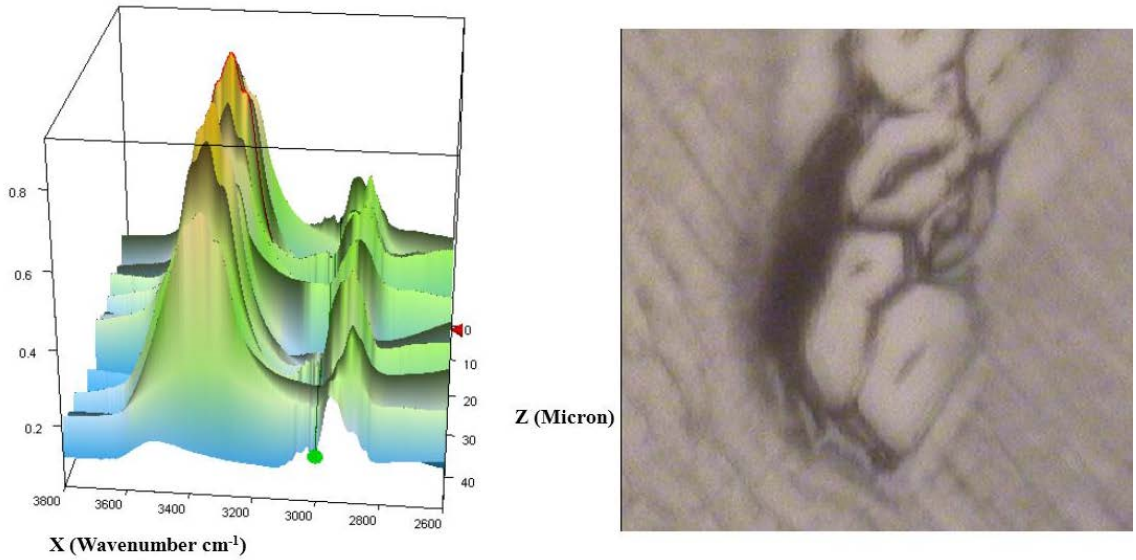

Figure 4. NaOH treated Chinese linen fibres in Hydropel

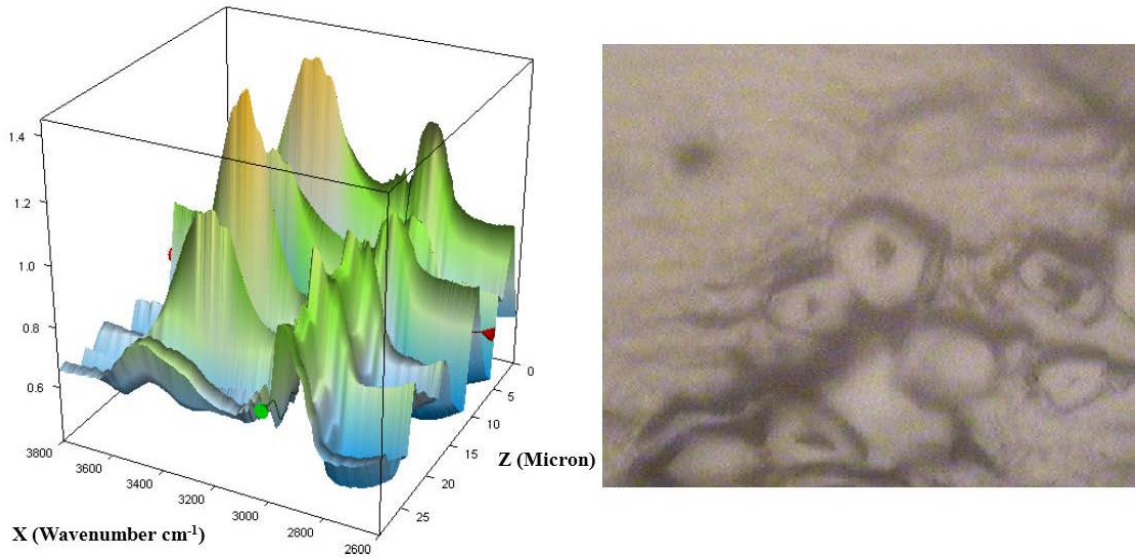

Figure 5. NaOH treated Chinese linen fibres in Hydropel and Acronal

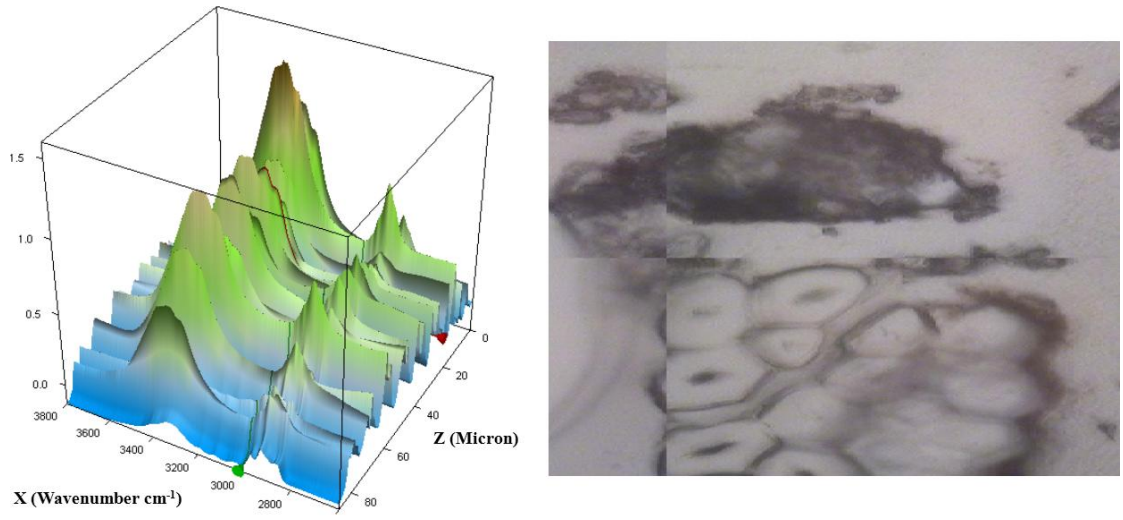

Figure 6. NaOH treated Chinese linen fibres in Soy-matrix

Figure 7 illustrates the intensity of the C=O bonds surrounding an NaOH treated Canadian linseed flax embedded in Hydropel and Acronal and Figure 8 indicates that there are 2 distinct peaks in the C-O wavelength region (1100-1200 cm-1) where the resin spectra have a peak at approximately 1185 cm^{-1} while the flax spectra have a peak at approximately 1175 cm^{-1}.

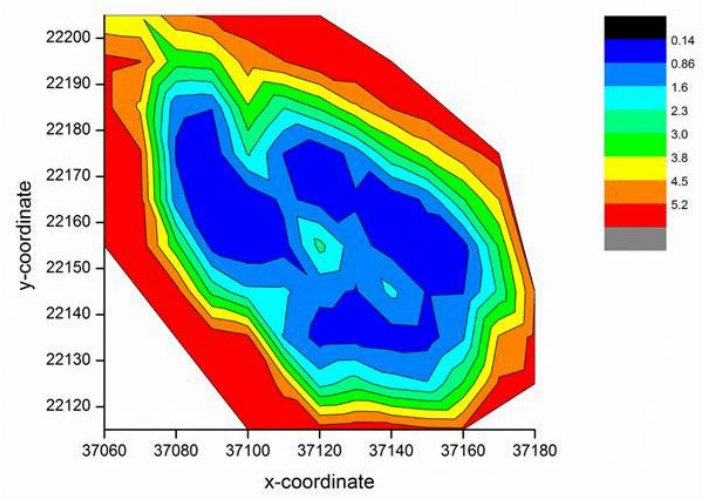

Figure 7. Approx. 1700 cm^{-1} C=O stretch of NaOH treated Canadian linseed fibre embedded in Hydropel and Acronal

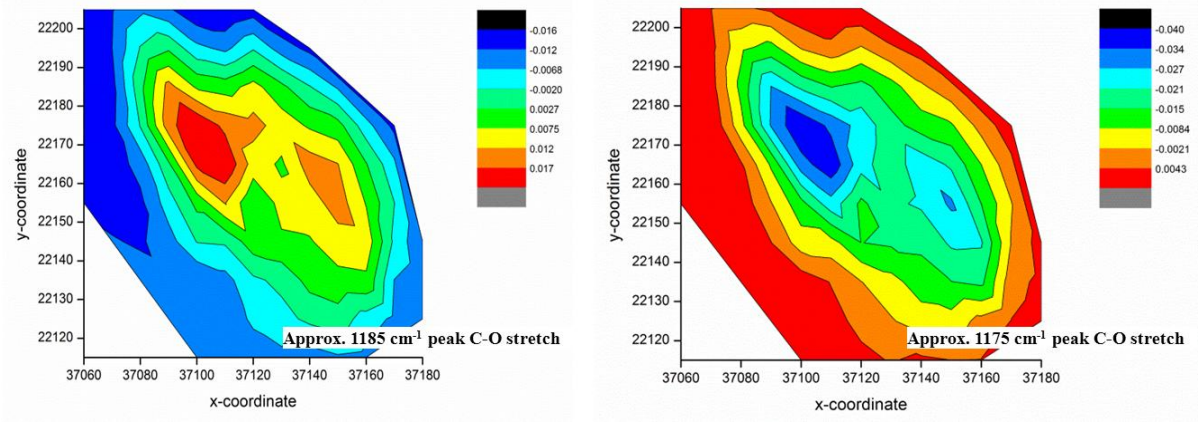

Figure 8. Intensity of C-O peaks at 1185 cm^{-1} (left) and 1175 cm^{-1} (right) of NaOH treated Canadian linseed fibre embedded in Hydropel and Acronal

5. Ongoing Research

The data compiled in the Mid-IR mapping exercise is currently being evaluated. Careful determination of the useful peaks for identifying the resin components and the different flax fibres must be checked and compiled. The usefulness of other data analysis methods such as principal component analysis (PCA) will be evaluated for determining the number of components contributing to the IR spectra. The STXM evaluation is in progress.

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