D5.2

Interim report on Testing of Fibres and Composites

Seventh Framework Programme
Capacities Programme
Proposal no: FP7 – 243456

Contents

1. Introduction

Fibre reinforced polymers find wide commercial application in the aerospace, leisure, automotive, construction and sporting industries. In recent years there has been much interest in developing natural fibre reinforced polymers for sustainable substitution of synthetic materials. However, natural fibres cannot be easily separated in to fibres of consistence quality. Also, natural fibres do not automatically have good interaction with polymers, which is required for optimal material performance. The UltraFibre project aims to address these 2 issues by developing 2 processing technologies for natural fibres:

- Ultrasonic processing for extraction and/or decortication of natural bast fibres with reduced standard deviation in tensile test data by 30%. During the project it was decided that a key goal of the ultrasonic processing should be to produce single plant cell fibres out of the bast fibre bundles.
- Plasma treatment processing for surface modification of natural fibres in order to obtain improved adhesion to polymer matrices conferring a 25% increase in mechanical properties compared with the untreated fibre.

This **Deliverable D5.2** is a report on the activities in WP5: testing and characterisation of ultrasonically and plasma treated natural fibres and their composites. It is prepared as an **interim report** as it was decided to continue testing of fibres throughout the project. In D5.3 a section on fibre testing will be added to cover future fibre testing activities.

The **objectives** for WP5 as stated in the Technical Annex 1 are as follows:

- To evaluate materials produced in WP2, WP3, WP4, WP6, and WP7
- To characterise the effects of ultrasonic treatment, SoftPlasma, and composite processing operations on the structure and morphology of the fibres, compounds and products.
- To test and characterise the moulded and extruded industrial development products

The **work-plan** for WP5 during the first 19 months as stated in the Technical Annex 1 focuses on analysis of fibres only (Tasks 5.1 and 5.2). However, in the end the composites properties count, and fibre properties may not present a fully clear prediction of composite properties. Therefore, at the partner meeting in Brussels (M16) it was decided that the evaluation of ultrasonic and plasma treatments should be performed through evaluation of corresponding fibre composites as well. Therefore, in Month 17 activities in Tasks 5.3 and 5.4 have started.

Task 5.1: Testing and characterisation of fibres after decortication
DLO-FBR will analyse the hydro-acoustically decorticated fibres from WP2, both chemically and physically. Their performance will be compared to fibres obtained through traditional means. It will be necessary to determine tensile elastic modulus and the breakage stress of the fibre, and the effects that mechanical processing and thermal history have on these properties. Fibre morphology will be determined using optical and scanning electron microscopy.

Task 5.2: Testing of fibres after plasma treatment
DLO-FBR will analyse plasma-treated fibres from WP3, both chemically and physically. Their performance will be compared to fibres obtained through traditional means and the unmodified ultrasound treated fibres.

Task 5.3: Fibre-matrix interactions
Fibre matrix interactions will be studied by modelling composite performance with composite theory, such as shear-lag, to characterise interfacial adhesion. Fracture behaviour of single fibres embedded in resins will be employed to measure the critical fibre length (SFFT) and to assess interfacial shear stress by fitting data to the shear lag model. These techniques will be employed to determine the efficacies of fibre treatments and additive formulation strategies in WP3 and WP4.

Task 5.4: Testing of compounds
The fibre quality in the compounds and moulded parts will be characterised using optical and scanning electron microscopy. It will be necessary to analyse the associated defectology and breakage of the fibre due to the processing conditions in addition to fibre average length and diameter. Iterative exchanges between WP7 and WP2, 3, 4, 5, and 6 will lead to optimisation of fibre extraction and melt processing conditions. Fibre length, stability, and degradation processes in polypropylene, poly(lactic acid), trans furan, and polyester formulations and products will be determined.

The physical performance of the new UltraFibre composites will be benchmarked against competitive technological solutions for the target applications. Design data will be generated using standard test methods for:

- Tensile strength, modulus, and elongation
- Charpy, Izod, and falling dart impact tests
- Three point bending modulus and strength
- Heat distortion temperature
- Flame resistance
- Extractable and leachable agents (odour / migration)
- Stability and recyclability

The **goal** of this project is to develop:

- **Ultrasonic processing** for extraction and/or decortication **of natural bast fibres with reduced standard deviation in tensile test data by 30%.** During the project it was decided that a key goal of the ultrasonic processing should be **to produce single plant cell fibres** out of the bast fibre bundles.
- **Plasma treatment** processing for surface modification of **natural fibres** in order to obtain improved adhesion to polymer matrices **conferring a 25% increase in mechanical properties** compared with the untreated fibre.

In section 2.1 the experimental procedures are described. Results of all fibre and composite characterization so far are presented in the next sections: fibres after ultrasonic treatment and after plasma treatment (sections 2.2 & 2.3), fibre-matrix adhesion using SFFT method (2.4) and composites (2.5). Issues encountered and solutions found are presented in section 2.6.

Conclusions are presented in Chapter 3.

Future work in WP3 is addressed in Chapter 4.

Annex 1 provides a typical procedure for batch compounding and injection moulding for better understanding of composite properties, as these procedures have not been presented in other deliverable reports published so far.

2. Results

2.1 Experimental methods

2.1.1 Selection of test methods

Related to Tasks 5.1 and 5.2, the most relevant fibre properties for reinforcement of polymers are:

- Fibre dimensions
- Surface characteristics
- Tensile properties

In the paragraphs below, the selection of test methods is discussed in more detail. Please note that in Deliverable 5.1 – Appendix A, background info and preliminary considerations regarding testing of the main natural fibre characteristics were presented already. Further, it may be noted that an overview of fibre analysis techniques available at UltraFibre partners was presented in Appendix B of Deliverable 5.1. The overview includes a short description of the methods as well as requirements related to material quantities needed and fibre dimensions.

To analyse fibre diameter reduction as a result of ultrasonic treatment, it was decided to use 2 methods: optical microscopy available at RAPRA and DLO-FBR and a Laserscan technology InControl has access to. Advantage of optical microscopy is that a quick scan of fibre dimensions can be performed. Disadvantage of optical microscopy is that collected information is rather qualitative. Advantage of the Laserscan method is that quantitative diameter data are obtained. Disadvantage of the Laserscan analysis is it is relatively time consuming and costly.
As the ultrasonic treatment is a wet process, fibres stick together again after drying. To separate the fibres before analysis, a Shirley trash separator, a high speed lab scale carding system, is used.

For analysis of fibre surface characteristics, 3 methods were selected:

- XPS: X-ray photoelectron spectroscopy provides information on elemental composition of the top few nm of a material. It is considered suitable to analyse the effect of plasma treatment, which is supposed to affect the very surface of a material only. XPS is time consuming and costly.
- FT-IR: Fourier transform infrared spectroscopy provides information on chemical bonds in a material and has a penetration depth of few micrometres from the surface. This methods is considered suitable for quickly analysing the effect of ultrasonic treatment and extraction on

the chemical composition of natural fibres. FT-IR is a quick and low cost technique.

- SEM: Scanning electron microscopy provides information on surface morphology of materials with a resolution for cellulosic materials of about 100 nm. This method would be suitable to evaluate morphology details of fibre (and materials in general). SEM is time consuming and expensive.

XPS and FT-IR analysis have been performed so far and methodology and test results will be presented in this report. SEM is scheduled for the coming period and results will be addressed in Deliverable 5.3 (due in Month 33).

Analysis of fibre tensile properties may be performed using a range of methods/procedures. A detailed analysis of issues related to tensile testing is presented in section 2.6. For the evaluation of fibre tensile strength in this project, a fibre testing method has been developed. The method analyses a collective of fibres, which is suitable for determining the trend of fibre strength (see section 2.1.7).

Fibre-matrix adhesion is a good indicator for the effectiveness of the plasma treatment. A good indication of fibre-matrix interactions (Task 5.3) can be obtained from flexural strength of composites, assuming that fibre strength in composites is similar. And flexural testing is a quick method. Obtaining a good indication of fibre-matrix adhesion is considered sufficient because in the end not adhesion counts but rather composite properties.
Detailed analysis of critical fibre length from single fibre composites (Task 5.3) is time consuming. Translation of critical fibre length into a quantified fibre-matrix adhesion would require single fibre strength, which requires a time consuming experimental procedure as well (also see section 2.6 for more details). Therefore, it has been decided at the partner meeting in Brussels (6-7th April 2011, reference Q5 report) that evaluation of fibre-matrix adhesion will be primarily based on composite flexural properties. Some single fibre tensile testing and single fibre composite fragmentation tests have been performed which show the potential and limitations of these methods (see sections 2.1.8, 2.1.9 and 2.4).

At the partner meeting in Brussels, it was decided that in the development stage of composites (Task 5.4) the following mechanical properties would be evaluated for 30 wt.% fibre reinforced composites:

- Flexural strength and stiffness
- Charpy impact strength

For analysis of final composite products (Task 5.6) it was decided to evaluate a wider range of properties:

- Flexural and Tensile properties
- Charpy impact strength
- Heat distortion temperature
- Scanning Electron Microscopy
- Flame resistance

Evaluation of final products is scheduled for Months 31-33 and will be addressed in Deliverable 5.3.

Task 5.5 relates to providing data from WP5 to WP8.

2.1.2 Fibre refining

Ultrasonically treated fibre samples as received were "clumped" together as a result of the wet processing. Fibre clumps had a 'thickness' of up to 5 mm (see Figure 1, fibre sample at right hand side). However, the lab scale Shirley device (Figure 2) cannot handle too thick fibre agglomerates, and thickness of a fibre layer is preferably less than 1 mm. Therefore (many) sections of fibres that were glued together were manually 'torn' apart in order to allow proper feeding to the Shirley device (Figure 1, fibre sample at left hand side). Fibres were fed parallel to feeding direction as much as possible in order to avoid fibre length reduction (left fibre sample in Figure 1).

Figure 1: Feeding of fibre samples to Shirley trash separator: fibres oriented parallel to feeding direction with maximum thickness of about 1 mm (left hand sample) and sample with about 5 mm thick fibre clumps (right).

Figure 2: Shirley trash separator.

Samples refined with Shirley trash separator are presented in Table 1 to Table 4.

Table 1: Ultrasonic pre-treatment conditions for flax (Ekotex sliver); sonication performed at RAPRA.

Sample code	Pre-treatment	(Static) Ultrasonic time (s)
R1	3% NaOH + 18 mM EDTA + 1% Lipsol at 40 °C for 4 h	300
R2a	0.3% NaOH + 18 mM EDTA + 1% Lipsol at 40 °C for 4 h	-
R2b	'', put through pump only for 4 cycles	-
R2c	''	30
R2d	''	60
R2e	''	120
R2f	''	180
R2g	''	240
R2h	''	300
R3a	0.3% NaOH + 1% Lipsol at 40 °C for 4 h	-
R3b	'', put through pump only for 4 cycles	-
R3c	''	30
R3d	''	60
R3e	''	120
R3f	''	300

Table 2: Ultrasonic pre-treatment conditions for flax (Ekotex sliver); sonication performed at RAPRA.

Sample code	Pre-treatment	(Static) Ultrasonic time (s)
R4b	40 °C water, no soaking	30
R6a	99 °C water, 1 h	-
R6b	99 °C water, 1 h	30
R6f	99 °C water, 1 h	300

Table 3: Ultrasonic pre-treatment conditions for flax (Ekotex sliver); sonication performed at RAPRA.

Sample code	Pre-treatment	Ultrasonic time (s)
S1	3% NaOH + 18 mM EDTA + 1% Lipsol at 99 °C for 1 h	-
S2	" "	30, static
S3	" "	300, static
S4	" "	300, flowing
S5	" "	Flowing only

Table 4: Pre-treatment conditions for flax (Ekotex sliver) and hemp (Hemp Technology tow) Ultrasonically treated for 300 s under flowing conditions; sonication performed at RAPRA.

Sample code	Pre-treatment
R12	Flax, 50 mm, soaked in water for 1h
R13	Flax, 50 mm, soaked in 1% Lipsol at 40 °C for 1 h
R14	Flax, 50 mm, soaked in 0.3% NaOH at 40 °C for 1 h
R15	Flax, 50 mm, soaked in 3% NaOH at 40 °C for 1 h
R16	Flax, 50 mm, soaked in 0.3% NaOH + 1% Lipsol at 40 °C for 1 h
R17	Flax, 50 mm, soaked in 0.3% NaOH + 18 mM EDTA at 40 °C for 1 h
R18	Hemp, soaked in 0.3% NaOH at 40 °C for 24 h

2.1.3 Optical microscopy

Fibres were placed between 2 glasses and fibre diameter was evaluated using an optical microscope (Figure 3). RAPRA uses a Brunell Microsopes SP400 universal microscope at a magnification of 200x with a digital camera mounted. DLO-FBR uses a Zeis Axioplan optical microscope at a magnification of 100x and an AxioCam Icc3 camera.

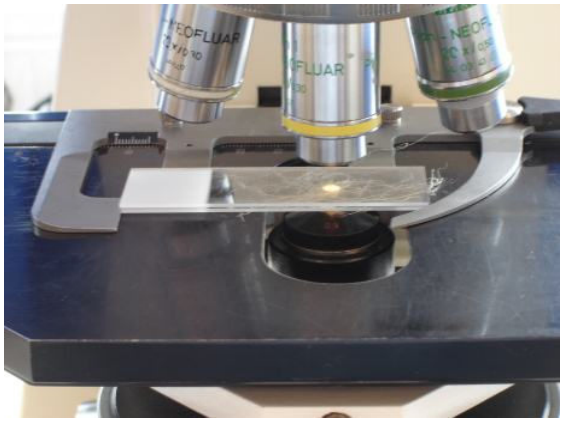

Figure 3: Evaluation of fibre diameters using optical microscope.

2.1.4 Laserscan analysis (at InControl)

The Laserscan equipment was developed for the wool industry to quantify fibre diameters. This equipment has been recalibrated for use with other fibres, mainly flax. The technique suspends fibre which is chopped to 2 mm lengths in a clear liquid. This suspension is then pumped across a laser cell and 2000 fibre diameter measurements are scanned automatically and then can be processed. The upper measuring limit of the Laserscan is 80 micrometer.

2.1.5 X-ray photoelectron spectroscopy (XPS)

Plasma treated fibre samples and an untreated reference were pre-dried in a vacuum oven at 50 °C overnight and stored in aluminum foil and a sealed PE bag. Next day, the samples were clamped in the sample holder and placed in the preparation chamber of the Jeol JPS-9200 XPS analyzer. Samples were kept there overnight under vacuum: $2*10^{-7}$ Pa. Subsequently, samples were transferred into the analysis chamber. Elemental analysis was performed using a Al Kα source with an X-ray power of 200 Watt, and an analyzer pass energy of 10 eV for narrow scans and 50 eV for wide scans. For all wide and narrow scans, a circular analysis area with a diameter of 3 mm is used.

XPS data is quantified using relative sensitivity factors and a model that assumes a homogeneous layer. The analysis volume is the product of the analysis area and the depth of information. Photoelectrons are generated within the X-ray penetration depth (typically microns), but only the photoelectrons within 3 times the photoelectron escape depth are detected. Which leads to an analysis depth of about 5-10 nm.

More detailed background info on the principle of XPS is presented in Figure 4.

The following fibre samples were tested:

- Plasma treated Ekotex flax fibres. Plasma treatments were performed at AcXys using a 12 cm ULD source at a N_2 flow of 200 L/min and a treatment time of about 30 s. Feed gasses were pure N_2, N_2 + 0.5% CO_2 and N_2 + 0.5% N_2O. Treated samples were stored in aluminum foil and a sealed PE bag until XPS analysis 17 days later. Untreated flax fibre (Ekotex sliver) was included as a reference.

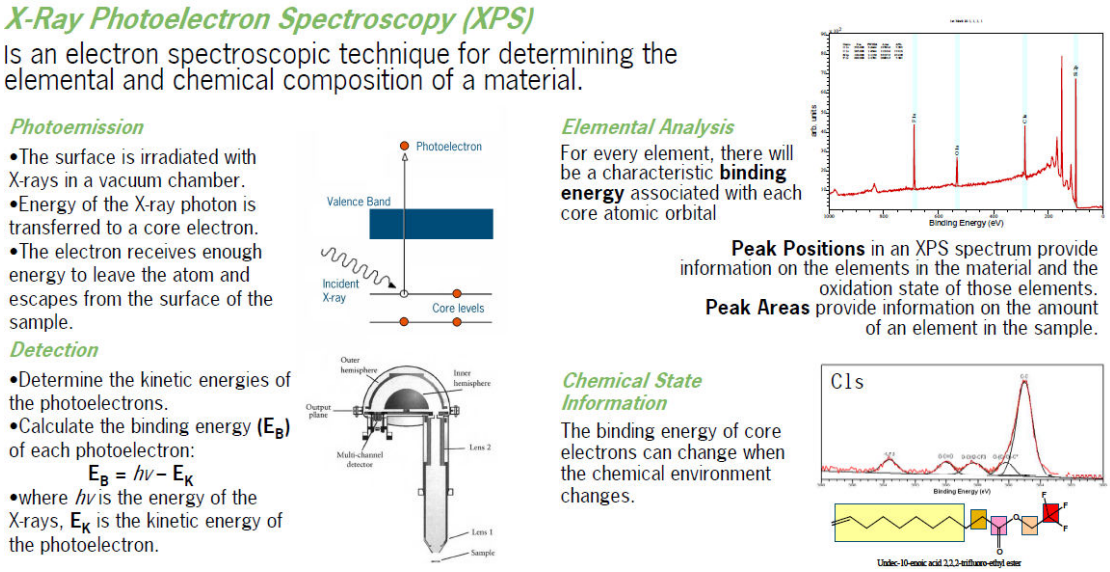

Figure 4: Background info on XPS technique.

2.1.6 Fourier transform infrared spectroscopy (FT-IR)

Shirley refined fibre samples were dried overnight at 105°C prior to FT-IR. Spectra were obtained using a Varian Scimitar 1000 FT-IR spectrometer equipped with a DTSG-detector and a PIKE MIRacle ATR with a diamond ω/ZnSe lens single reflection plate (Figure 5). The measurement resolution was set at 4 cm^{-1}, and the spectra were collected in the ATR (Attenuated Total Reflection) mode in the range 4000-650 cm^{-1} with 64 co-added scans.

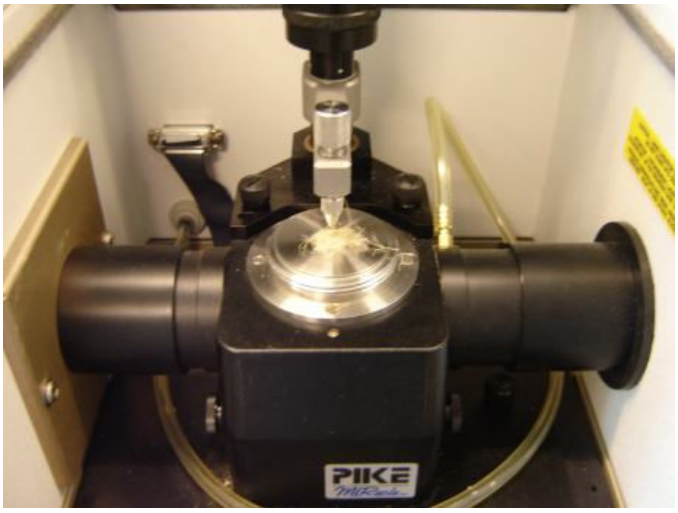

Figure 5: Evaluation of fibres using FT-IR.

2.1.7 Collective fibre strength testing

A fibre sample is collected and combed to orient the fibres parallel. This fibre sample is clamped in Pressley clamps at a span length of 3.2mm (Figure 6). Clamps are closed using a 1Nm momentum key. Subsequently, the sample is transferred to a Zwick universal testing machine using specially designed holders (Figure 7). Fibres are loaded at 1 mm/min until fracture and using a pre-load of 1 N. The typical range of breaking force is 20 – 60 N.

The broken fibre sample is collected and weighed at an accuracy of 0.00001 g. Effort is made to keep fibre weight as constant as possible. Usually fibre weight was in the range 0.00160 – 0.00250 g. The cross section of the fibre collective was calculated from:

$$D = \frac{\left(\frac{m}{ro}\right)}{L} * 10 \quad (1)$$

where m = fibre weight, ro = fibre density (1.4 g/cm^3), and L = fibre length in the clamps (14 mm).

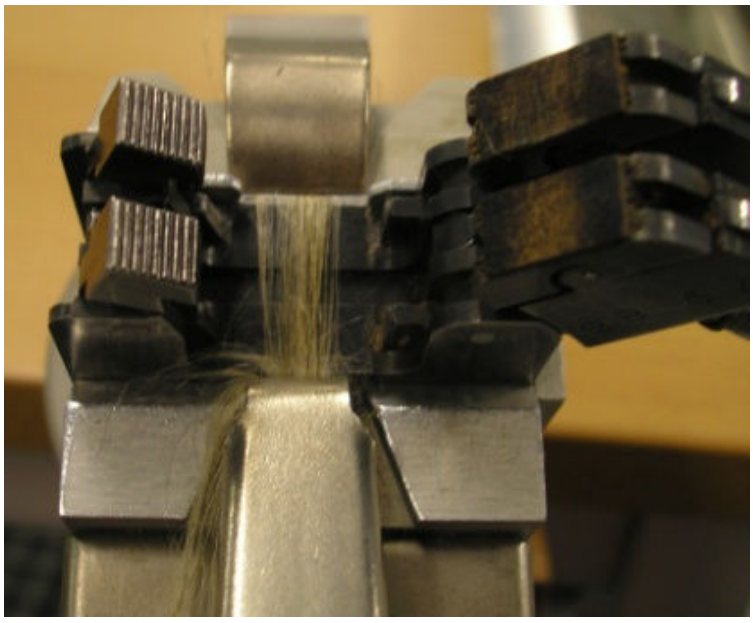

Figure 6: Collective fibre sample ready for clamping in Pressley clamps from Stelometer fibre strength testing system.

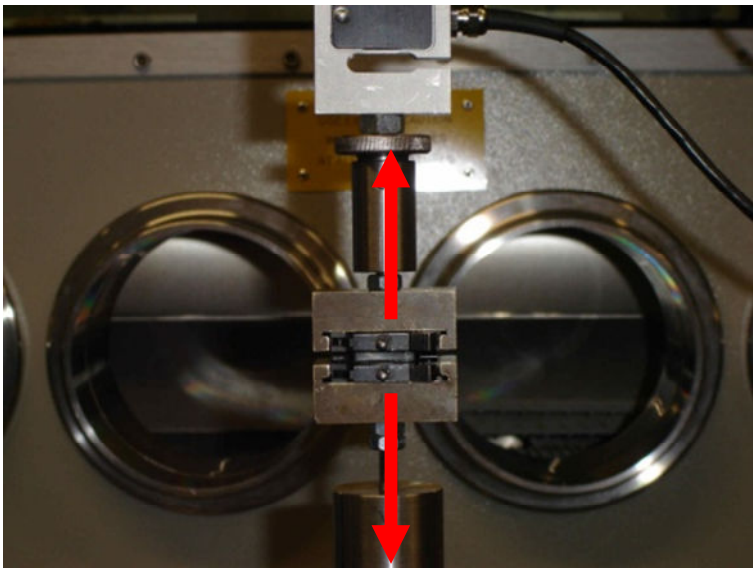

Figure 7: Specially designed holders for Pressley clamps in universal tensile machine.

2.1.8 Single Fibre testing

Individual technical fibres without visual weak spots were hand-selected, and glued on a paper frame using tape (Figure 8). The cross sectional area of each fibre was determined from 3 * 2 perpendicular visual diameter measurements (see Figure 9) assuming an elliptical cross section and using a Carl Zeiss Axioplan microscope at a magnification of 100x. Next, the paper frame with the glued fibre was carefully fixed in the Pressley clamps at 3.2 mm clamp distance and the paper frame was cut to set free the fibre. Tape was added on the clamp jaws to avoid breaking the fibres at the clamp edge. Fibres were tested on a Zwick tensile machine, using a 100 N load cell with a maximum error of 0.5 % from 0.4 N upward. Fibre strength is calculated from the breaking force and the average cross section of the 3 ellipses. The typical range of breaking force for the single flax fibres is 0.2 – 1 N.

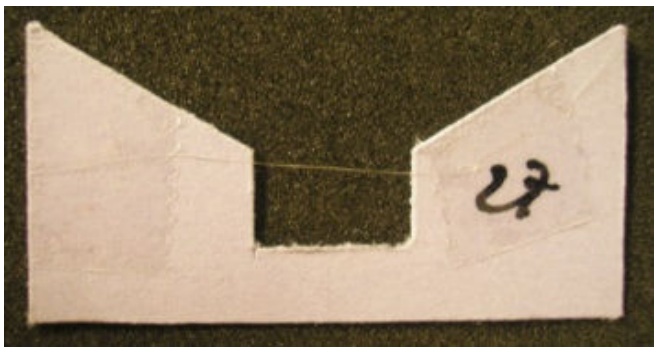

Figure 8: Single flax fibre glued onto paper frame.

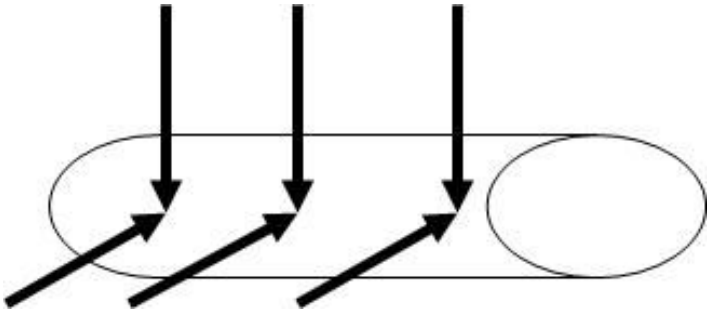

Figure 9: Visualisation of positions where fibre diameter was determined.

2.1.9 Single Fibre Fragmentation test (SFFT)

Sheets of PP and PLA were compression moulded in a PHI Hydraulic Hot Press. Granules were pre-heated in an aluminium mould with dimensions 100 * 50 * 0,1 mm (kitchen grade aluminium foil) at 190 °C for 8 min. Subsequently, pressure was slowly increased to 25 ton in 4 min and maintained for a minute before cooling to room temperature under pressure. Single fibres without visual weak spots were selected from untreated and N_2 treated flax fibres and glued on the polymer sheets using Type-ex, leaving at least 8 mm space between the fibres (Figure 10). Attention was paid to fix the fibres as straight as possible. Another polymer sheet was then put on the top of the one with the fibres, and the resulting 'sandwich' was pre-heated at 190°C for 8 min. Subsequently, pressure was slowly increased to 15 ton in 4 minutes and maintained for a minute before cooling to room temperature under pressure. Samples were cut to 4 mm wide SFFT samples, using a sharp knife and a ruler.

The single fibre composites were then loaded in a home built tensile rig (Figure 11). Load was increased by manual rotation of the screw, until the specimen showed no further fibre fracture (Figure 12). The composite is then put under the optical microscope in order to measure fragmented fibre lengths and corresponding diameters. At least 200 fibre fragments per composite were taken into account for determination of critical fibre length.

Critical L/D is determined from the average L/D of the fibre fragments following the equation:

$$\frac{L}{D}\text{critical} = \frac{4}{3}.\frac{L}{D}\text{average} \quad (2)$$

The fibre strength at critical fibre length is calculated from the following formula:

$$\frac{\sigma l}{\sigma_c} = (\frac{lc}{l_l})\text{^}1/m \quad (3)$$

Where m = Weibull modulus, σl = fibre tensile strength at length l_l, being 3.2 mm in this case (see section 2.1.8), and σ_c = fibre strength at critical fibre length, l_c. The Weibull modulus, m, is a dimensionless parameter, which is used to describe variability in strength of materials. It is the slope in the plot of Ln(-Ln(1-P)) versus Ln(σ_f) where P = failure probability and σ_f = fibre stress (S. van der Zwaag, Journal of Testing and Evaluation, 1989, 292-298).

The apparent interfacial shear strength, τ, can be determined from Kelly-Tyson theory (A. Kelly, W.R. Tyson, J Mech Phys Solids 13, 1965, 329-350):

$$\tau = \frac{\sigma_c . d}{2 . l_c} \quad (4)$$

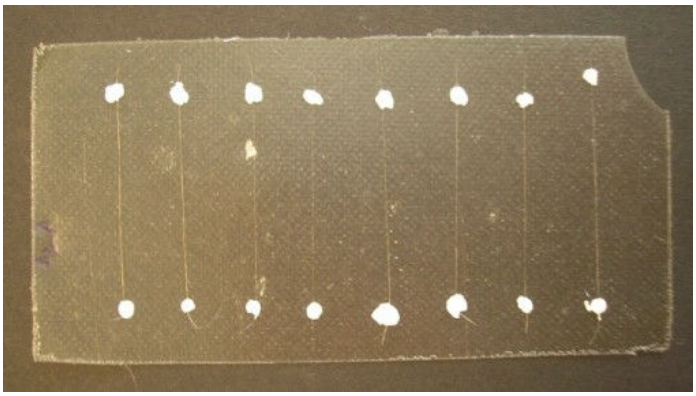

Figure 10: Single flax fibres in PLA sheet before cutting to 4 mm wide SFFT samples.

Figure 11: Device for manual loading of SFFT samples. A grid on the screw allows monitoring of the applied elongation.

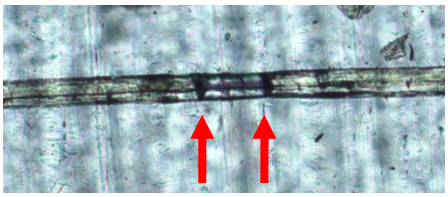

Figure 12: Fragmented flax fibre in PP matrix. Fractures in fibre are indicated by red arrows.

2.1.10 Flexural testing

The flexural properties were measured on a Zwick universal testing machine according to ISO 178 at a support length of 64 mm (Figure 13) and a crosshead speed of 2 mm/min for the modulus and 10 mm/min for the strength. The flexural strength and modulus were determined from 5 specimens per batch.

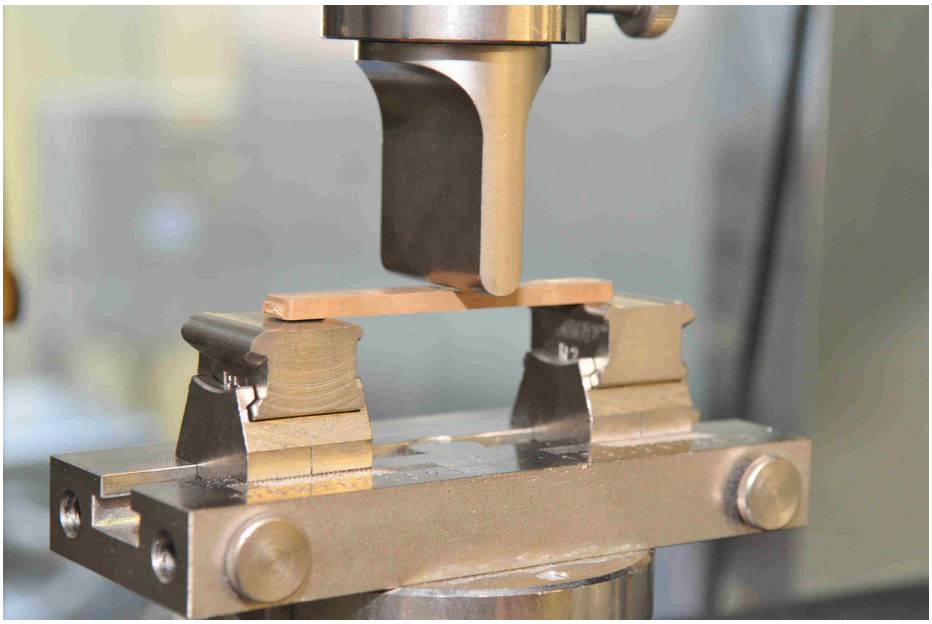

Figure 13: Flexural testing set-up.

2.1.11 Charpy impact testing

The Charpy unnotched impact strength was determined using a Ceast Resil 50 pendulum impact tester according to ISO 179/1fU using an impact hammer of 4 J at a speed of 2.9 m/s (Figure 14). The Charpy impact strength was determined from 10 specimens per composition.

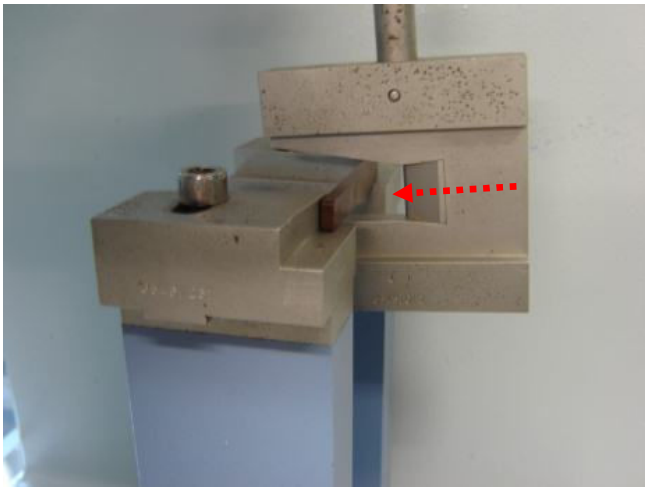

Figure 14: Charpy impact hammer blowing (red arrow) standard injection moulded composite test specimen.

2.2 Characterisation of fibres after Ultrasonic treatment (WP2)

The goal of WP2 is to produce natural bast fibres with reduced standard deviation in tensile test data by 30% and to produce single plant cell fibres.

2.2.1 Fibre refining

When refined fibres using the Shirley trash separator, fine fibres are collected in one compartment, coarse fibres are collected in a second compartment (Figure 15). The relative amounts of refined and coarse fibres are indicated in Table 5. In first instance, it was concluded that the fine fibre content could be related to fibre pre-treatment: The larger the fine fibre content, the more effective the pre-treatment + ultrasonics treatment on fibre refining. After completing the first Shirley treatment for all fibre samples R1-R3f, it seemed that the amount of coarse fibres also depended on the way that fibres are fed to the carding drum. The 'contact' time of fibre and carding drum is much longer for a fibre parallel to feeding direction than for a fibre perpendicular to feeding direction, and the chance for a fibre to be refined will increase with contact time. However, parallel positioning of the fibres is limited by fibres being 'glued' together while in rather random orientation as a result of the wet processing. Whereas the R2a fibres in Figure 1 are rather parallel in the as received state because of just soaking pre-treatment, most fibre samples as received had random orientation, see Figure 16 representing R1.
As the carding process is parallel to the feeding direction, it may be concluded that non-parallel fibre feeding causes severe fibre fracture.

Figure 15: Shirley refined Ekotex flax sliver (left picture) and Ultrasonically treated Ekotex flax fibre coded R1 (right). On each picture: unrefined fibre at left, fine fibre top right and coarse fibre bottom right.

Figure 16: Ultrasonically treated fibre sample R1 after drying, showing fibres glued together in random orientation.

Table 5: Relative yield of 'fine' and 'coarse' fibre after Shirley refining.

Sample code	Refined fibre (g)	Coarse fibre (g)	Fine fibre content
Ekotex reference	4.16	0.95	81.4%
Ekotex reference duplo	14.54	4.44	76.6%
R1	34.68	7.13	82.9%
R2a	22.64	3.27	87.4%
R2b	18.22	5.48	76.9%
R2c	15.19	5.8	72.4%
R2d	15.88	5.98	72.6%
R2e	13.83	5.8	70.5%
R2f	17.77	3.66	82.9%
R2g	24.76	4.67	84.1%
R2h	18.51	4.25	81.3%
R3a	16.03	4.27	79.0%
R3b	14.51	3.5	80.6%
R3c	13.25	2.09	86.4%
R3d	19.21	2.44	88.7%
R3e	19.69	3.38	85.3%
R3f	17.2	3.13	84.6%

The fibres are very fluffy after refining, and the human eye cannot make differences between the different ultrasonically treated fibres.

Starting from sample R4 onward, apparent 'fine' fibre content after Shirley refining on average dropped dramatically (see Table 6), also for reference flax

fibres. The actual fibre fineness after Shirley refining, however, seemed not to change. It is concluded that the fibres are mainly collected in the coarse fibre bin. It must be mentioned that after Shirley refining, the 'fine' hemp fibre is more coarse than the 'coarse' flax fibre.

Table 6: Relative yield of 'fine' and 'coarse' fibre after Shirley refining (2).

Sample code	Refined fibre (%)	Coarse fibre (%)	Dust + shives (%)
Ekotex flax reference, 3	33.7	66.4	
Ekotex flax reference, 4	27.0	73.0	
R4b	45.4	54.6	
R6a	38.0	62.0	
R6b	14.1	85.9	
R6f	30.9	69.1	
S1	30.3	69.7	
S2	45.9	54.1	
S3	31.2	68.8	
S4	36.9	63.1	
S5	46.2	53.8	
Hemp Technology, tow	8.4	81.9	4.0

2.2.2 Chemical composition

In WP2, both chemicals and ultrasonics have been applied to fibres in order to obtain cleaned and refined fibres. The question was whether ultrasonics could increase the efficiency of chemicals to extract binding components from the fibres in order to achieve better fibre refining. FT-IR is used as a quick method to obtain an indication of fibre chemical composition. Figure 17 shows the absorption spectra of the untreated flax reference and the 300 s ultrasonically treated flax samples with different chemical agents used. DLO-FBRs experience that it is impossible to obtain perfectly reproducible FT-IR absorption scans for such fibres like flax is confirmed. The lower signal in the 1550-1700 cm^{-1} region indicates that lignin components are extracted after OH treatment (R1, R2h, R3f). Surprisingly, this effect seems less significant for 3% NaOH than for 0.3% NaOH. Further, the 1720-1740 cm^{-1} peak, corresponding to C=O structure, shows remarkable changes. The increase of the peak for the R1 sample may be due to selective alkaline extraction of phenolic compounds and pectin extraction by EDTA, making the ester groups of hemicellulose become more predominant. On the other hand, the 0.3% NaOH pre-treated samples rather show a decrease of the 1720-1740 cm^{-1} peak, the decrease being more predominant for the R3f sample which was not subjected to EDTA extraction.

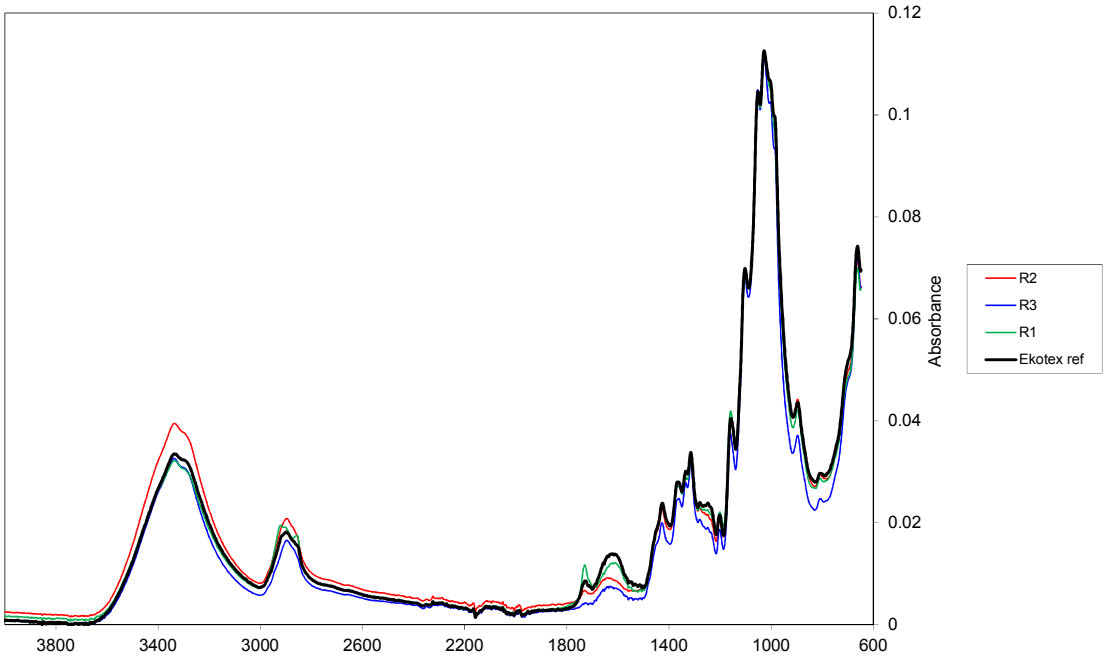

Figure 17: FT-IR absorption spectra for untreated flax (Ekotex ref), and ultrasonically treated fibre sample: 3% NaOH+18mM EDTA (R1), 0.3% NaOH+18 mM EDTA (R2) and 0.3% NaOH (R3).

FT-IR analysis of a selection of chemically and ultrasonically treated fibre samples and the untreated reference shows that the use of chemicals changes the chemical composition of fibres, ultrasonics do not add to the change (Figure 18 and Figure 19). Analytically speaking: the peak height in the 1500-1800 cm^{-1} area reduces when going from untreated (Ekotex) to just chemical treatment (R2a, R3a), peak height of R2a and R2h and R3a and R3f are basically the same. The same result is obtained in a duplo performed by RAPRA (Figure 20).

TGA analysis by RAPRA showed that so far no effect of ultrasonics and use of chemicals on fibre thermal stability can be concluded.

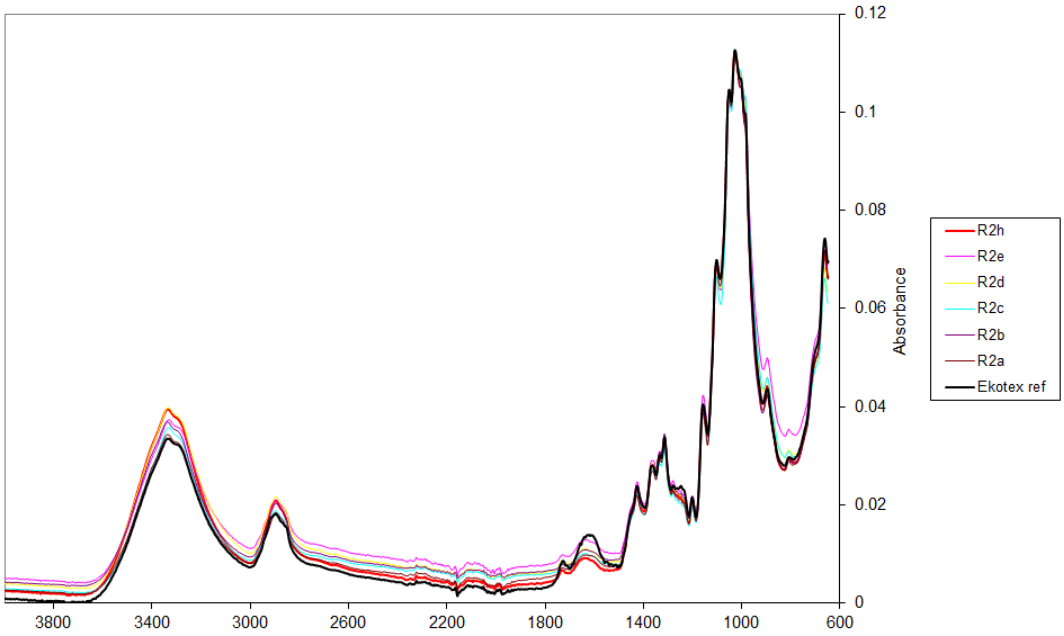

Figure 18: FT-IR absorption spectra of untreated (Ekotex ref), chemically treated (R2a, R2b), and chemically + ultrasonically treated (R2c-R2h) flax fibres.

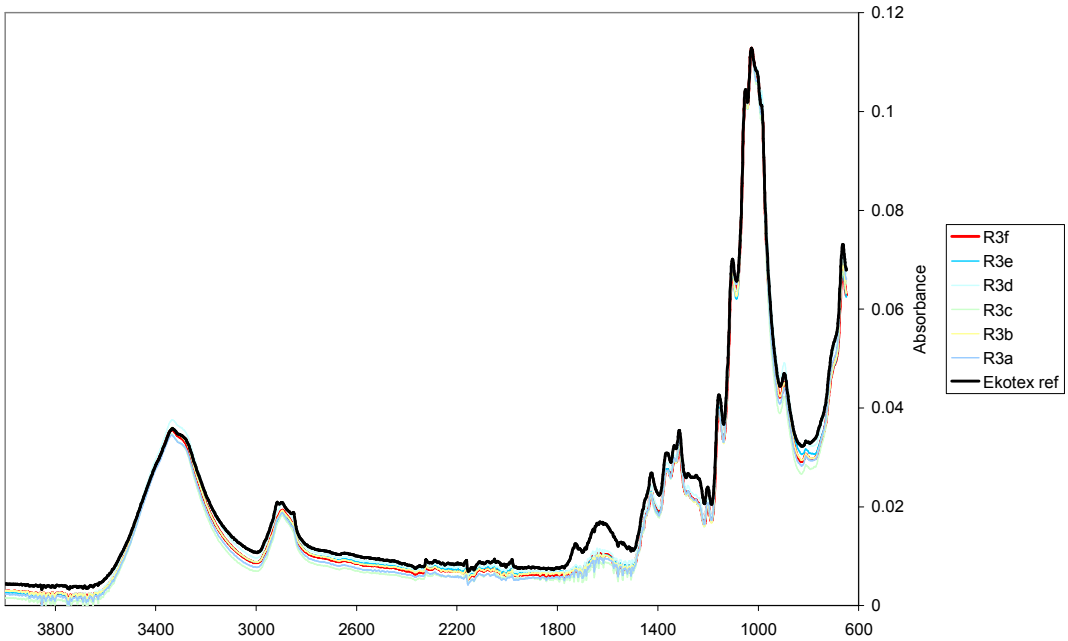

Figure 19: FT-IR absorption spectra of untreated (Ekotex ref), chemically treated (R3a, R3b), and chemically + ultrasonically treated (R3c-R3f) flax fibres.

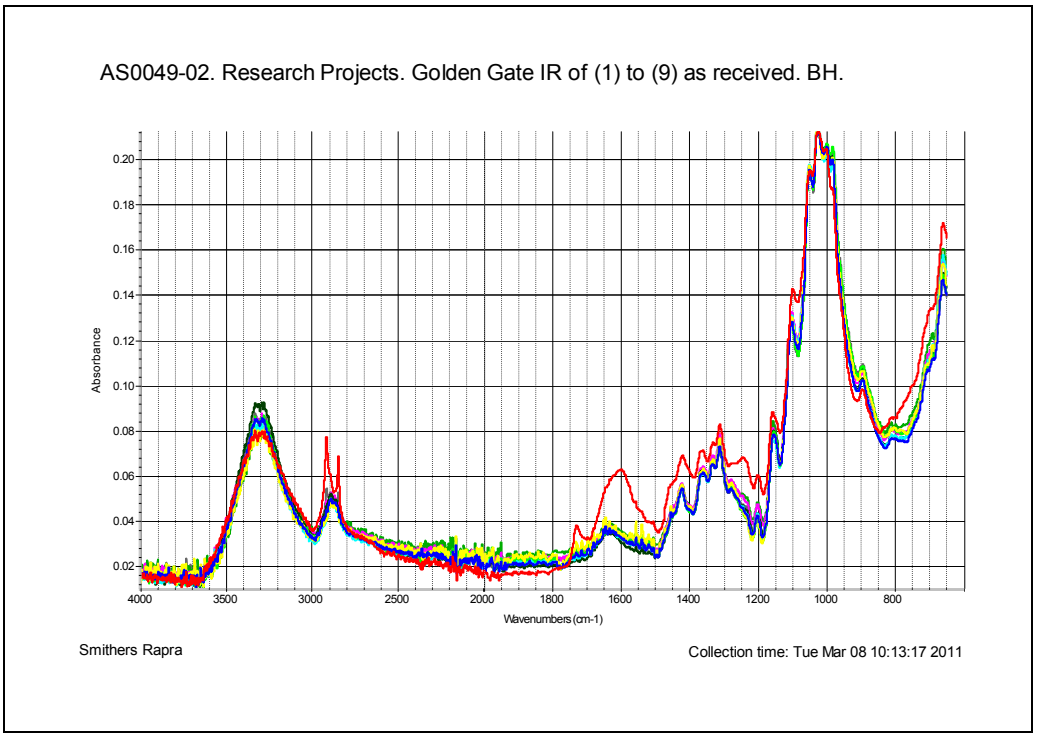

Figure 20: FT-IR absorption spectra of untreated (red), chemically treated (green, light green, turquoise), and chemically + ultrasonically treated (all other lines) flax fibres. Analysis by RAPRA.

2.2.3 Fibre diameter

InControl has evaluated the fibre diameter of untreated and chemically (NaOH) and ultrasonic (US) pretreated fibres using Laserscan. One form of presentation is shown in Figure 21 and illustrates the wide range of diameters of natural fibres which presents some difficulty in presentation when looking for a single mean figure. The Laserscan characterisation technique appeared to give some useful results, so a series of fibre samples prepared by RAPRA were analysed using the Laserscan. Figure 22 shows the output from the Laserscan. Differences in diameter seem small when considering fibre diameter number distributions. However, the composite 'sees' volume of the fibres, therefore volume distribution of fibre diameter has to be evaluated (Figure 23). Clear effects of NaOH and US can be observed. The effect will be larger when considering that the upper measuring limit of the Laserscan is 80 micrometer. The frequency value of the Ekotex reference at 80 micrometer indicates that fibres with larger diameter are present. If these coarse fibres would be included in the evaluation, the maximum frequency level of Ekotex reference would be lower.

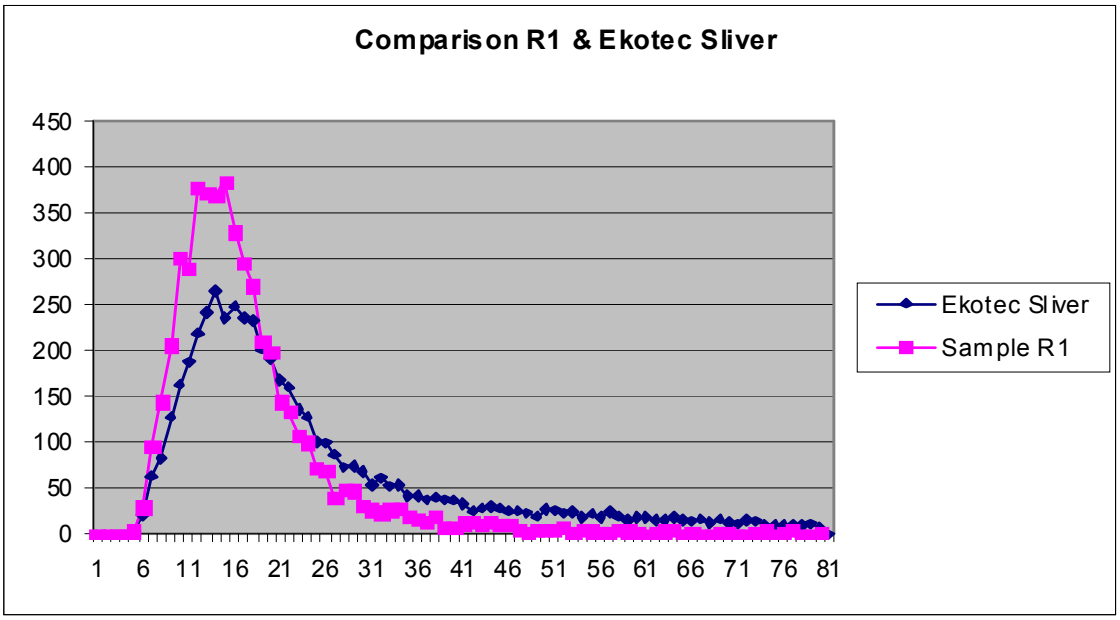

Figure 21: Diameter distribution of untreated (Ekotex) and chemically and ultrasonically (R1) treated flax fibres, measured with Laserscan (InControl)

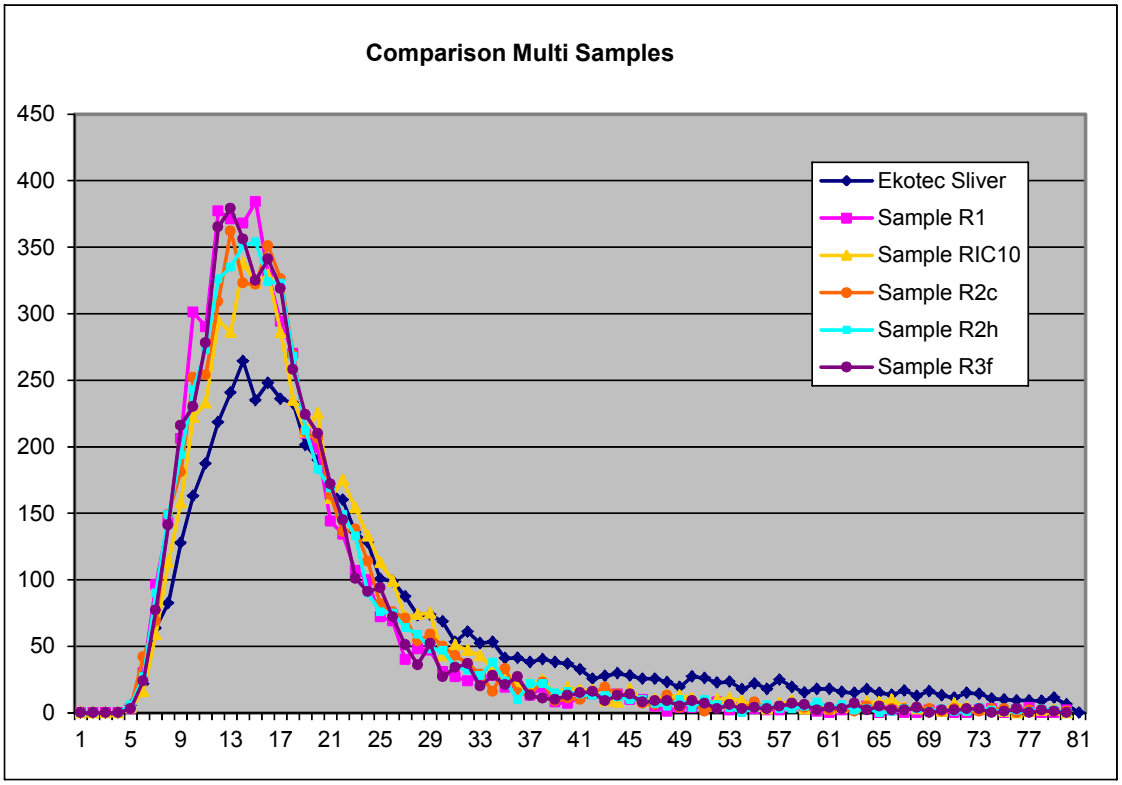

Figure 22: Diameter distribution of untreated (Ekotex), just ultrasonically treated (RIC10) and chemically and ultrasonically (R1-R3f as coded in Table 1) treated flax fibres, measured with Laserscan (InControl).

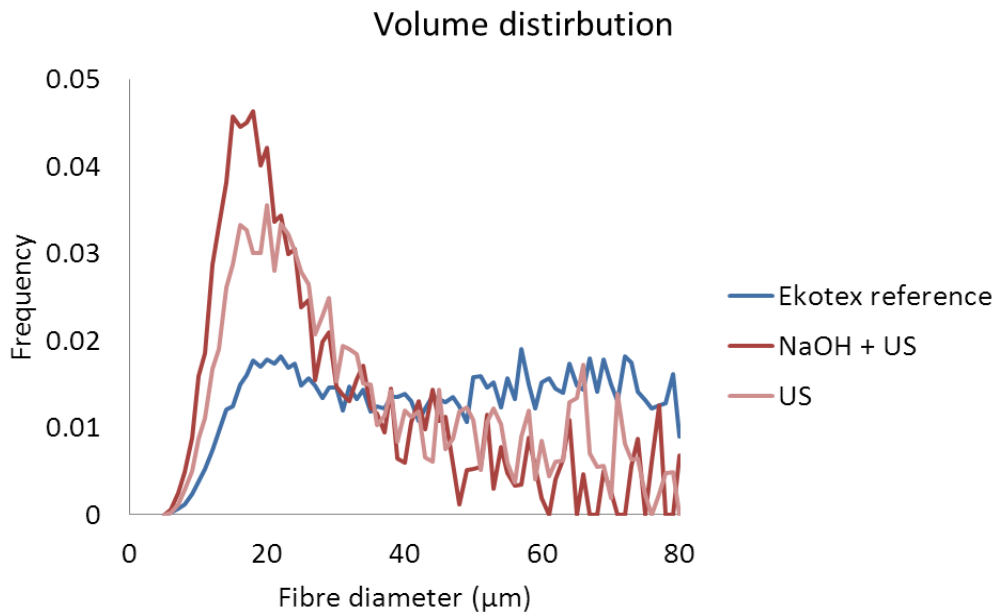

Figure 23: Volume distribution of diameter of untreated (Ekotex) and chemically (NaOH) and ultrasonically (US) treated flax fibres, measured with Laserscan (InControl).

Fibre diameter reduction after Shirley refining is confirmed with optical microscopy (Figure 24). Shirley treatment results in a significant yield of single plant cell fibres already. From 7 pictures it is concluded that about 40% of fibres by volume are single plant cells after Shirley refining only. Refining of chemically + ultrasonically treated fibres exhibits about 75 volume% of single plant cell fibres (evaluation of 7 pictures). This result indicates that the chemically + ultrasonically treated fibres will refine more easily than untreated fibres in an (extrusion) compounding process.

Pictures in Figure 24 are representative of the fibre diameter range of each sample.

(A) (B) (C)

Figure 24: Optical micrographs of Ekotex reference (A), refined Ekotex (B), refined chemically and ultrasonically treated fibre (C). Full width of each picture is 2075 pixels = about 0.97 mm.

2.2.4 Fibre strength

After mechanical refining using the Shirley machine, fibre length has decreased depending on pre-treatment conditions (Figure 25 and Figure 26). The correlation between fibre strength and fibre length (Figure 27) suggests that length reduction is a result of lower fibre strength. Whereas fibre length below 1.5 cm does not allow proper fibre strength analysis using the method described in section 2.1.7, these fibres are in principle still long enough for reinforcing polymers, the reinforcing potential also depending on fibre strength and fibre-matrix adhesion.

Figure 25: Fibre length fractionation after Shirley refining.

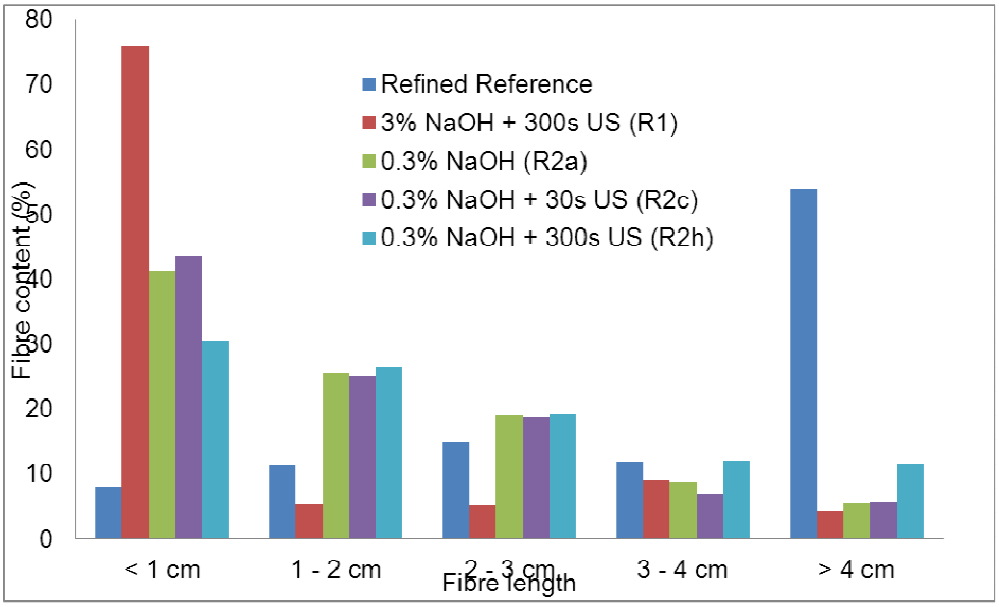

Figure 26: Fibre length distribution of untreated and pre-treated fibres after Shirley refining.

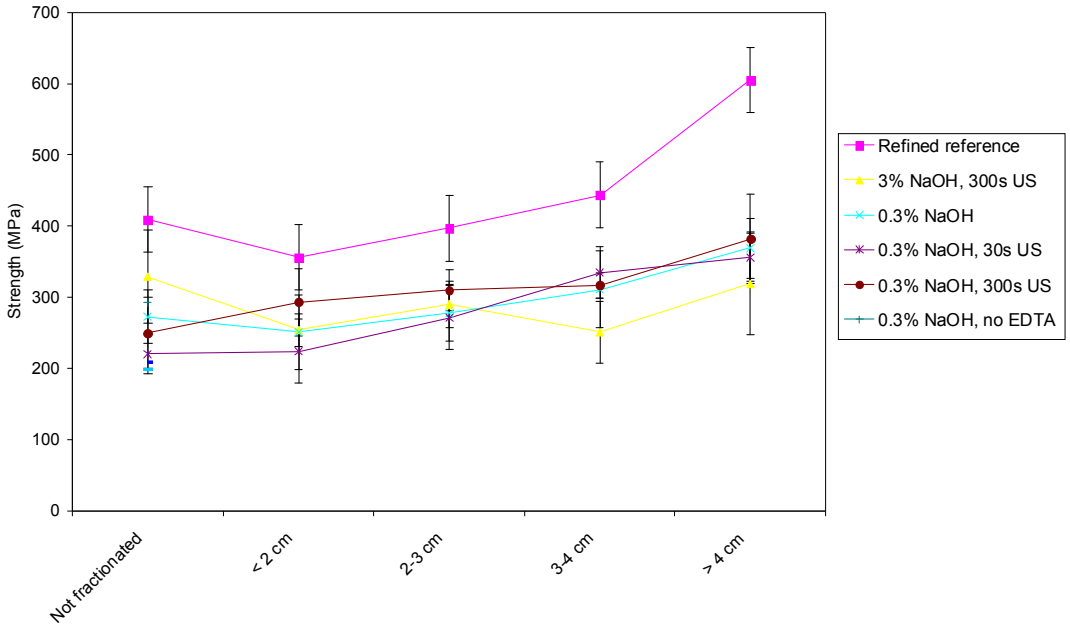

Figure 27: Tensile strength of collective of untreated and pre-treated fibres for indicated fibre length fractions.

Fibre strength after all treatments evaluated decreases compared to the just Shirley refined reference (Figure 28 – Figure 30). Even soaking in hot water or ultrasonic treatment in water reduces fibre strength. For the effect of treatment conditions on fibre strength no clear trend could be observed so far. This may suggest that not all relevant processing parameters have been included in the

evaluation so far. It may be noted that a few samples have a reduced variation in strength data, however this may be just statistics as no correlation to treatment conditions can be observed here and average fibre strength has decreased at least 35%.
Because of the difficulty in translating the fibre strength data to composite performance, it was decided during the meetings in Brussels that composites will be made based on ultrasonically pretreated fibres in order to find an answer to what level fibre strength reduction poses a problem or not.

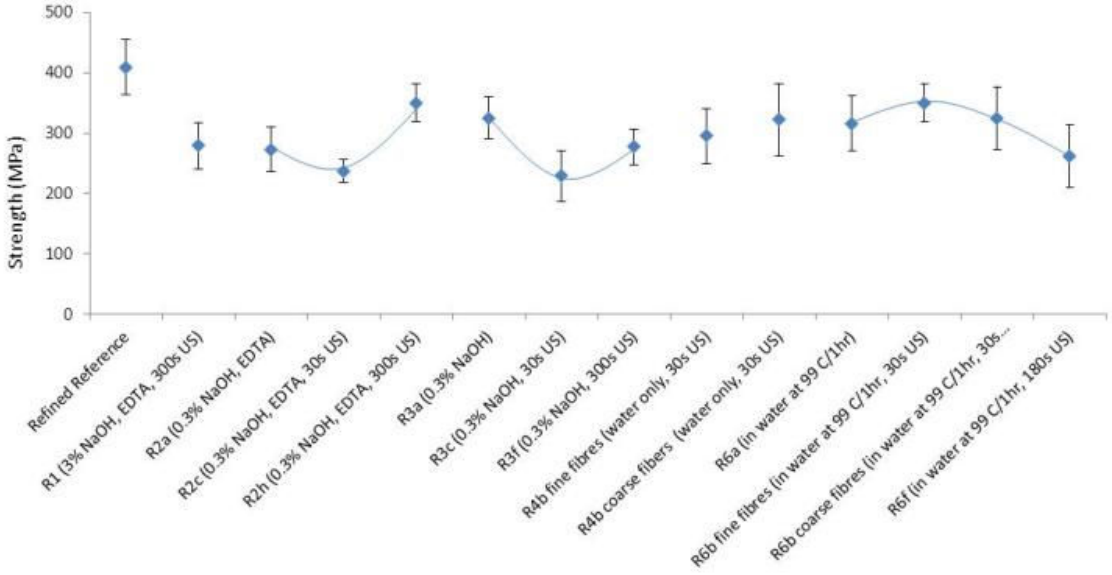

Figure 28: Tensile strength of collective of flax fibres, ultrasonically treated under static conditions, and Shirley refined.

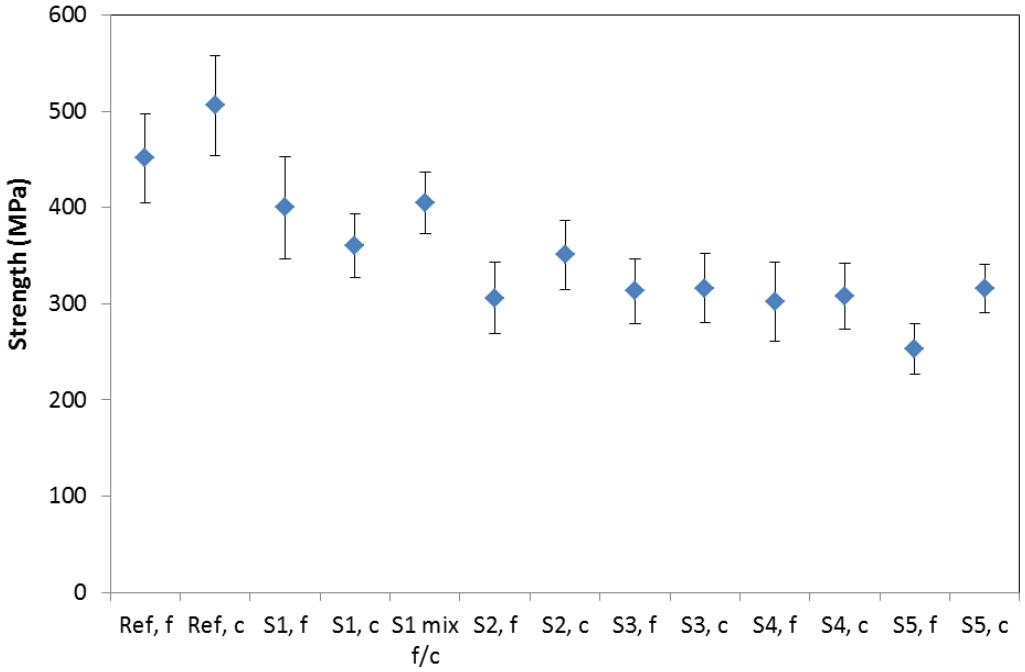

Figure 29: Tensile strength of collective of flax fibres, ultrasonically treated under conditions as indicated in Table 3. f and c refer to fine and coarse fibre fraction, respectively.

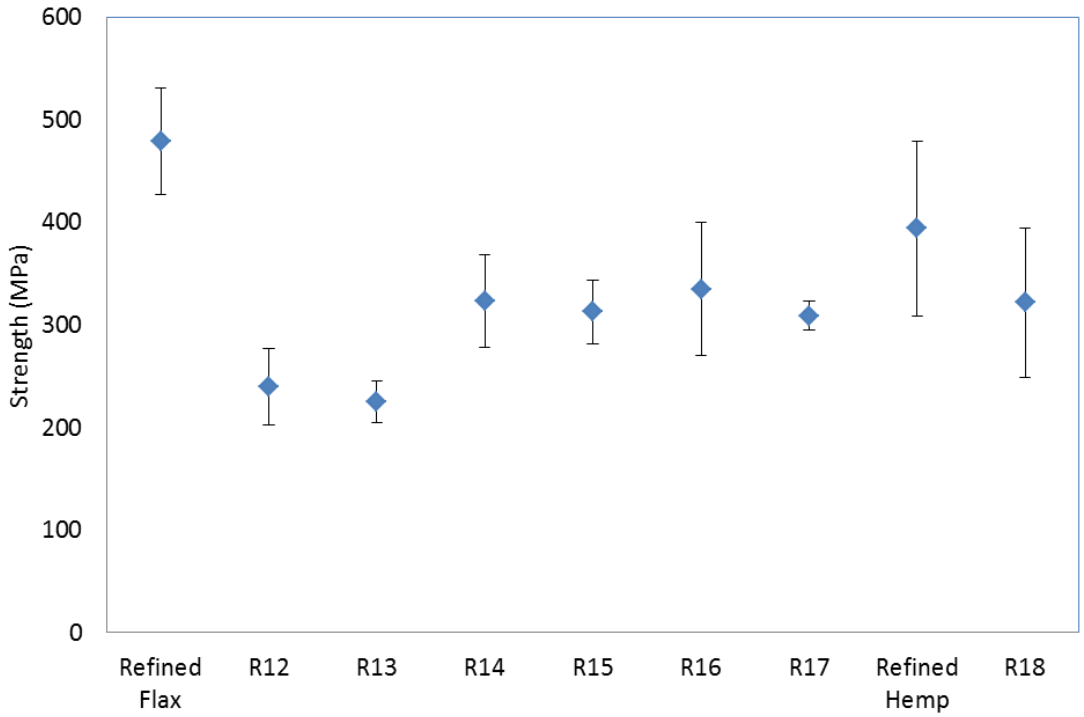

Figure 30: Tensile strength of collective of flax and hemp fibres, ultrasonically treated under flowing conditions, and Shirley refined.

2.2.5 Conclusions on Ultrasonically treated fibres

- Chemical and ultrasonic treatment facilitate the production of single plant cell fibres, as was one of the goals in the project. Soaking of flax fibres in a solution of 3% NaOH, 18 mM EDTA and 1% Lipsol for 4 h and subsequent ultrasonic treatment for 300 s and Shirley refining resulted in about 75% single plant cell fibres by volume.
- Chemical analysis using FTIR shows some effect of pre-treatment (NaOH, NaOH+EDTA), but no effect of ultrasonics on fibre composition.
- Chemical and ultrasonic treatments performed so far seem to reduce fibre strength. Real fibre performance needs to be evaluated in composites.
- No reduction in variation of strength performance could be concluded so far.

2.3 Characterisation of fibres after Plasma treatment (WP3)

The goal of WP3 is to produce natural bast fibres with a modified surface which exhibits improved adhesion to polymer matrices conferring a 25% increase in mechanical properties compared with untreated fibres. This goal needs to be examined by the analysis of fibre reinforced composites (section 2.4 and 2.5). Treated fibres themselves however still need to be characterized in order to make sure that plasma treatment does modify the fibre surface and that it does not negatively affect strength.

2.3.1 Fibre surface modification

Ekotex reference fibres were treated using standard plasma treatment equipment at AcXys' facilities. Three different feed gasses were used: N_2, N_2 + 0.5% CO_2 and N_2 + 0.5% N_2O. More details about the treatment procedures followed will be addressed in Deliverable 3.3 report. Plasma treated fibres and an untreated reference were dried at 50 °C under vacuum and analysed with XPS 2.5 weeks after plasma treatment, showing a significant change in Carbon, Oxygen and Nitrogen element composition at the fibre surface (Table 7), which is derived from element peak surfaces in XPS scanning spectra (Figure 31). At the same time, collective fibre strength of plasma treated flax fibres is retained (Figure 32).

Table 7: Elemental composition of untreated and plasma treated flax fibre surface (upper few nm) using XPS.

	Oxygen	Carbon	Nitrogen
Flax, untreated	18.6	78.3	1.0
Flax, N_2 plasma	14.8	71.4	12.6
Flax, N_2+CO_2 plasma	36.7	50.4	6.7
Flax, N_2+N_2O plasma	41.9	52.2	2.1

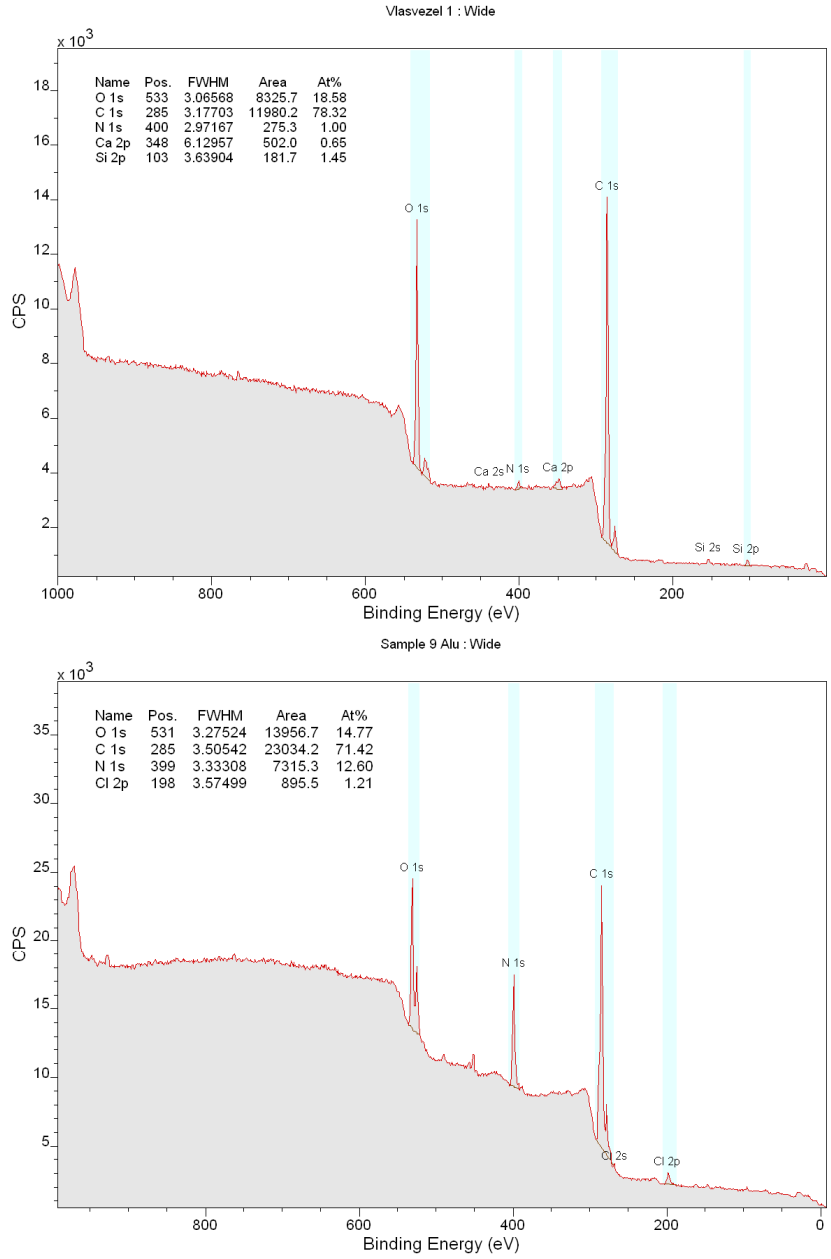

Figure 31: XPS spectra of untreated (upper) and N_2 plasma treated flax (lower picture).

Drying of the N_2+CO_2 plasma fibres at 105 °C resulted in lower Oxygen and Nitrogen content and higher Carbon content compared to treated fibres dried at 50 °C: 31.8, 5.5 and 61.5 %, respectively, indicating a loss of the effect of plasma treatment.

2.3.2 Fibre strength

The plasma treatment of flax and hemp has no significant effect on the collective fibre strength of the fibres (Figure 32 and Figure 33).

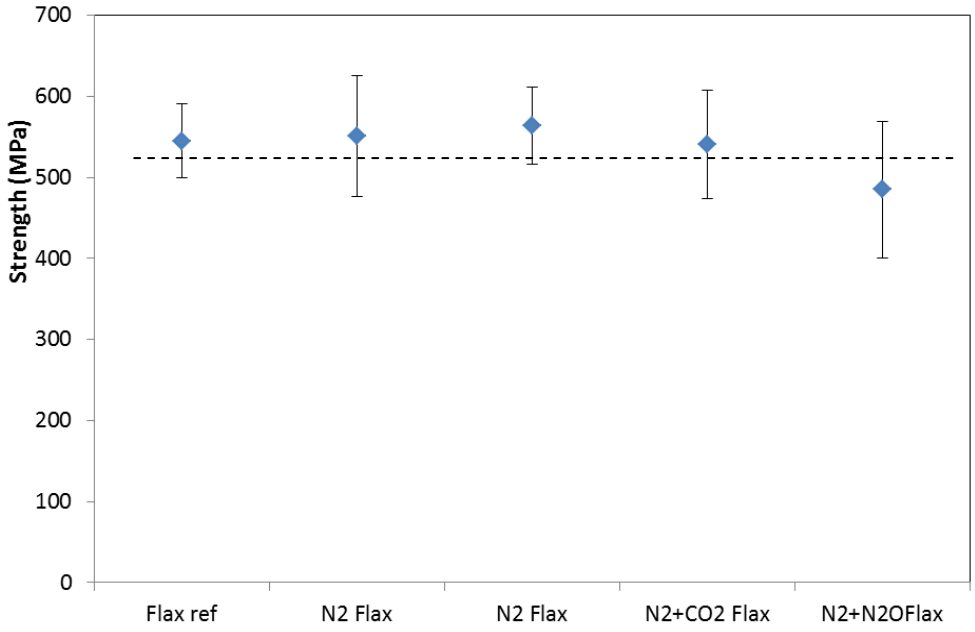

Figure 32: Collective fibre tensile strength of untreated and (AcXys) plasma treated flax fibres. Dashed line representing level of untreated fibres.

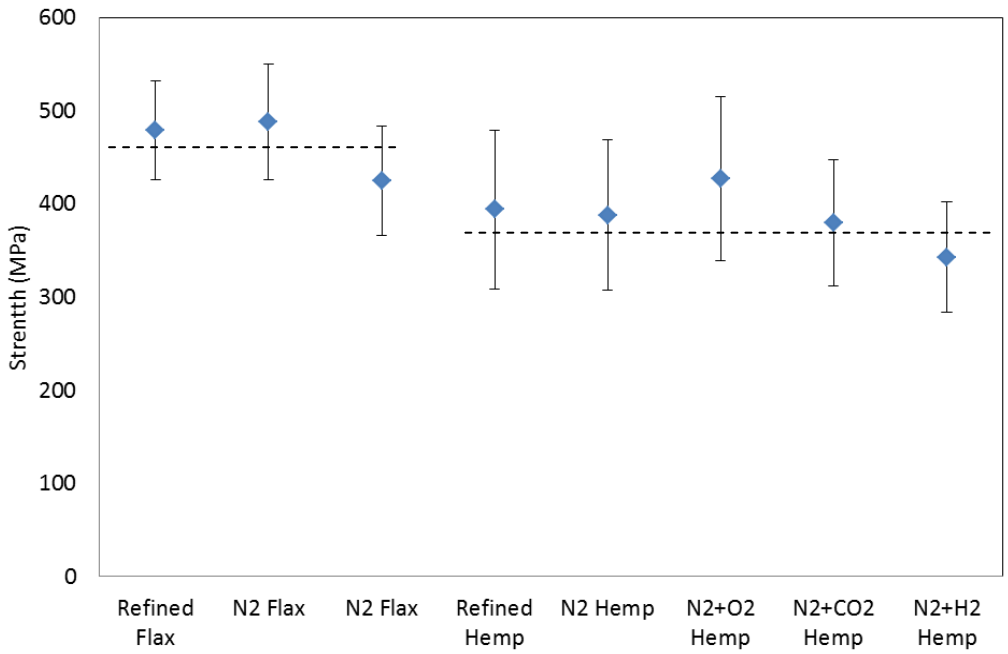

Figure 33: Collective fibre tensile strength of Shirley refined and (DLO-FBR) plasma treated and untreated flax and hemp fibres. Dashed lines representing level of untreated fibres.

2.3.3 Conclusions on Plasma treated fibres

- Using plasma treatment, modification of flax fibre surface is achieved while retaining fibre strength.
- For hemp it is shown that plasma treatment did not affect fibre strength, modification of flax fibre surface needs to be tested.

2.4 Characterisation of Fibre-Matrix adhesion using SFFT (Task 5.3)

Evaluation of fibre-matrix adhesion using Kelly-Tyson equation nr 4 requires critical fibre length and fibre strength at critical fibre length.

Single fibre tensile tests were performed on untreated and N_2 treated flax. Strength, average cross section and calculated Weibull modulus are presented in Table 8. Tensile strength of single fibres is much higher than of a collective of fibres (see Figure 33) because of the volume effect. A slight decrease in average tensile strength may be observed for N_2 plasma treated fibres, in particular because of the lower average diameter, but a real weakening effect of plasma on fibres cannot be concluded because of the high standard deviation. The systematic error in fibre strength is estimated to be 41 MPa only, based on a variation of +/- 1 pixel in diameter, and a maximum error of 0.5% for the force at 0.4 N and above. In consequence, the high standard deviation for each fibre tested cannot be explained by the accuracy of diameter measurements nor by the accuracy of the load cell.

Table 8: Tensile properties of single flax fibres tested. Between brackets the standard deviation is presented.

	Untreated Flax	N_2 treated Flax
Tensile strength (MPa)	1055 (428)	1018 (427)
Diameter (μm)	24.2	20.3
Weibull modulus	2.27	2.43

The fibre strength at critical fibre length can be determined using equation 3, requiring Weibull modulus values, m. Weibull modulus was determined from the slope in the plot of Ln(-Ln(1-P)) versus Ln(σ_f) (see for example Figure 34) and presented in Table 8.

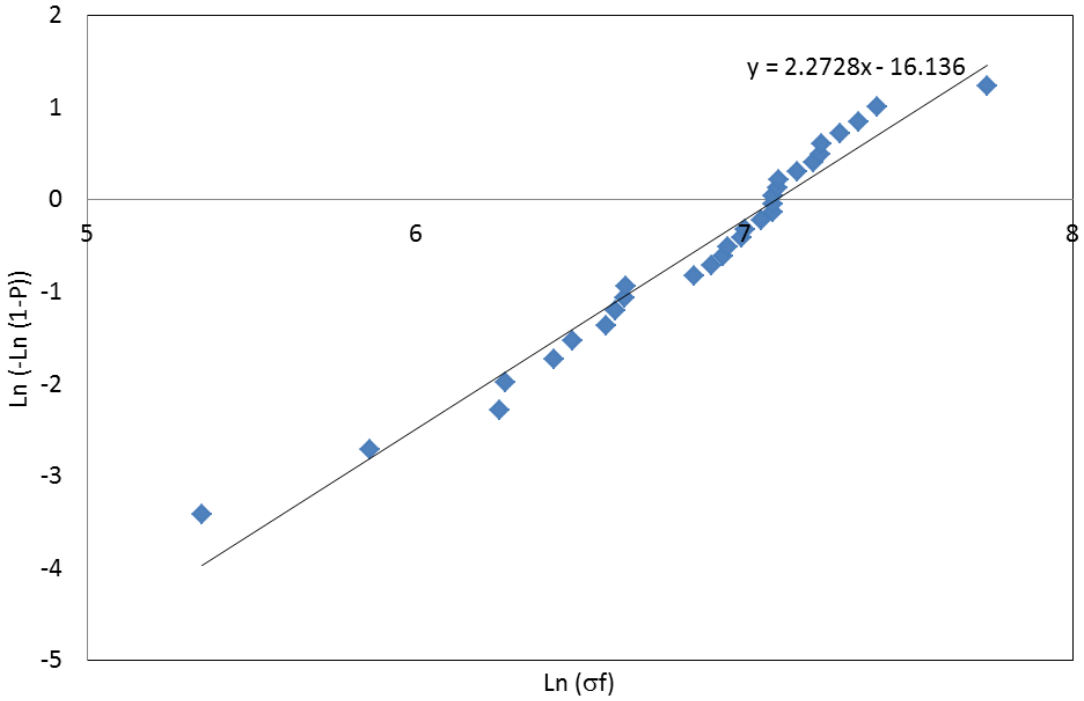

Figure 34: Weibull plot of experimentally determined probability of fibre failure versus fibre strength at 3.2 mm span length.

Critical fibre length is derived from single fibre composite fragmentation tests (SFFT). Both untreated and N_2 treated flax fibre-PP and –PLA composites were analysed. Critical fibre length is calculated from L/D values of over 200 fibre fragments per composite using equation 2. Distributions of L/D values are presented in Figure 35. The distribution curves are similar to those found for flax-PP before (M.J.A. Van den Oever, H.L. Bos, Advanced Composites Letters 7 (3), 1998, 81-85). Small L/D values are caused by weak spots in the fibre, high values result from locally weak fibre-matrix interfaces, resulting from possible contamination of the fibre surface. In real composites similar effects occur.

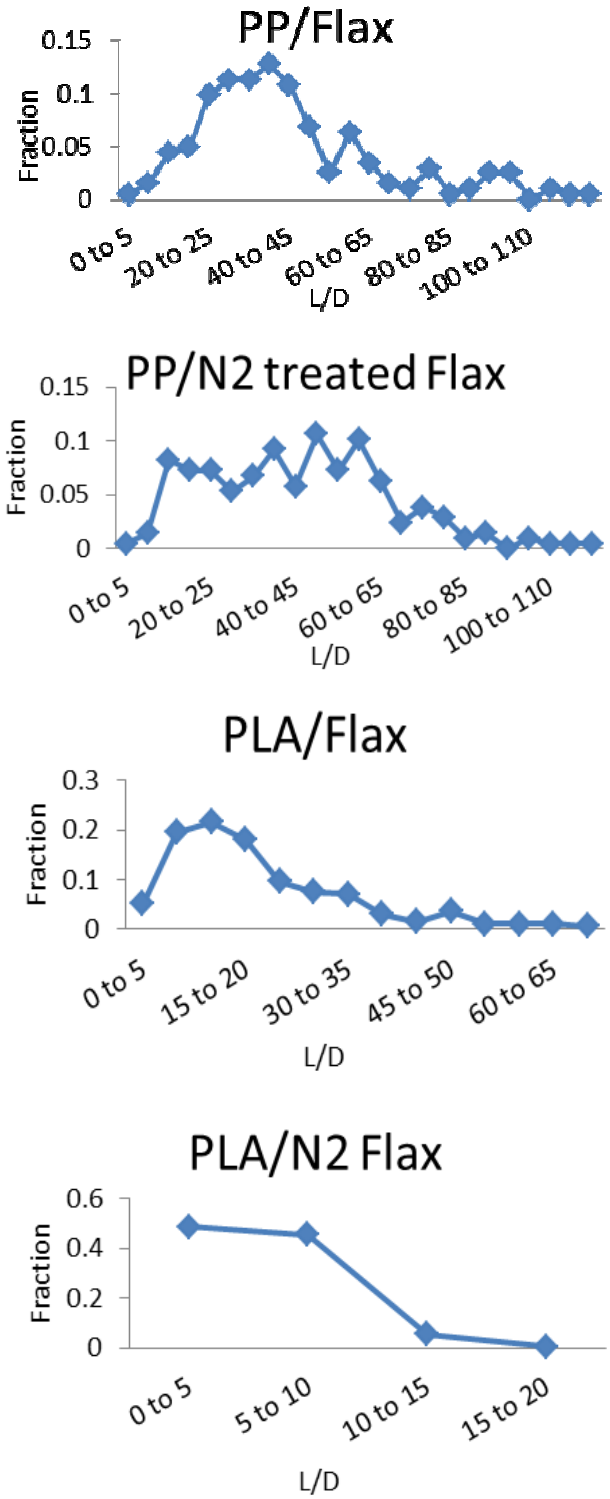

Figure 35: Distribution of L/D ratio for untreated and N_2 treated single flax fibre-PP and PLA composites.

From the average L/D values, critical L/D values are determined (Table 9). A uniform critical fibre length is calculated from the average diameter of the fibre fragments (Table 9). The shear strength results indicate that N_2 plasma treatment has a positive effect on adhesion to both PP and PLA polymer. The τ values for flax-PP are very similar to those found by Van den Oever and Bos, τ values for flax-PLA seem unrealistic. Based on contact angles with water of 65° for PLA, and 106° for PP, a better interaction may be expected between flax and PLA. However, using Von Mises criteria for the maximum shear strength of a polymer, a maximum τ value for PLA of around 38 MPa (=tensile strength/$\sqrt{3}$) is expected. High values obtained for shear strength in PLA could also partially be explained by the high quantity of cracks initiated by bubbles in the PLA composite samples cracks may suggest fibre break where only the polymer is broken. This method may be improved by making SFFT samples containing less initial voids, however, this development is outside the scope of this project.

Table 9: Properties resulting from SFFT and calculated shear strength.

	Flax-PP	N_2 Flax-PP	Flax-PLA	N_2 Flax-PLA
Average L/D	47.8	43.4	19.3	5.5
Critical L/D	63.8	57.9	25.2	7.4
Average D (μm)	25	19	20	21
Critical length, L_c (mm)	1.62	1.11	0.50	0.15
Average strength at L_c (MPa)	1426	1573	2384	3542
Shear strength, τ (MPa)	11.2	13.6	46.3	239.6

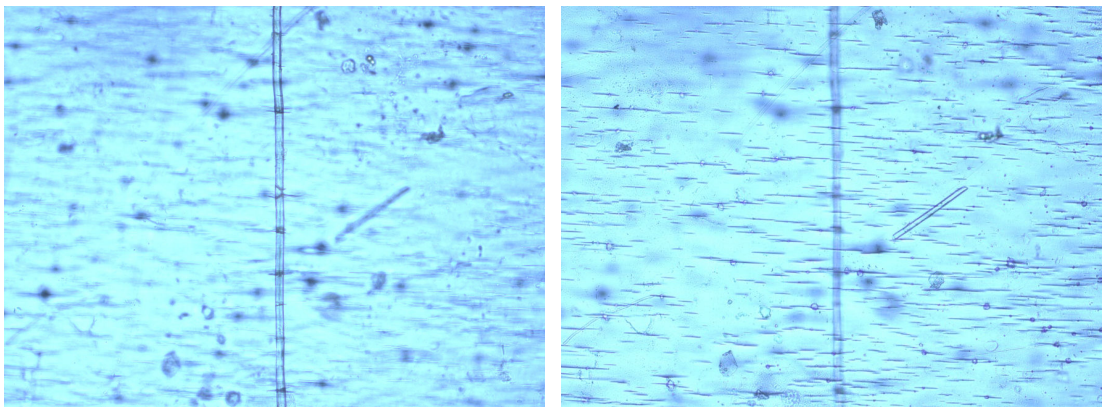

Figure 36: Flax-PLA SFFT sample showing cracks in the fibre (left) and the PLA matrix surface (right picture).

The critical fibre lengths appear very short, in the range 1.1 – 1.6 mm for flax-PP and even shorter for PLA. These fibre length values indicate the order of magnitude required for reinforcement of polymers.

The SFFT method cannot be applied for thermosetting resins like furan or UP resins due to too low failure strain to allow complete fibre fracture without fatal resin failure.

2.4.1 Conclusions from SFFT fibre-matrix adhesion analysis

- SFFT analysis is a suitable method to analyse adhesion of fibre-PP composites. A positive effect of N_2 plasma treatment on adhesion to PP was observed. Improvement of adhesion was less compared to MAPP results in literature.
- Results indicate that single plant cell fibre length required for effective reinforcement of PP is in the range of 2 mm. Improved adhesion reduces the length required for effective reinforcement.
- Suitable SFFT analysis method of PLA matrix may be developed, however this is beyond the scope of this project.

2.5 Characterisation of Composites (WP4, WP6)

The goal of the project is to produce natural bast fibres with:

1) a refined diameter and lower variation in strength properties (using ultrasonic treatment) compared to conventionally decorticated fibres
2) a modified surface (using plasma treatment) which exhibit improved adhesion to polymer matrices conferring a 25% increase in mechanical properties compared with untreated fibres.

Evaluation of the effect of ultrasonic fibre treatment on composite properties is scheduled for the next period.

2.5.1 Natural fibre-PP

A first series of Shirley refined and plasma treated flax fibres was tested in PP and PP/MAPP polymer matrix. Untreated fibre was evaluated as a reference. All composites contained 30 wt.% of fibre. In Figure 37 – Figure 39, flexural modulus, flexural strength and Charpy impact strength are presented. Compositions are indicated in the figure caption. The MAPP content refers to the total composite. Conclusions from these results are:

- Plasma treatment and MAPP hardly have an effect on flexural modulus of batch kneaded compounds. This is as expected.
- N_2 plasma treatment has a positive effect on fibre-PP matrix adhesion, resulting in a 23 % increase of composite flexural strength compared to untreated fibre. This effect is close to the effect of using about 1% MAPP, resulting in a 29 % increase of flexural strength. The intensity of plasma treatment however seems an important parameter. The positive results were obtained with a treatment of 6 passages at 2 sides, treatment of 2 passages at 1 side does not show an effect of composite strength. Plasma treatment intensity needs to be evaluated in more detail.
- Plasma treatment does not have a positive effect on flax-PP Charpy impact strength, MAPP does.

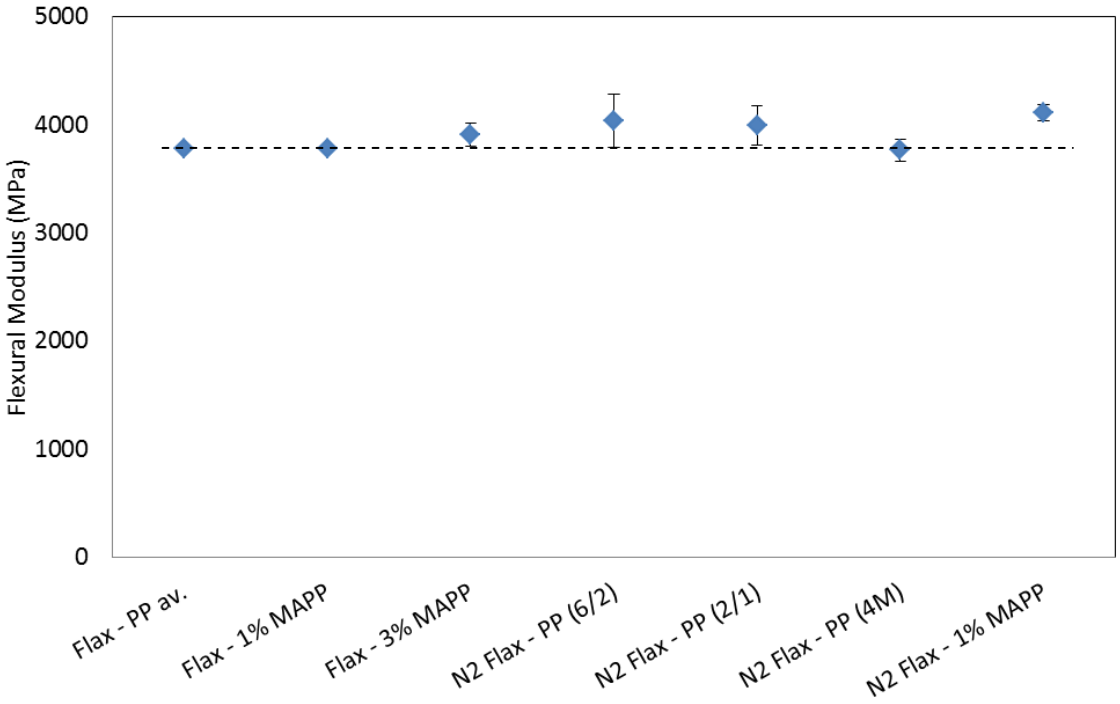

Figure 37: Flexural modulus of flax-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated flax-PP composites.

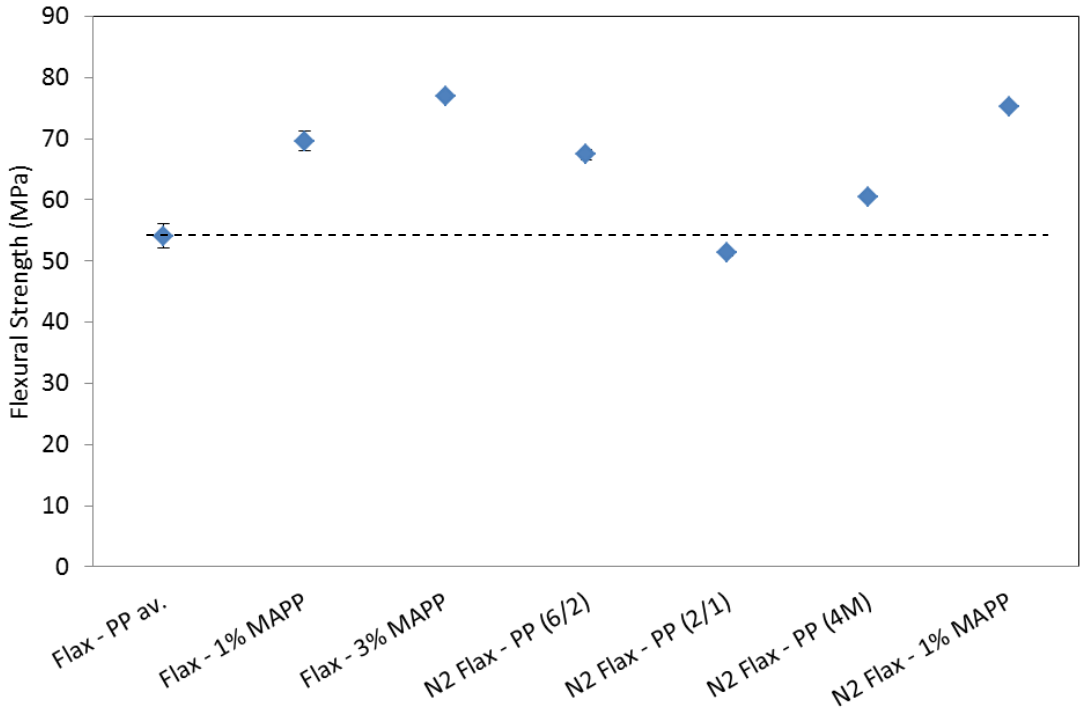

Figure 38: Flexural strength of flax-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated flax-PP composites.

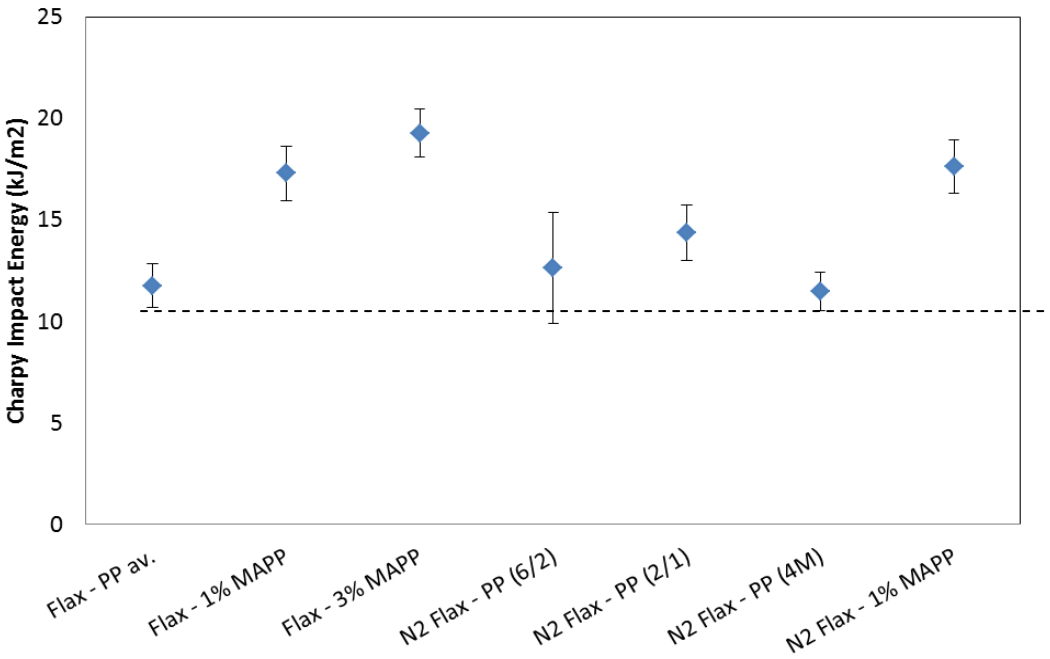

Figure 39: Impact strength of flax-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated flax-PP composites.

A series of Shirley refined and plasma treated hemp fibres was tested in PP and PP/MAPP polymer matrix. Untreated fibre was evaluated as a reference. All composites contained 30 wt.% of fibre. In Figure 40 – Figure 42, flexural modulus, flexural strength and Charpy impact strength are presented. Conclusions from these results are:

- Plasma treatment (N_2, $N_2 + O_2$, $N_2 + CO_2$, $N_2 + H_2$) has no effect on hemp-PP composite strength, indicating that no effect on hemp-PP adhesion is achieved. The effect of MAPP is as expected.
- On the other hand, plasma treatment does have a significant effect on hemp-PP composite flexural modulus. Modulus increase is in the range 10 – 23 %, similar to the increase due to addition of MAPP.
- Considering Kelly-Tyson model for composite (tensile) strength and Cox-Krenschel model for composite E-modulus, no explanation can be given for the increase of hemp-PP composite modulus while strength does not increase. From optical micrographs of Shirley refined flax and hemp fibres and of untreated and plasma treated hemp and flax-MAPP composites (Figure 43), it may be concluded that hemp fibre refine further during compounding and injection moulding (Table 10). This would create fresh fibre surface and reduced effectiveness of the plasma treatment. But it does not explain why hemp-PP modulus increases while strength does not.

- Like for flax-PP, plasma treatment does not have a positive effect on hemp-PP Charpy impact strength.

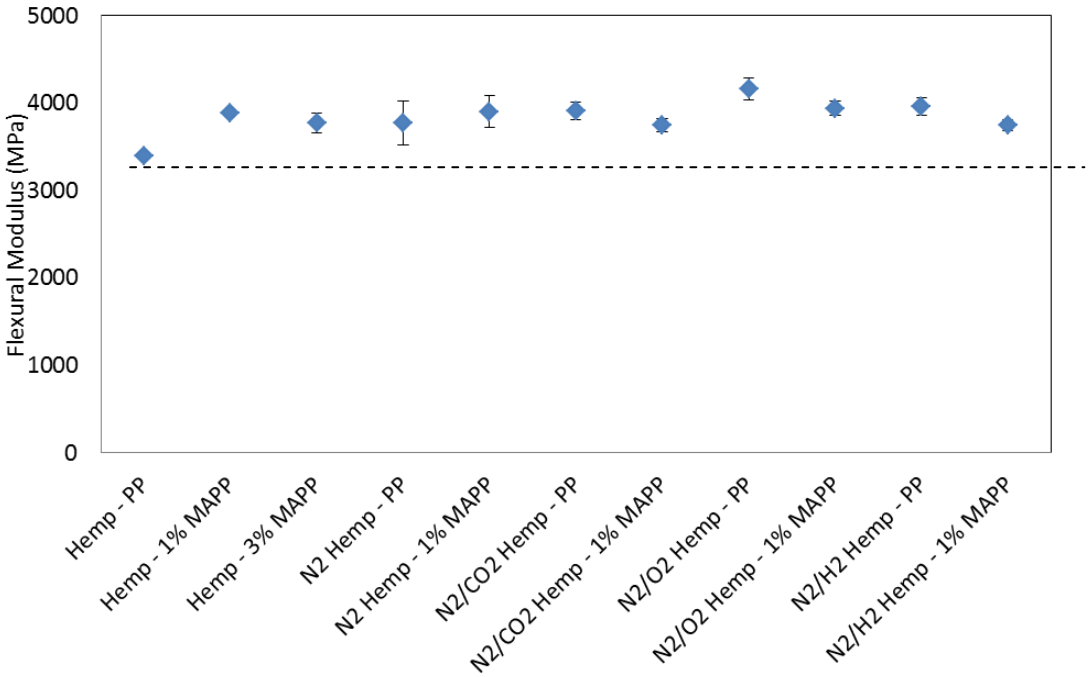

Figure 40: Flexural modulus of hemp-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated hemp-PP composites.

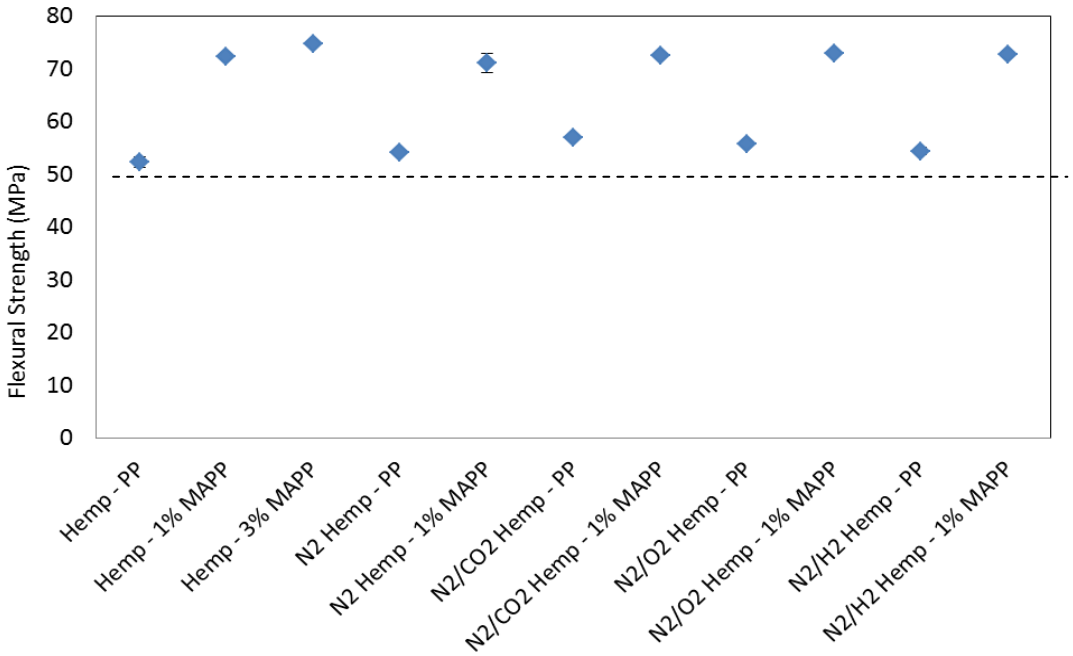

Figure 41: Flexural strength of hemp-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated hemp-PP composites.

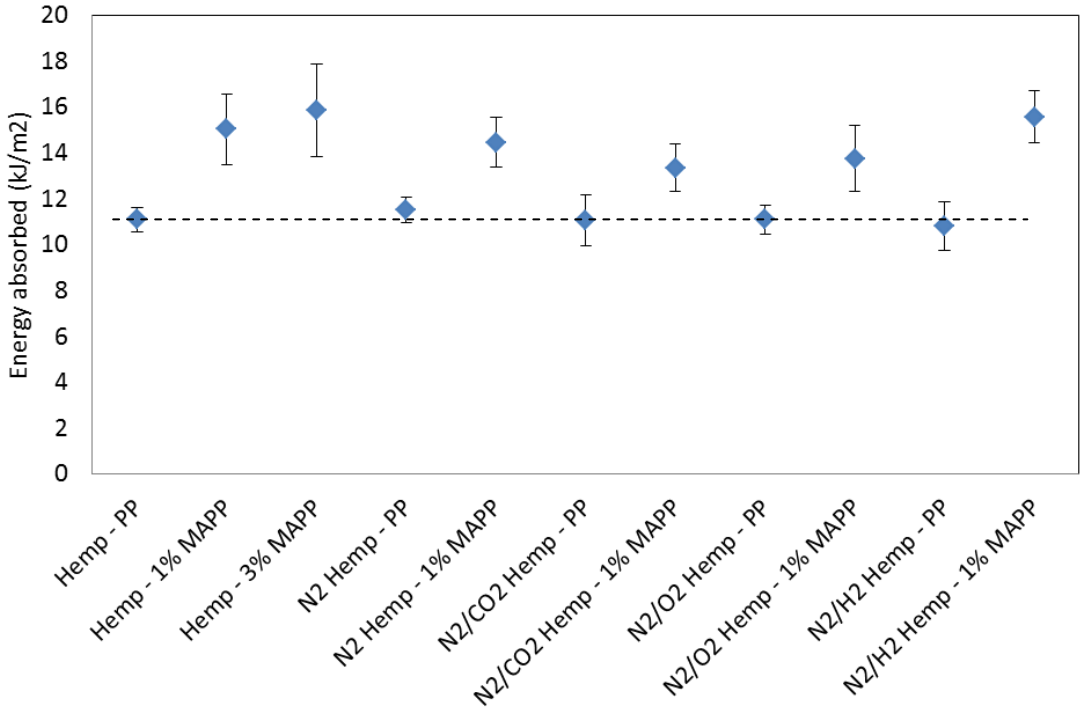

Figure 42: Impact strength of hemp-PP composites: effect of plasma treatment and MAPP. Dashed line represents level of untreated hemp-PP composites.

Table 10: Fibre diameter values collected from 30 fibres, after refining and in injection moulded 1% MAPP composites. Standard deviation between brackets.

	After refining (μm)	Untreated fibre	N_2 plasma treated fibre
		In composites (μm)	
Hemp	42 (17)	35 (10)	37 (17)
Flax	20 (10)	20 (5)	20 (4)

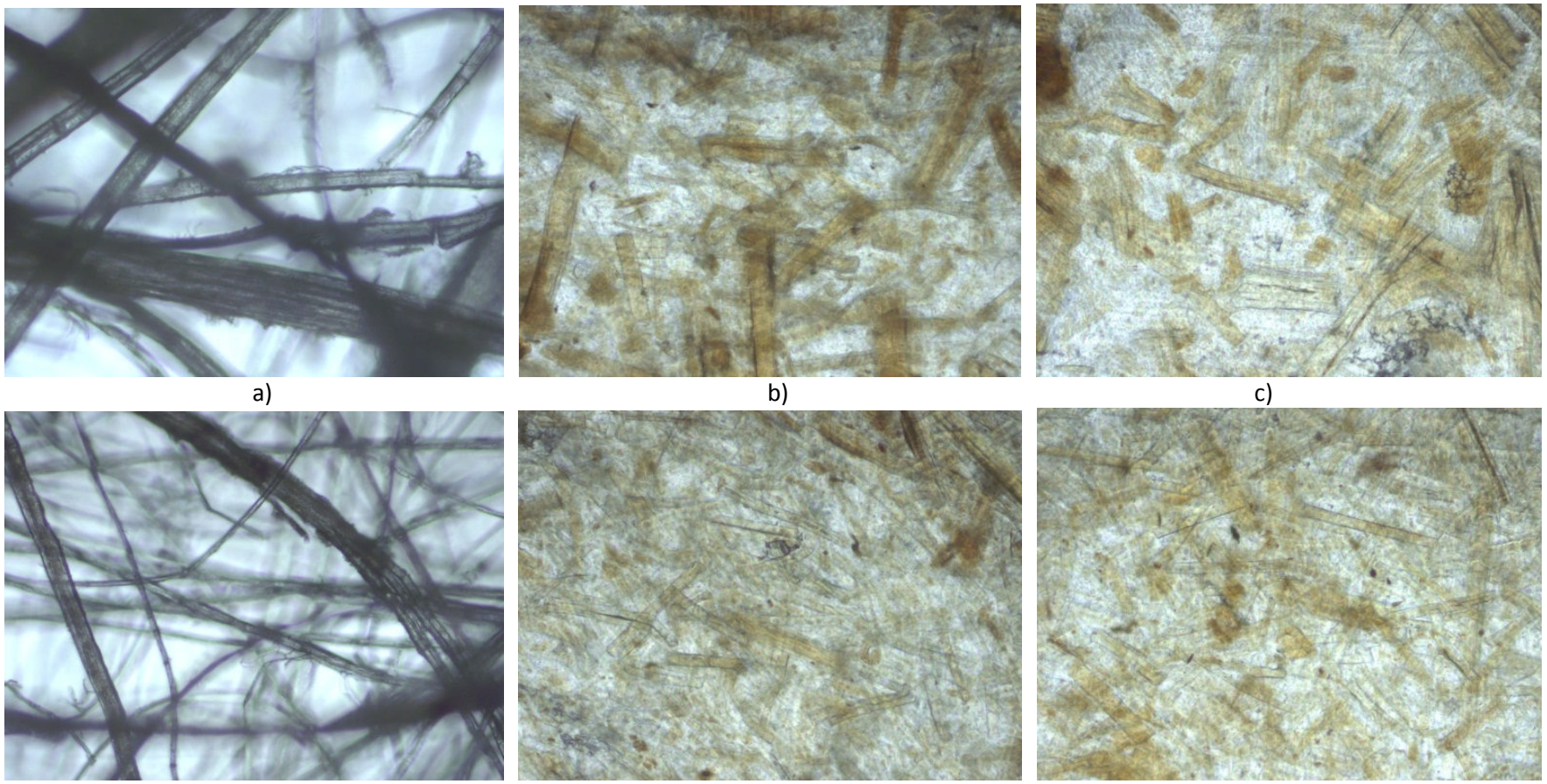

Figure 43: Micrographs of Shirley refined fibre (a), untreated fibre-PP-1%MAPP (b) and N2 plasma treated fibre-PP-1% MAPP (c) for hemp (upper) and flax fibre (lower 3 pictures). Full width of each picture equals 508 μm.

2.5.2 Natural fibre-PLA

A series of Shirley refined and plasma treated hemp fibres is tested in PLA matrix. Untreated fibre was evaluated as a reference. All composites contained 30 wt.% of fibre. In, flexural modulus, flexural strength and Charpy impact strength are presented. Conclusions from these results are:

- Difficult to see a consistent trend so far.
- N_2 Plasma treatment results in improved flax-PLA composite modulus, but no improved strength, similar to the hemp-PP composites.
- Plasma treatment based on N_2, N_2 + O_2 and N_2 + CO_2 feed-gasses seems to result in a significant improvement of hemp-PLA composite strength, up to 24 %. It must be noted, however, that the strength values of the untreated hemp-PLA are low compared to the value for flax-PLA.
- Overall, N_2 + H_2 plasma treatment seems to have a negative effect on hemp-PLA composite performance.
- No significant trend for the effect of plasma treatment on hemp-PLA Charpy impact strength can be observed.

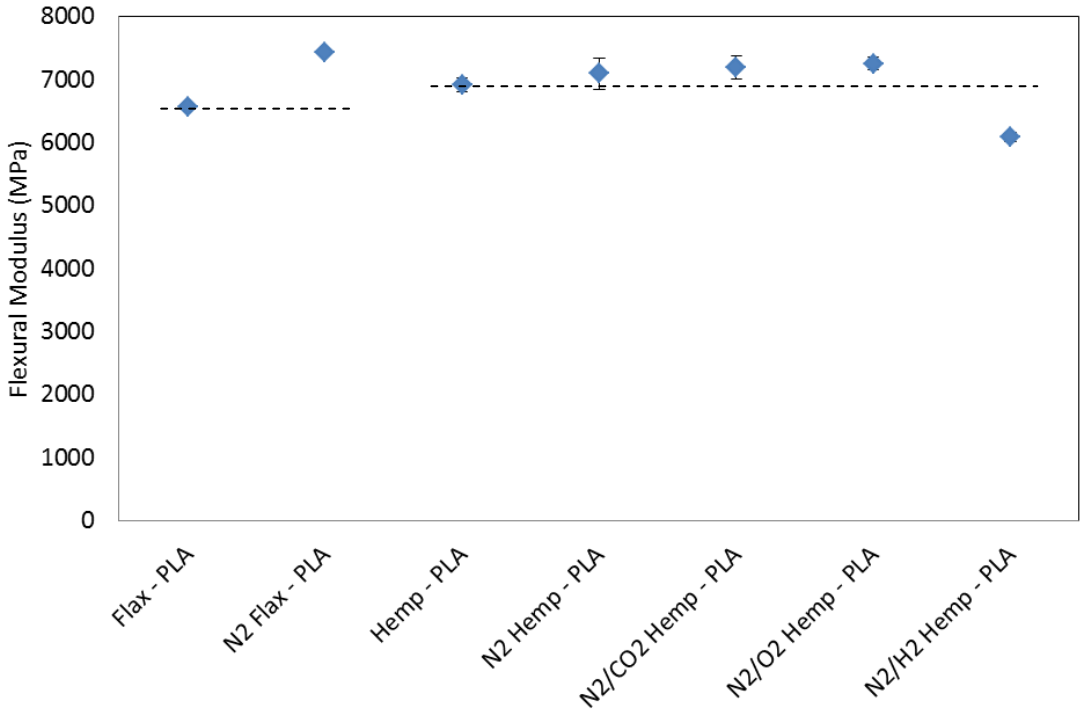

Figure 44: Effect of plasma treatment on Flexural modulus of (Shirley refined) Flax and Hemp-PLA composites. Dashed line represents level of untreated fibre composites.

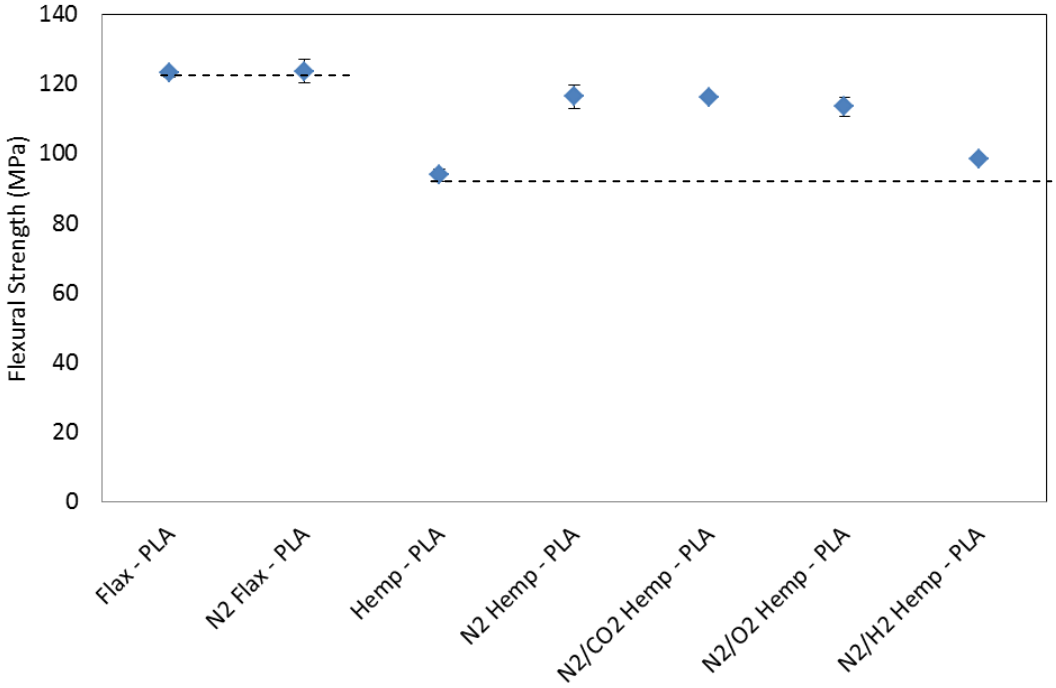

Figure 45: Effect of plasma treatment on Flexural strength of (Shirley refined) Flax and Hemp-PLA composites. Dashed line represents level of untreated fibre composites.

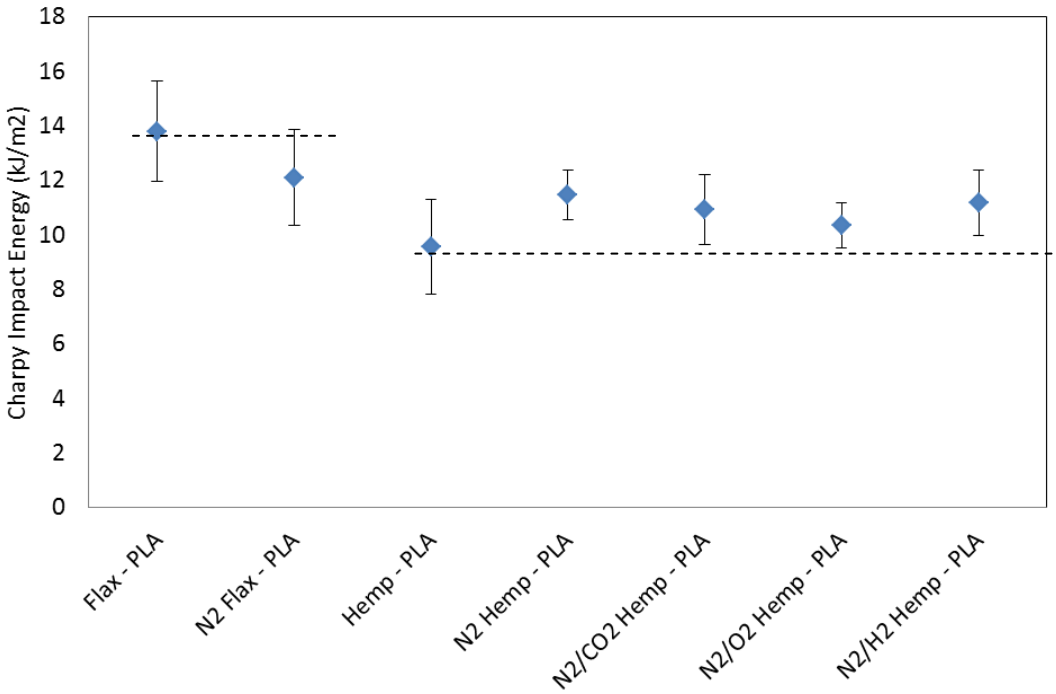

Figure 46: Effect of plasma treatment on Charpy impact strength of (Shirley refined) Flax and Hemp-PLA composites. Dashed line represents level of untreated fibre composites.

2.5.3 Natural fibre-UP

Preliminary trials with flax fibre non-woven and unsaturated polyester (UP) using the SMC process were performed by MoveVirgo. Trials were meant to evaluate SMC processing using natural fibres. First successful flax-UP composite specimen contained about 5-10% of fibre. The composite was tested for tensile properties, showing a strength of 20 MPa and a modulus of 6.5 GPa. The poor performance is due to low fibre content. Probably also uneven fibre dispersion and poor fibre wetting contribute to the low composite strength. New series of trials will have to address fibre content, fibre dispersion and fibre wetting.

2.5.4 Conclusions on Composites

- N_2 plasma treatment of flax has resulted in a 23 % increase in PP composite strength, while retaining composite modulus and Charpy impact strength. This is close to the 25% goal set in Technical Annex 1. Using 1% MAPP resulted in a 29% increase in flax-PP strength.
- Plasma treatment intensity seems to be an important parameter and needs to be investigated in more detail.
- For plasma treated hemp fibre-PP composites an increase of flexural modulus by 10 – 23 % was observed, strength remained at the same level as for untreated hemp-PP. This effect cannot be explained using Kelly-Tyson model for composite (tensile) strength and Cox-Krenschel model for composite E-modulus.
- Plasma treatment of hemp based on N_2, N_2 + O_2 and N_2 + CO_2 feed gasses shows a significant improvement of hemp-PLA composite strength, up to 24 %. The strength values of the untreated hemp-PLA may need to be checked.
- Plasma treatment does not have a significant effect on flax and hemp reinforced PP and PLA composite Charpy impact properties.
- Ultrasonically treated fibres have not been evaluated in composites so far.
- Preliminary trials on flax-UP composites suggest that fibre content, fibre dispersion and fibre wetting need to be addressed in order to achieve good composite strength performance.

2.6 Issues & solutions

The fibre diameter analysis method, required for tensile testing of single natural fibres as described in Technical Annex 1, as it was available at DLO-FBR at the start of the project was very time consuming for a series of reasons:

- Fibres need to be glued on a cardboard frame for diameter analysis because of the very short working distance of regular optical microscopes.
- Fibres may break when part of the cardboard frame is cut away, which is necessary for diameter analysis from 2 perpendicular sides, so prior to fibre testing.
- The available (regular) microscopes require 'manual' evaluation of the fibre diameter.

Therefore, DLO-FBR evaluated the possibilities to source a vision system with long working distance, which would allow analysis of fibre diameter after they are fixed in the clamps for tensile testing already. Thus avoiding analysis of fibres which break before testing and avoiding the time consuming gluing of fibres onto a cardboard frame.

A 'long distance' vision system was foreseen to be required to analyse fibre cross section of individual fibres prior to actual tensile testing. A number of issues and considerations came up:

- Supplier of long distance vision systems does not offer equipment for rent.
- Buying such a system (costs about € 17.000) raises issues related to bearing costs and ownership.
- Contracting a third party may be more expensive, as the fibre strength needs to be investigated directly after fibre diameter analysis in order to avoid permutation of the many samples.
- An indication of fibre-matrix adhesion (Task 5.3) for which the strength of individual fibres would be required, can be derived from flexural strength properties of composites.

At the UltraFibre partners meeting in Brussels the following solution was proposed and accepted:

- Fibre-matrix adhesion will be derived from flexural strength properties of composites.
- For the evaluation of fibre strength in Task 5.1 and 5.2, a collective fibre tensile testing method will be used. The method was developed at DLO-FBR and combines the use of Pressley clamps from the so called Stelometer test equipment (Figure 6) and a universal tensile testing machine using special clamp holders (Figure 7). The testing of a collective of fibres using of the Pressley clamps allows the determination of fibre cross section from test fibre sample mass.

3. Conclusions

Below, conclusions from analysis work up to month 20 are reported. Testing and characterization results to be collected in months 21-33 will be reported in Deliverable 5.3, due in month 33.

Related to WP2: Ultrasonic treatment

- Chemical and ultrasonic treatments facilitate the production of single plant cell fibres, as was one of the goals in the project. Single plant cell fibre content after Shirley refining could be increased to up to 75 % by volume compared to 40 % for untreated fibres.
- Ultrasonic treatment did not cause a change in chemical composition and thermal stability of fibres, which was concluded from FTIR and TGA analysis.
- Chemical and ultrasonic treatments performed so far seem to reduce fibre strength. Real fibre performance needs to be evaluated in composites.
- No reduction in variation of strength performance could be concluded so far.

Related to WP3: Plasma treatment

- Using plasma treatment, modification of flax fibre surface is achieved while retaining fibre strength.
- For hemp it is shown that plasma treatment did not affect fibre strength, modification of flax fibre surface needs to be tested.
- Plasma feed gas composition and plasma intensity will need further development.

Related to Task 5.3: Fibre-matrix interactions

- SFFT analysis is a suitable method to analyse adhesion of fibre-PP composites. A positive effect of N_2 plasma treatment on adhesion to PP was observed. Improvement of adhesion was less compared to MAPP results in literature.
- Results indicate that single plant cell fibre length required for effective reinforcement of PP is in the range of 2 mm. Improved adhesion reduces the length required for effective reinforcement.
- Suitable SFFT analysis method of PLA matrix may be developed, however this is beyond the scope of this project.

Related to WP4: Composites

- Ultrasonically treated fibres have not been evaluated in composites so far.
- N_2 plasma treatment of flax has resulted in a 23 % increase in PP composite strength, while retaining composite modulus and Charpy impact strength. This is close to the 25% goal set in Technical Annex 1. Using 1% MAPP resulted in a 29% increase in flax-PP strength.

- Plasma treatment intensity seems to be an important parameter and needs to be investigated in more detail.
- For plasma treated hemp-PP composites an increase of flexural modulus by 10 – 23 % was observed, strength remained at the same level as for untreated hemp-PP. This effect cannot be explained using Kelly-Tyson model for composite (tensile) strength and Cox-Krenschel model for composite E-modulus.
- Plasma treatment of hemp based on N_2, $N_2 + O_2$ and $N_2 + CO_2$ feed gasses shows a significant improvement of hemp-PLA composite strength, up to 24 %. The strength values of the untreated hemp-PLA may need to be checked.
- Plasma treatment does not have a significant effect on flax and hemp reinforced PP and PLA composite Charpy impact properties.
- Preliminary trials on flax-UP composites suggest that fibre content, fibre dispersion and fibre wetting need to be addressed in order to achieve good composite strength performance.

4. Future Work (Months 21 to 33)

For the coming period the following activities are planned:

- Mechanical properties analysis of already prepared PP composites based on ultrasonically treated fibres in order to evaluate the effect of chemical pre-treatment and ultrasonics on composite performance.
- Laserscan analysis of fibre diameter will be performed to evaluate the effect of ultrasonics on fibre refining.
- SEM of ultrasonic and plasma treated fibres in order to evaluate fibre morphology.
- SEM of treated fibre composites in order to better understand the effect of treatment on fibre-matrix adhesion and composite performance.
- XPS of recently plasma treated fibres produced to qualify surface modification.
- Depending on the results from the trials mentioned above, further fibre treatments (WP2 and WP3, a.o. ultrasonic processing conditions, further plasma feed gas composition and plasma treatment intensity) will be performed and composites will be prepared (WP4 and WP6). These fibres and composites will be analysed in order to collect relevant information.
- Components that will be produced in WP7 will be tested.
- Testing results will be described in Deliverable 5.3 report, which is due in Month 33.

Annex 1 Typical procedure for batch compounding and injection moulding

Polymer granules were melted in a Haake Rheomix batch kneader (Figure 47) at a set temperature of 185 °C at a rotor speed of 100 RPM during 2.5 min under a constant flow of pre-dried nitrogen. Subsequently, fibres were fed to the polymer melt and compounded up to a total time of about 13 min. The temperature of the polymer melt was determined using a thermocouple.
Before compounding, PLA was dried in a Gerco granules dryer (Gerco Apparatenbau GmbH & Co KG, Sassenberg, Germany) at 80 °C with pre-dried air before melt compounding for at least 4 h.

Figure 47: Haake Rheomix batch kneader.

Composites were granulated using a KT handlings device (Figure 48) and dried overnight in a Gerco granules dryer at 80 °C with pre-dried air and injection moulded to flexural/impact test bars with dimensions 80*10*4 mm^3 using a Demag ERGOtech 25-80 (Figure 49). All composite specimens were conditioned for at least 7 d at 23 °C and 50 % RH before further analysis.

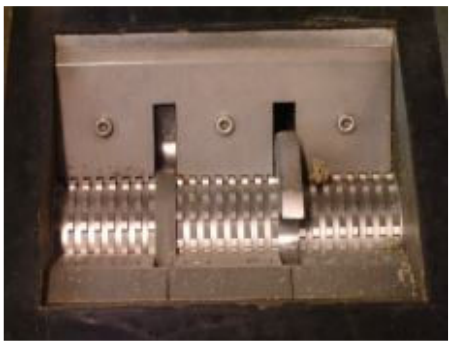

Figure 48: Granulating section of KT handlings granulator.

Figure 49: Demag ErgoTech 25-80 injection moulding machine.