D5.3

Report on Testing of Composites and Products

UltraFibre

SEVENTH FRAMEWORK PROGRAMME

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 consistent 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 D5.3** is a **report on testing of compounds, mouldings and products** and covers analysis activities in WP5 since submission of Deliverable 5.2 in Month 20.
Although D5.2 covered all activities of Tasks 5.1 and 5.2, it was decided that further fibre testing may be useful in the course of the project in order to provide answers to particular research questions. Therefore, scanning electron microscopy (SEM) method of fibre surfaces will be addressed in this report, results were already presented in D3.3.

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 **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.

The **work-plan** for WP5 during the period Month 20-33 as stated in the Technical Annex 1 focuses on analysis of fibre-matrix interaction (Task 5.3), compounds (Task 5.4) and components (Task 5.6).

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

Task 5.5: Supply of design data for industrial applications
Data generated in WP5 will be used to assemble a design guide in support of the industrial application in WP8 and the wider industrial exploitation of the UltraFibre formulations.

Task 5.6: Testing of components
Products and materials from industrial scale up trials will be tested and characterised. Their performance will be compared to existing industrial components.

Comments to execution of Tasks:

Tasks 5.3: A particular way of evaluating fibre-matrix adhesion and its results was presented in D5.2 (sections 2.1.9 and 2.4). Further, in D5.2 (section 2.1.1) it was explained why flexural strength will be used as the indicator for evaluating fibre-matrix adhesion. Flexural strength is a key parameter which is quantified in Task 5.4 and 5.6 anyway.

Task 5.4: During the partner meeting in Brussels (Month 16), it was decided that during the development stage of injection moulded composites, flexural strength and stiffness and Charpy impact strength will be evaluated for 30 wt.% fibre reinforced composites (also see D5.2 section 2.1.1).
At the partner meeting in Wageningen (Month 23) it was decided that DLO-FBR would make a mould for making lab scale SMC composite samples in order to efficiently evaluate the effect of plasma treatments on UP composite properties. Optimisation of SMC composition (fibre content, flow additives) and moulding conditions (temperature) was performed in consultation with RAPRA and Movevirgo.

Task 5.5: Results from this task will be addressed in a booklet/CD-ROM/PDF-document which will be composed later on in the project.

Task 5.6: For analysis of final composite products 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

During the partner meeting in Wageningen (Month 23), it was decided that SMC composite products should be characterized for water absorption as well. For reason of timing, water absorption method will be addressed in D6.1. The issues of Extractable and leachable agents and Stability and recyclability will be addressed in (section 2.3) of this report.

In order to make the Deliverable reports as clear and simple as possible, the **presentation and discussion of test results, which are directly related to the experimental development and scaling up work will be presented in**

Deliverable reports 3.4, 4.3 and 6.1. Results which are not directly linked to these Deliverable reports are presented in this report.

- In section 2.1 the experimental procedures are described.
- Results of fibre characterization related to WP2 are presented in section 2.2.
- Results of development work on ultrasonically treated fibres for PP composites related to WPs 2 and 4, as well as considerations on their stability, recycling and extractables (WP5), are presented in sections 2.3.
- Section 2.4 refers to the characterization of SMC composites, which will be addressed in D3.4.
- Issues encountered and solutions found are presented in section 2.5.
- Conclusions are presented in Chapter 3.

2. Results

2.1 Experimental methods

2.1.1 Selection of test methods

Considerations for selecting particular test methods have been addressed in Deliverable 5.2, section 2.1.1. The experimental methods for characterisation of fibres and composites which were described in Deliverable 5.2 include:

- Fibre refining (rather a preparation method)
- Optical microscopy
- Laserscan analysis
- X-ray photoelectron spectroscopy (XPS)
- Fourier transform infrared spectroscopy (FT-IR)
- Collective fibre strength testing
- Single fibre testing
- Single fibre fragmentation tests (SFFT)
- Flexural testing
- Charpy impact testing

New analysis methods include those relevant to characterize final composite product properties as addressed in the Technical Annex 1 and also D5.2, section 2.1.1. For reason of convenience, in subsequent subsections, all methods to characterize final composite products have been described:

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

As the fibre surface analysis using SEM is new since publication of D5.2, this experimental method has been included in section 2.1.2.
Next to the Laserscan method addressed in D5.2, a different automated laser fibre diameter measurement system, called QICPIC, was evaluated (section 2.1.3).

As some of the moulded SMC composite materials showed some degree of warping, a simple method has been established to provide an indicator for warping (section 2.1.10).

2.1.2 Scanning electron microscopy (SEM)

SEM micrographs were made at room temperature by DLO-FBR using a FEI Magellan 400 scanning electron microscope (FEI, Eindhoven, NL) after covering the material surfaces with a 10 nm layer of platinum using a Jeol sputter coater. Material surfaces analysed include: 1) untreated and treated hemp and flax fibres, 2) Charpy impact fracture surfaces of injection moulded and 3) Charpy impact fracture surfaces of SMC composites.

2.1.3 Fibre diameter analysis (QICPIC)

An automatic laser fibre diameter measurement system "QICPIC" was used. It produces visual images of each fibre tested and can measure from 10µm to 30mm; a useful range for fibres with a powerful, dedicated analysis software package. Fibres can be measured dry or in a liquid. The software allows use of a size and aspect filters and can give number, volume and length presentations which all give different perspectives on the characteristics of the sample. The equipment offers complementary information to the Laserscan information (D5.2).

2.1.4 Flexural testing

The flexural properties of SMC specimens and products were determined by DLO-FBR using a Zwick universal testing machine according to ISO 178 at a support length of 64 mm (Figure 1) 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.

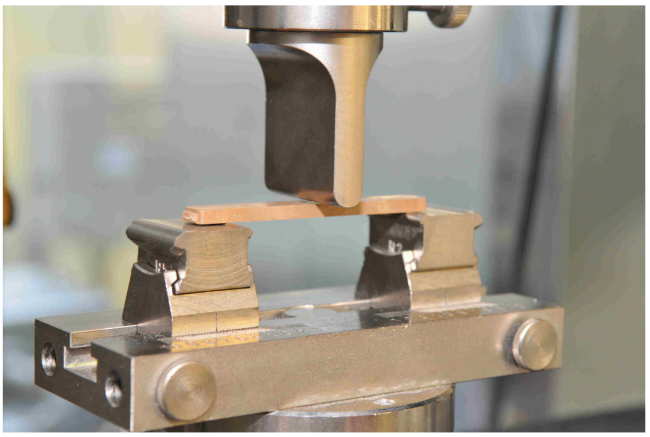

Figure 1: Flexural testing set-up.

The flexural properties of SMC composites prior and after water absorption were determined by RAPRA in general accordance with BS EN ISO 178:2003 using a Houndsfield universal testing machine. The test pieces were cut from the SMC plaques supplied by means of a high speed copy routing machine and were of

nominal dimensions 80 x 10 mm and actual thickness. The test pieces were conditioned at ambient temperature for a minimum of 88 hours prior to test and tested in the same atmosphere on a universal test machine which was calibrated to grade 1. Support span was 59 mm and test speed was 2 mm/min. The modulus was calculated from the slope of the initial part of the stress-strain curve using the software supplied with the test machine. Calculated nominally between 0.05 and 0.25% with no variation in method.

The flexural properties of injection moulded specimens were determined by CESAP using a Galdabini Sun 2500 universal testing machine according to ISO 178-1 at a support length of 64 mm and a crosshead speed of 2 mm/min for the elastic modulus. The modulus was determined from 5 specimens per batch.

2.1.5 Tensile testing

The tensile properties of SMC specimens and products were determined by RAPRA in general accordance with BS EN ISO 527-2:1996 using a Houndsfield universal testing machine. Type 1B Dumbbells of nominal width of 10 mm and actual thickness were cut from the plaques supplied by means of a high speed copy routing machine. The dumbbells were conditioned at ambient temperature for a minimum of 88 hours prior to test and tested in the same atmosphere. Standard wedge action jaws were used on the universal test machine, which was calibrated to grade 1, and a Video Extensometer was used to measure the change in length of the initial 50 mm gauge length. Grip-to-grip separation was 115 ±1 mm, test speed was 10 mm/min. The tensile strength and elongation at break were determined from 5 specimens per batch.

The tensile properties of injection moulded specimens were determined by CESAP on Galdabini Sun 2500 universal testing machine according to ISO 527-1-2 at a grip length of 120 mm, an extensometer length of 50 mm, (Figure 2) and a crosshead speed of 5 mm/min for the strength and elongation at break. The tensile properties were determined from 5 specimens per batch.

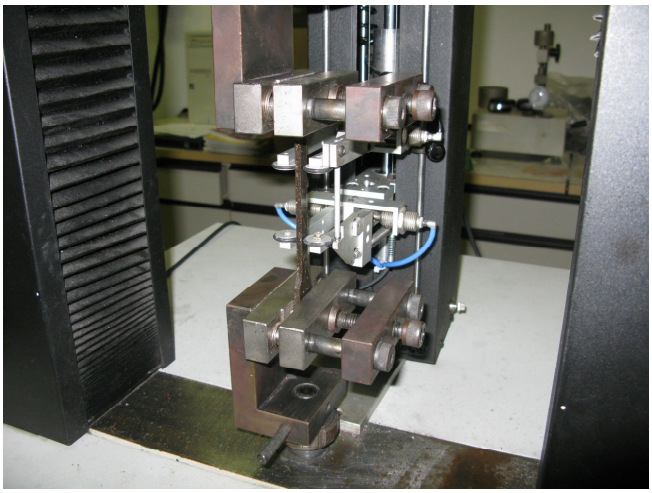

Figure 2: Tensile testing set-up.

2.1.6 Charpy Impact testing

The Charpy unnotched impact strength of SMC specimens and products was determined by DLO-FBR 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 3). The Charpy impact strength was determined from 10 specimens per composition.

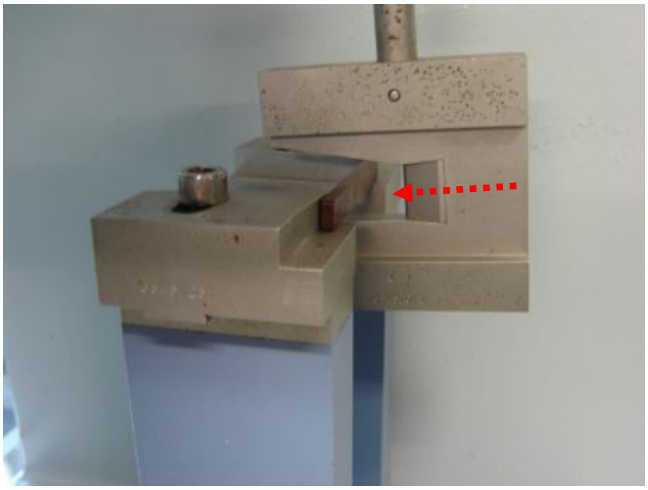

Figure 3: Charpy impact hammer blowing (red arrow) standard injection moulded composite test specimen.

The Charpy notched impact strength of injection moulded specimens was determined by CESAP using a CEAST 6545 pendulum impact tester according to ISO 179/1eA using an impact hammer of 2.0 J at a speed of 2.9 m/s. The Charpy impact strength was determined from 10 specimens per composition.

2.1.7 Heat distortion temperature (HDT)

Heat Deflection Temperature of SMC specimens and products was determined according to ISO 75-1,2 using a Ray-Ran HDT-Vicat softening point apparatus (Ray-Ran Test Equipment Ltd, UK). Specimens were positioned flatwise and stress applied was 1.8 MPa (Figure 4). The heating rate was 2 °C/min. HDT temperature was taken as the temperature at which the strain at the surface of the test specimen was 0.1%, which corresponds to a deflection of 0.19mm at the used support length of 64mm.

SMC specimen thickness varied in the range 3.34 – 3.85 mm. The deflection corresponding to 0.1% strain herewith varied from 0.18 – 0.20 mm. Due to this small variation, 0.19 mm deflection was taken for all tests. The required force to achieve a stress of 1.8 MPa varied in the range 2.05 – 3.16 N. In order to apply stress accurately, samples were individually loaded at 1 g (0.01N) accuracy.

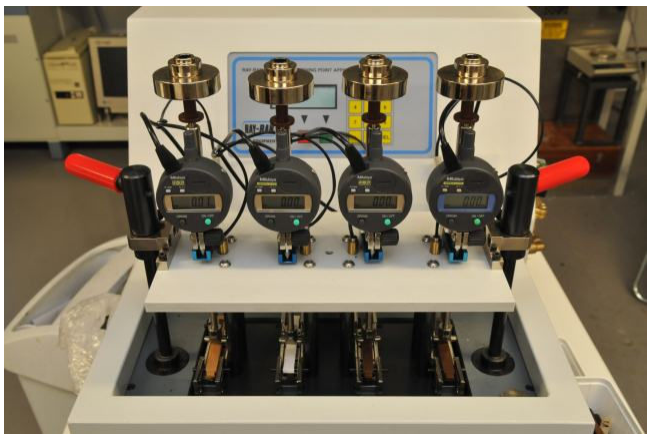

Figure 4: HDT testing equipment.

Heat Deflection Temperature of injection moulded specimens was determined by CESAP according to ISO 75-1-2 using a CEAST 6520 Vicat-HDT equipment. Specimens (127x12.7x3.2 mm) were positioned edgewise and stress applied was 1.8 MPa. The heating rate was 2 °C/min. HDT temperature was taken as the temperature at which the deflection of the specimen was of 0.2%, which is 0.26 mm at the used support length of 101 mm.

2.1.8 Flame resistance

UL 94 flammability test of injection moulded specimens was determined by CESAP using a CEAST flammability chamber. A composite specimen (127x12.7 mm, 1.6 mm of thickness) is positioned vertically. A layer of cotton fibre is placed under the specimen at 300 mm distance (Figure 5). A flame of 20 mm height is applied by a methane fuelled Bunsen which is positioned at a slope of 45° under the specimen (Figure 5) and placed on a slide such that the flame can be easily moved to and from the specimen. The flame is applied for 10 s, and as soon as the flame on the specimen extinguishes, a second flame

application is carried out for another 10 s. After that, the flame of the Bunsen is pushed away from the specimen, flame propagation time is determined. The test is conducted on 5 specimens conditioned 48 h at 23°C and on 5 specimens conditioned 168 h at 70°C.
The classifications V0 and V1 are obtained if, after each application of the flame, the specimen ceases to burn within 10 s or 30 s, respectively. Classification is V2 if during application of the flame, glowing material burns the cotton layer below the specimen; NC (not classifiable) if the specimen burns completely after that the flame is pushed away.

Figure 5: Flame test set up: Positioning of specimen (left), application of flame (right).

2.1.9 Water absorption

Prior to ageing, samples were coated on the edges only, with a resin supplied by the client. Samples were aged in de-ionised water at ambient temperature for periods of 0, 2, 4, 6 and 8 weeks.

2.1.10 Warping of SMC composites

SMC plaque were put on a table and pushed to the table at one end. The distance between the table and the test plaque at the other end was quantified using an electronic calliper (Figure 6). Warping is defined as the ratio of this distance and the length of the composite.

Figure 6: Quantification of warping of SMC composites.

2.2 Characterisation of fibres (WP2, WP3)

The goal of WP2 is to produce natural bast fibres with:

- A reduced fibre diameter to allow for improved extrusion compounding and compound properties
- A cleaner fibre surface to achieve better bonding with polymer matrices.

To explore the range of possibilities of the QICPIC analysis equipment, chopped flax fibre was analysed and the results clearly identified the 2, 4 & 6 mm fibre batches show in Figure 7. Images of some of the individual fibres are shown in figures 8 - 13. Firstly as a group, then an enlarged view of one from each group. The images clearly show some fibrillation which appears to increase the shorter the fibres are chopped. This will be investigated further. Figure 14 shows the fibre diameter as approximately 28 µm. The equipment offers complementary information to the Laserscan information used earlier therefore trials will now be undertaken with processed fibres.

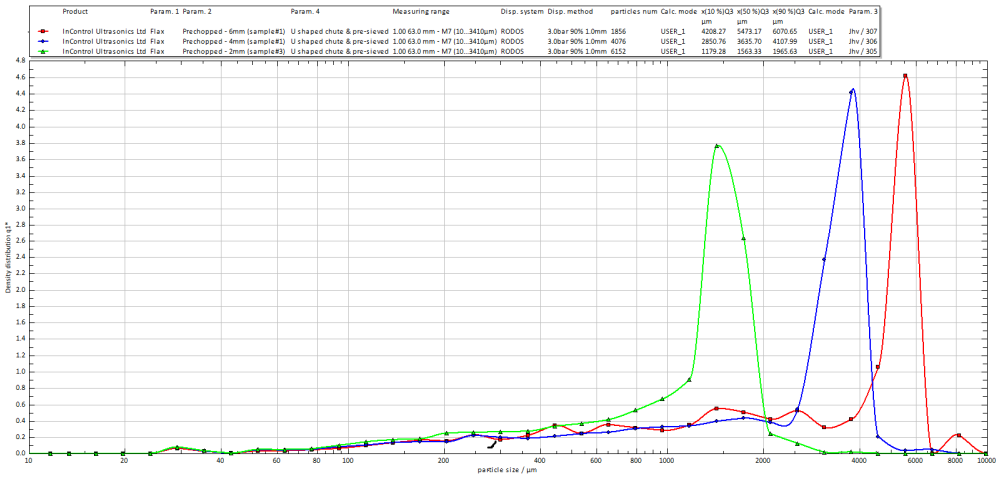

Figure 7: 2, 4 and 6 mm Chopped flax fibre length

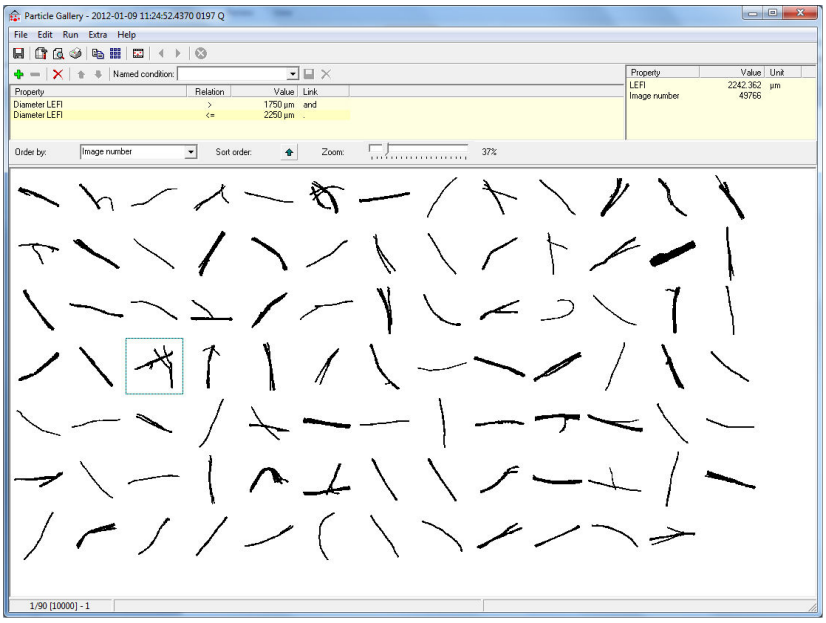

Figure 8: Images of 2 mm chopped flax fibres.

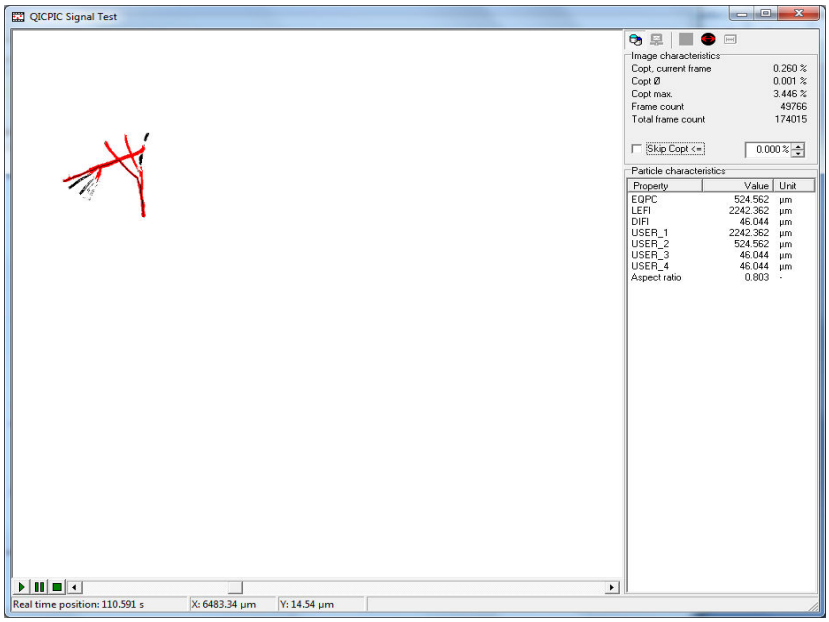

Figure 9: Enlarged image boxed in Figure 7.

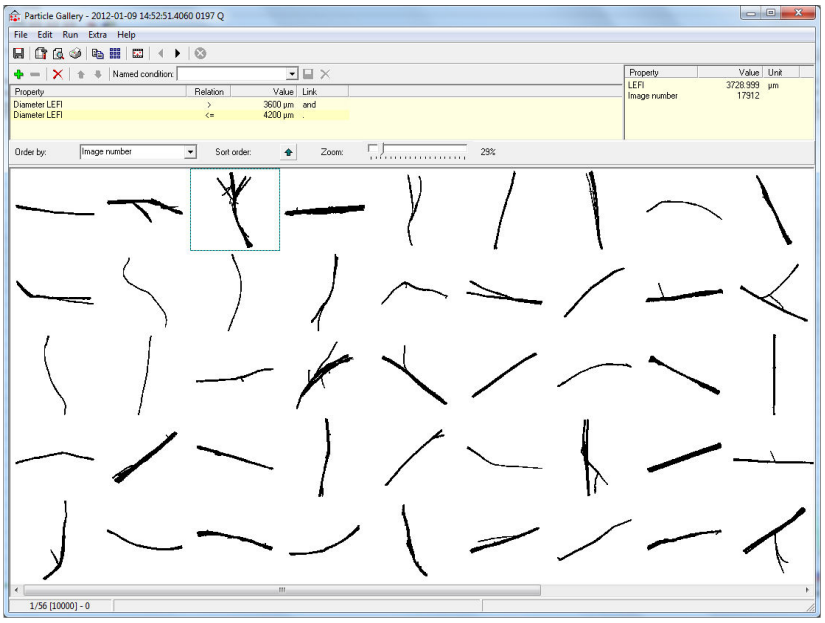

Figure 10: Images of 4 mm chopped flax fibre.

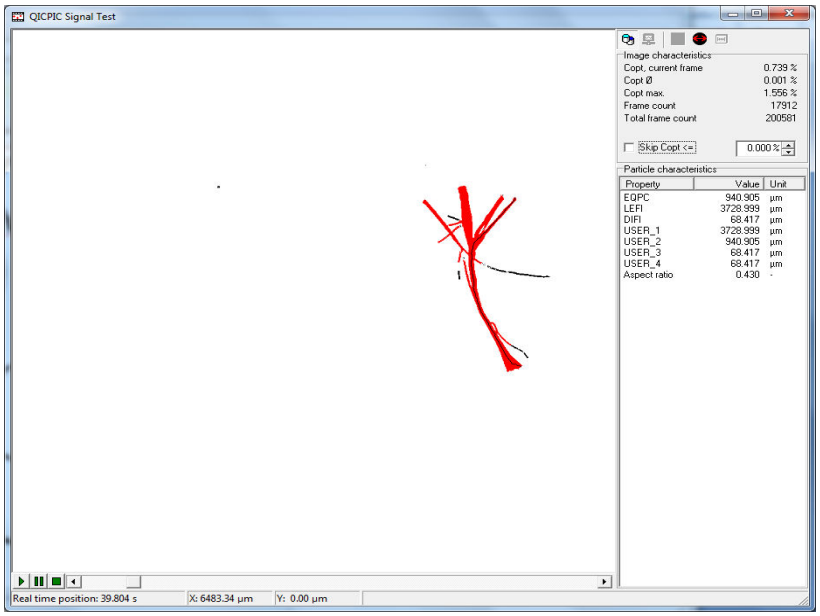

Figure 11: Enlarged image boxed in Figure 9.

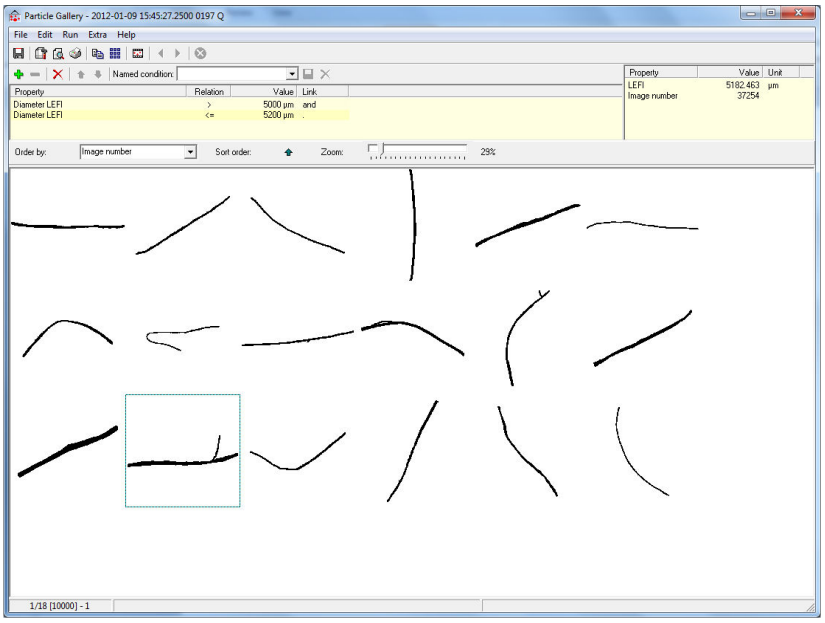

Figure 12: Images of 6 mm chopped flax fibre.

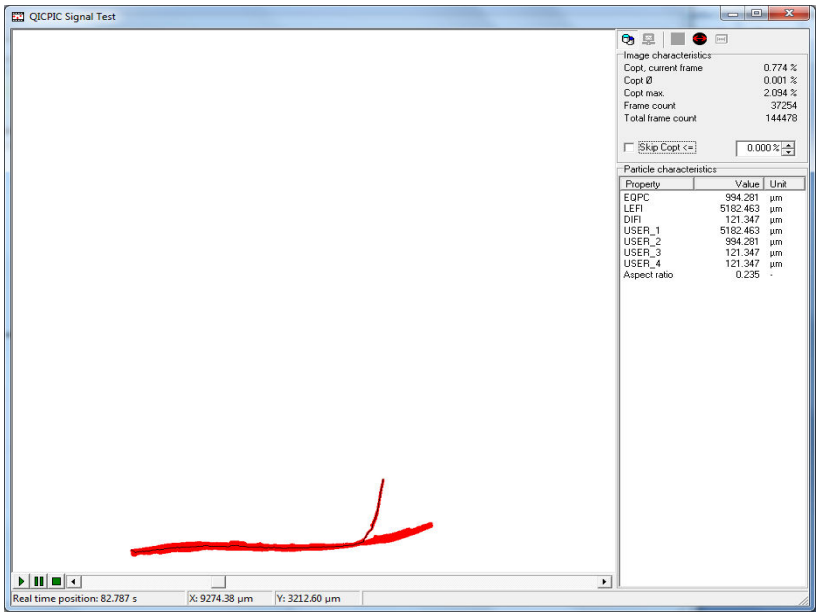

Figure 13: Enlarged image boxed in Figure 11.

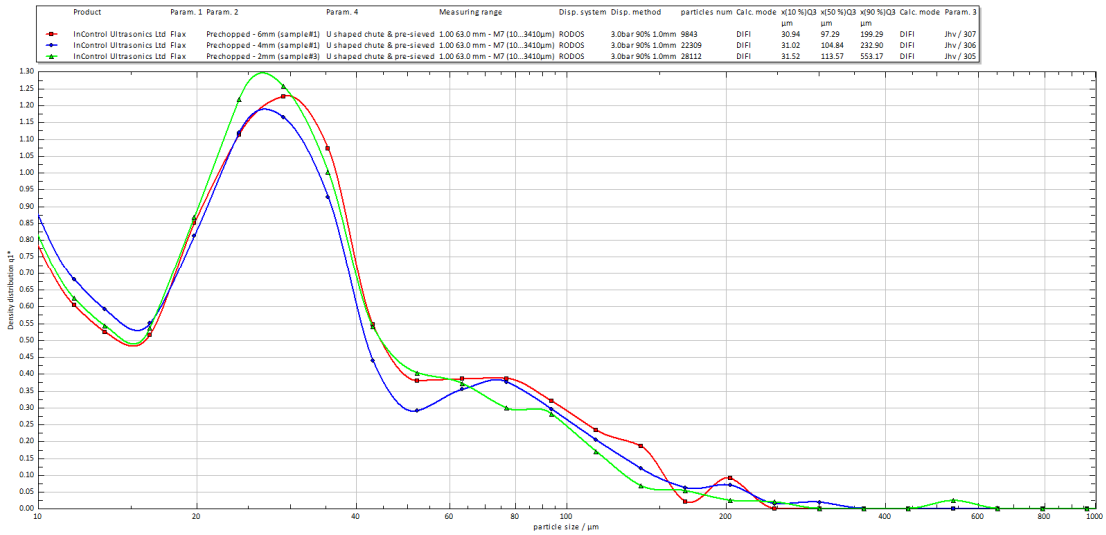

Figure 14: Diameter of chopped 2, 4 and 6 mm flax fibre.

Further results on fibre analysis will be addressed in D7.1.

2.3 Characterisation of PP Composites (WP2, WP4)

The goal of the project is to produce natural bast fibres with a refined diameter and lower variation in strength properties as compared to conventionally decorticated fibres using ultrasonic treatment.

Composites based on untreated not refined and refined & ultrasonically treated flax and hemp fibres were prepared by RAPRA. Composites were injection moulded by DLO-FBR and analysed for flexural and Charpy impact strength. For flax, flexural strength has improved by 14% from 62MPa for untreated unrefined flax to 70MPa for refined flax treated with 0.3% NaOH and 1% Lipsol and 300s sonication (Figure 15, Table 1); this procedure being the optimum condition investigated. The same treatment shows an optimum in both the flexural modulus (Figure 17) and Charpy impact strength which shows a 33% improvement (Figure 19).

For hemp, largest improvement is observed for Shirley refining, showing an increase from 58 to 65 MPa (Figure 16, Table 2). Treatment of refined hemp with NaOH (0.3%)/lipsol (1%)/EDTA (18mM) and no sonication shows a rise of 4 MPa; this treatment was also optimum for the flexural modulus (Figure 18) and Charpy impact strength (Figure 20), increase of impact strength, however, is low.

It may be concluded that within this series, both chemical pretreatment and ultrasonics have a slightly positive effect on composite flexural strength. The effect of pretreatment on variation in properties is ambiguous, for the flax fibre composite series variation tends to increase, for hemp variation in composite

performance tends to decrease. Best score achieved is a 60% reduction in variation in composite flexural strength, however, this may be an artifact.

Table 1: Mechanical properties of Flax-PP/MAPP composites: Effect of chemical and ultrasonic pretreatment.

	-	Water US	Lipsol US	0.3% NaOH US	3% NaOH US	0.3% NaOH-Lipsol US
Flex Strength (Mpa)	61.6	62.1	66.2	68.2	65.2	70
Std Dev.	0.2	1	1	0.8	1.3	0.6
Flex Modulus (Mpa)	3148	3076	3280	3308	3267	3391
Std Dev.	10	145	53	62	58	102
Charpy Impact (kJ/m2)	16.9	17.4	19.6	21.2	17.5	22.5
Std Dev.	1.0	0.9	1.7	1.6	1.3	2.0

Table 2: Mechanical properties of Hemp-PP/MAPP composites: Effect of chemical and ultrasonic pretreatment.

	-	Shirley	0.3% NaOH	0.3% NaOH-Lipsol US	0.3% NaOH-Lipsol-EDTA	0.3% NaOH-Lipsol-EDTA US
Flex Strength (Mpa)	57.7	64.5	63.3	65.1	69.4	67.7
Std Dev.	0.9	0.5	1.7	0.6	0.5	0.2
Flex Modulus (Mpa)	2811	3192	3114	3187	3282	3310
Std Dev.	86	21	110	69	60	69
Charpy Impact (kJ/m2)	15.4	15.1	15.9	16.6	18.2	17.7
Std Dev.	1.4	1.3	1.6	0.6	2.0	1.2

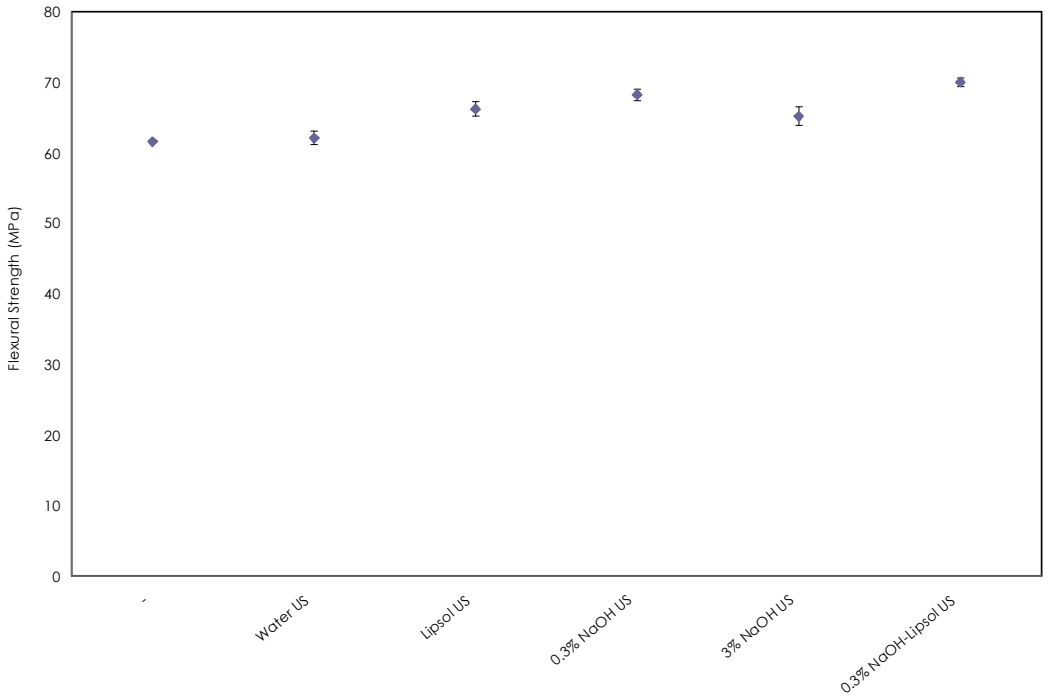

Figure 15: Flexural strength of Flax-PP/MAPP.

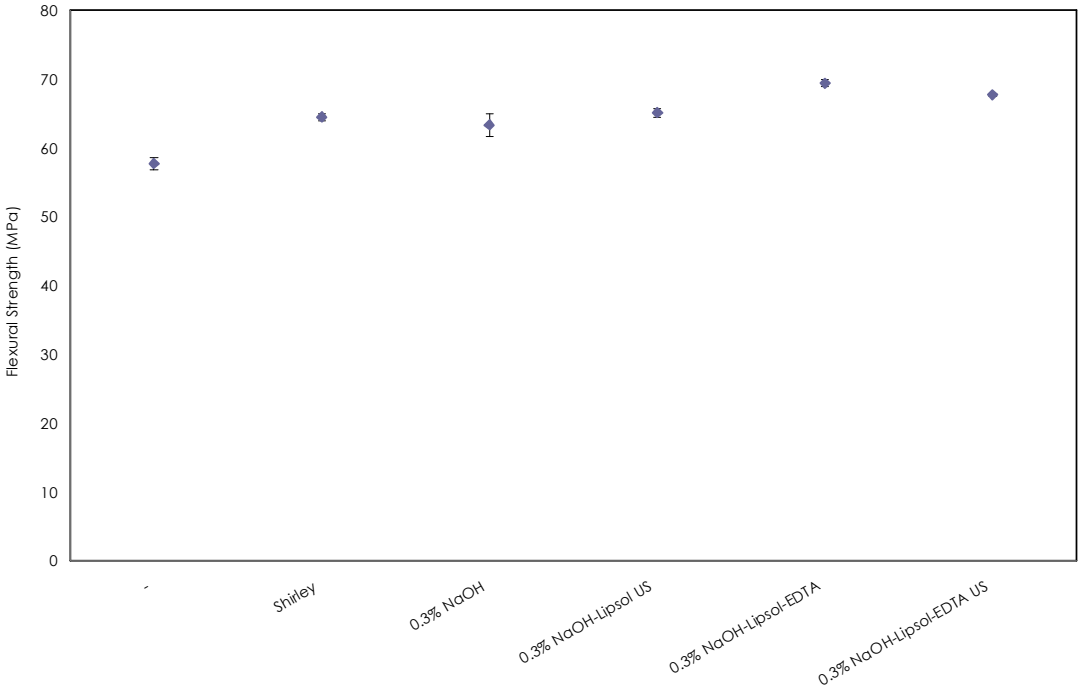

Figure 16: Flexural strength of Hemp-PP/MAPP.

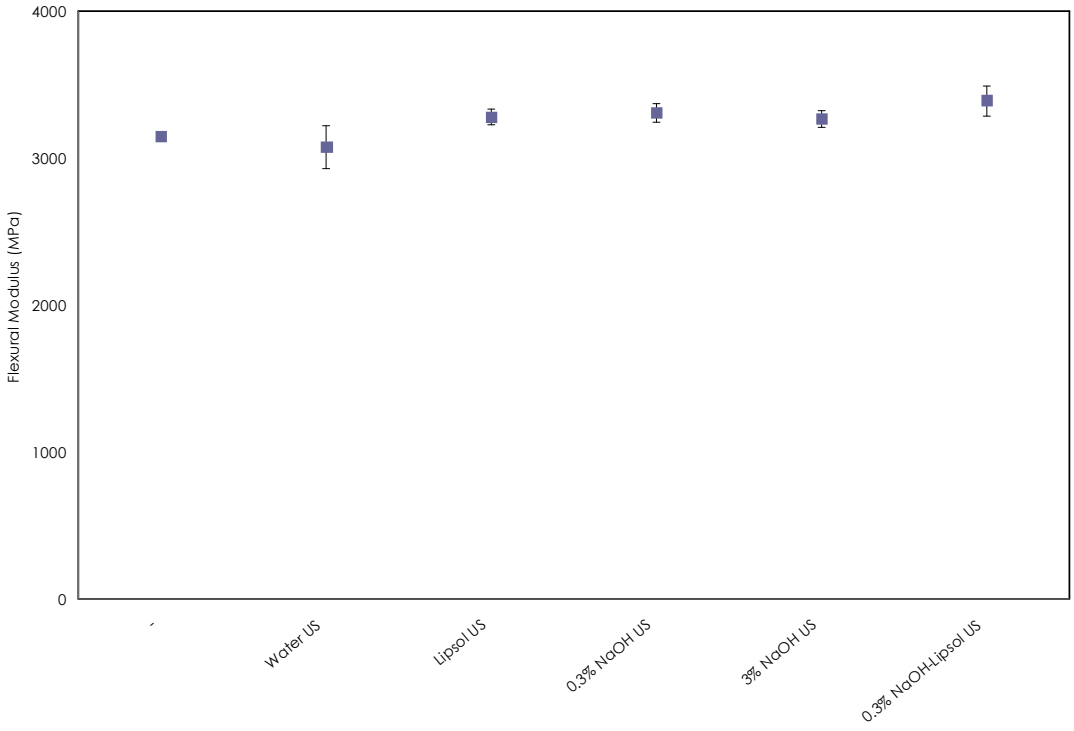

Figure 17: Flexural modulus of Flax-PP/MAPP.

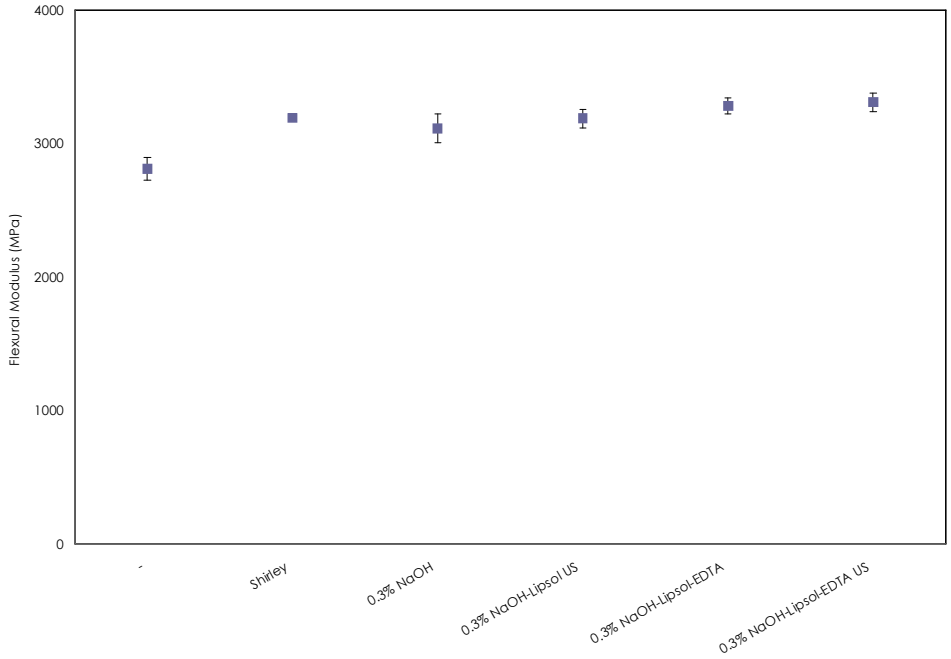

Figure 18: Flexural modulus of Hemp-PP/MAPP.

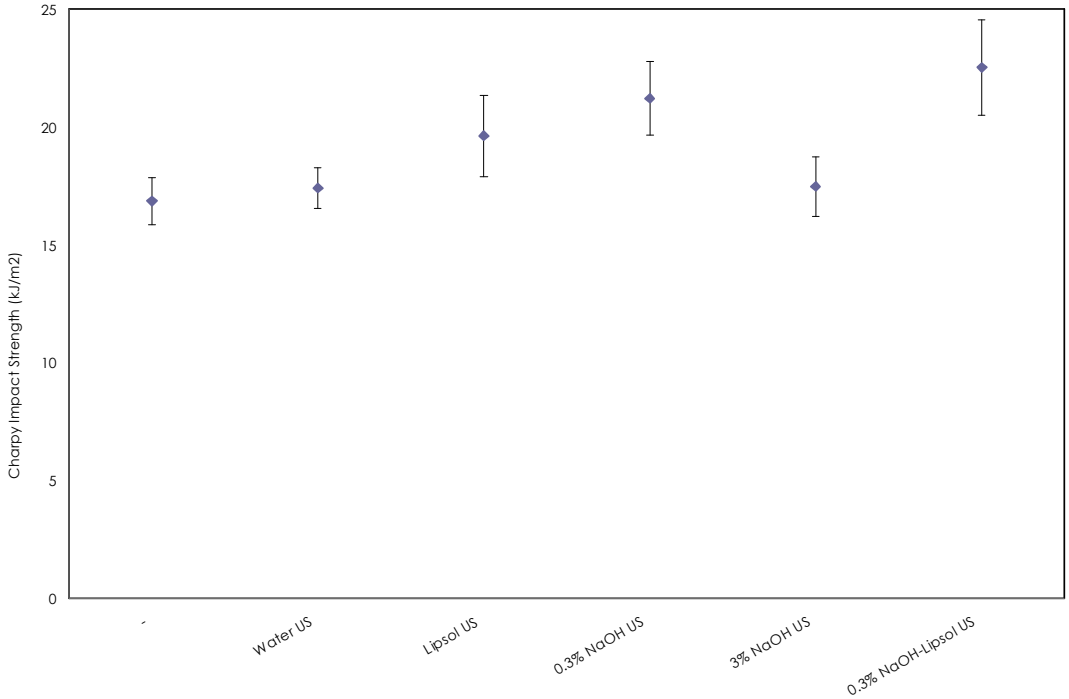

Figure 19: Charpy impact strength of Flax-PP/MAPP.

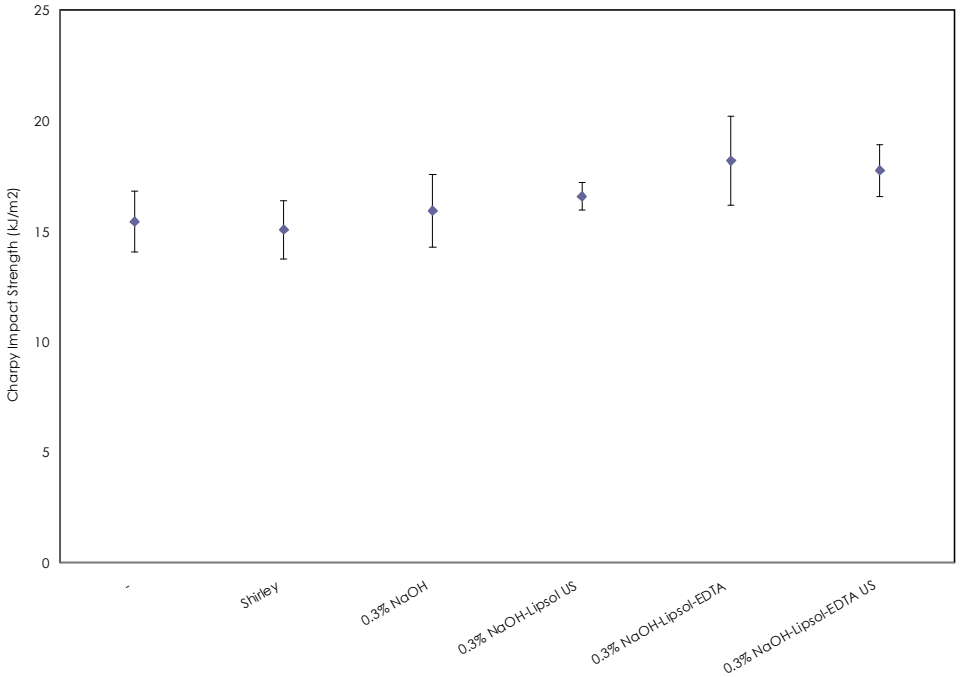

Figure 20: Charpy impact strength of Hemp-PP/MAPP.

Stability and recyclability

For stability and recyclability no standard tests are known and actually GreenGran have never received a questions related to this issue. Natural fibre thermoplastic composites can be recycled like all other thermoplastic compounds. Mechanical recycling studies show that degradation during a number of mechanical recycling cycles is limited, although impact strength was not addressed [1]. Selling argument for natural fibre composites is thermal recycling advantage compared to glass fibre composites. In addition, in contrast to glass fibre composites, mechanical recycling does not wear the barrel of the moulding device.

Extractable and leaching agents

Extractables are not expected at dry conditions (RH < 95%). If natural fibre composites will be applied in water, reduction in properties (D3.4) will be larger issue than extractables which are of vegetal origin and biodegradable.

[1] A. Arbelaiz, B. Fernández, J.A. Ramos, A. Retegi, R. Llano-Ponte, I. Mondragon. Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling. Composites Science and Technology 65 (10), 2005, 1582–1592.

2.4 Characterisation of SMC Composites (WP3, WP6)

The goal of the project is to produce natural fibres with a modified surface using an atmospheric plasma treatment which exhibit improved adhesion to polymer matrices conferring a 25% increase in mechanical properties compared with untreated fibres.

In reports D3.3 and D5.2 it was shown that plasma treatment of flax and hemp fibres resulted in an increase in flexural strength of up to 23-24% for PP and PLA composites. In the present reporting period, the effect of plasma on natural fibre reinforced unsaturated polyester (UP) composites has been addressed. Composite manufacturing technology selected is sheet moulding compound (SMC).

Procedures to make SMC composites and related results will be presented in D3.4.

2.5 Issues & solutions

This Deliverable 5.3 report is suggested to include the test results of composite products from Work Packages 4, 6 and 7. The due date of this D5.3 report is Month 33, however, which is prior to the ending dates of WPs 6 and 7: Month 35. Therefore, it was proposed (and accepted) to postpone the due date for D5.3 to M35.

In order to make Deliverable reports most clear and simple by directly relating the presentation and discussion of test results to the experimental development and scaling up work in one and the same report, it was decided to report WP5 activities as follows:

- D5.3: Description of analytical methods used by DLO-FBR, RAPRA, InControl, CESAP. Now due in M35.
- Analysis results in same report as experimental development work and/or scaling up work, that is in: D3.4, D4.3, D6.1, D7.1.

3. Conclusions

In order to present the results of the project as clear as possible, it was decided to present and discuss the test results directly related to the experimental development and scaling up work in one and the same report: Deliverable reports D3.4 (Plasma treated hemp fibre based unsaturated polyester SMC composites), D4.3 (Ultrasonically treated hemp fibre based extrusion compounds) and D6.1 (Scaling up of ultrasonics and plasma).

Below, conclusions are reported on testing activities which are not addressed in aforementioned Deliverable reports and which were obtained since the previous Deliverable 5.2 report.

- Both chemical pretreatment and ultrasonics have a slightly positive effect on composite flexural strength, within the series performed. The effect of pretreatment on variation in properties is ambiguous: 1) for the flax fibre composite series variation tends to increase, 2) for hemp fibre variation in composite performance tends to decrease after chemical and ultrasonic treatment. Best score achieved is a 60% reduction in variation in composite flexural strength, however, this may be an artifact.
- No issues with stability and recyclability of natural fibre reinforced thermoplastics are expected based on 1) scientific literature and 2) absence of questions from industry related to these subjects.
- No issue with extractables are expected at dry conditions (RH < 95%). At wet conditions (under water applications), extractables are of vegetal origin and will biodegrade.
- Analysis results related to unsaturated polyester (UP) composites will be presented in D3.4.
- Further analysis results related to ultrasonically treated fibres and polypropylene (PP) extrusion compounds will be presented in D4.3 and D6.1.

3.1 Further work

Results of analysis work on fibres, composites and products will be presented and discussed in Deliverable reports 3.4, 4.3 and 6.1.