UltraFibre

Overview of technology, results and commercial benefits

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SEVENTH FRAMEWORK PROGRAMME

UltraFibre

- Overview of technology, results and commercial benefits

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Introduction

This book is intended to give the reader an overview of the technologies developed during the EC funded project called "UltraFibre", in particular to provide:

- An introduction to the different techniques (Ultrasonics and atmospheric plasma treatments)
- Results and technical benefits
- Options for scale-up and financial costing
- Summary of Life Cycle Assessment (LCA)
- Case studies

1.1 Background

Fibre reinforced polymers find wide commercial application in the aerospace, leisure, automotive, construction and sporting industries. **Figure 1.1** shows the natural fibre reinforced polymer products for Mercedes.

***Figure 1.1**: Examples of natural fibre composites used in automotive applications*

In recent years there has been much interest in developing natural fibre reinforced polymers for a sustainable substitution of synthetic materials and also to develop markets for the non-food crop industry sector. The major impediment to growth facing the European natural fibre sector is the high processing costs needed to produce the fibres themselves. While natural fibres can be used for a wide variety of applications, other fibres are considerably more cost-effective. The growth in the agro-materials / energy crop sector is causing competition for land with food production and this is driving up the costs of both food and non-food crop products. There is an urgent need for more sympathetic integration of food and non-food production; this can be partially achieved through improved process efficiency and productivity. Natural fibre crops cannot be easily separated into fibres of consistent quality. Therefore, to commercially exploit past research investment on the world market and for Europe to reap the sustainability benefits that will result from expansion of the non-food crop sector, new research was required to reduce processing costs and to improve fibre quality, consistency, and efficiency.

The fibre composites industry is running into difficulties of supply at the moment. The worldwide shortage of carbon fibre has been well documented and is a result of a number of factors, including increased demand from China and India. The shortage is driving up the price of fibres, which is hitting manufacturing industries, already under pressure from the emerging world economies. As a result, a project to investigate and encourage the use of natural fibres in composites was extremely timely. Research and development into the application of natural fibres in composites is fragmented, meaning that each fibre research group is attempting individually to address the problem. However, the R&D issues are more fundamental and in the “pre-competitive domain”. Typical generic technical problems are fibre-polymer bonding, fibre treatment, thermal behaviour, production problems, *etc.*.. Sequential and fragmented R&D has inevitably led to inefficient allocation of limited funds and duplicated R&D work. To solve the problems facing the natural fibre sector, input is needed from agro-science, biochemistry, polymer science, chemical engineering, mechanical engineering, production engineering, product design, marketing and management. Thus, a collaborative European wide approach was needed to make a step change in the industrial production of natural fibres. In order for European industry to survive against competition from low-wage economies, it has to innovate and become more knowledge-based.

1.2 The UltraFibre project

In order to address the challenges outlined in the previous section, a group of trade associations formed a consortium of research and industrial partners to investigate ways to reduce processing costs and to improve fibre quality and consistency. Funding was successfully sort from the European Commission and on 1st January 2010 the project named “UltraFibre” began.

The aim of the UltraFibre was to develop industrially scalable processes to enable natural fibre growers to process their products into consistent, high quality fibres suitable for supply into the composite materials processors and end-user markets.

Two main techniques were investigated during the UltraFibre project:

1) Ultrasonics (see **chapter 2**)

2) Atmospheric Plasma treatments (see **chapter 3**)

1.3 Project objectives

Deliver a scalable, economic, continuous, clean- Ultrasonic technology to provide tonnage quantities of high quality fibre, conferring:

- A greater percentage of cleaner and refined elemental fibres, thus improving the quality of bast fibre for the reinforcement of polymer products
- A 25% reduction in production costs

Integration of an Atmospheric Plasma fibre treatment process conferring:

- A 25% increase in mechanical properties compared with the untreated fibre
- Commercial thermoplastic and thermosetting composites in targeted end-user applications

1.4 Project overview

The three-year project (UltraFibre) was part-funded by the European Commission under the Seventh Framework Programme and aimed to undertake research to reduce the costs associated with the processing of natural fibres, whilst improving fibre quality, consistency and efficiency. More than €1.7 million of direct financial assistance was provided by the European Commission throughout the duration of the project.

UltraFibre aimed to assist European natural fibre SMEs in reducing their costs, increasing the yield and quality of natural fibre production, thus improving the state of the art for natural fibre composite materials within the EU. The UltraFibre project aimed to realise these goals by developing an ultrasonic and atmospheric plasma treatment systems for improved adhesion between polymeric materials and the natural fibres.

The UltraFibre consortium is comprised of Trade Associations, Small/Medium size enterprises (SMEs) and research partners (RTDs):

Trade associations:

- ASSOCOMAPLAST (Italy)
- European Industrial Hemp Association (Germany)
- British Plastics Federation (UK)

SMEs:

- AcXys Technologies SA (France)
- Movevirgo Limited (UK)
- ICMA (Italy)
- CESAP (Italy)

RTDs:

- Smithers Rapra (UK),
- GreenGran BV (Netherlands)
- InControl Ultrasonics Ltd (UK)
- Wageningen UR – Food and Biobased Research (Netherlands)

1.5 Technical and commercial benefits

The UltraFibre technology resulted in:

- High quality elementary natural fibres
- Atmospheric Plasma treated fibres with improved adhesive properties compared with the untreated fibres
- Yielding higher quality commercial thermoplastic and thermosetting composites
- Bio-composites with improved mechanical properties for new high-tech applications

Figure 1.2: *From field to product*

The results of the project enable:

- Natural fibre growers to process their products into consistent, high quality fibres suitable for the supply into the composite materials processors and end user markets
- The promotion of the economic prosperity of natural fibre cultivators
- The promotion of the cooperation between material suppliers, converters, farmers, research centres and end users of the plastic products
- Increased competitiveness of European industry
- The improvement of skill levels throughout the supply chain

1.6 Book overview

The following chapters provide an overview of the technologies investigated during the project, key results / benefits, options for scale-up, lifecycle assessment and case studies:

- Chapter 2 – Ultrasonic treatment
- Chapter 3 – Plasma treatment
- Chapter 4 – Natural fibre polymer processing
- Chapter 5 – Life Cycle Assessment and case studies
- Chapter 6 – Contact details and useful references

2

Ultrasonics Applied to Fibre Processing

2.1 Introduction to the technique

2.1.1 Understanding basic high power ultrasonics

High power ultrasonics is mechanical energy transmitted by resonant horns. High power ultrasonic equipment comprises a power generator, which transmits a high voltage, high frequency (20 kHz) current to a piezoelectric transducer. The resonant transducer converts the electrical signal to a mechanical vibration. The mechanical vibration is transmitted to the work piece by one or more resonant horns screwed together to form a single resonant transducer/horn stack (or stack). Typical power levels range from 0.5 kW to 6 kW.

The elements are transducer, flanged booster, interstage and end horn (or probe or cell). Each element is resonant at the chosen operating frequency usually 20 kHz, as is the complete stack. The horns are metallic, typically a titanium alloy (Ti64). The resonance enables energy to be stored in the horns and to transfer energy between elements and the work piece or load.

The primary application of such equipment is for welding or 'flowing' thermoplastics. The vibrational energy causes melting by friction heating; if the material is brittle it can be pulverised or ground into a powder. Horns sharpened to a knife edge give enhanced slitting or cutting. A typical set up would comprise a stack held vertically in a pneumatic press to apply a downwards compressive force on two halves of a component to be welded, it will have a joint designed to dissipate energy, the plastic melts, flows, joins and then cools under load. Pressure and time are the two main variable control parameters.

Essentially high power ultrasonics is mechanical vibrational energy transmitted by resonant low loss metal alloy horns.

2.1.2 Elements of high power ultrasonic equipment

2.1.2.1 Generator

The generator supplies electrical energy to the transducer stack and contains an automatic phase lock loop to deliver the power at the stack frequency. **Figure 2.1** shows three 3 kW/20 kHz generators in a panel.

2.1.2.2 Transducer stack

The transducer stack is the complete resonant head comprising a transducer, flanged booster, interstage, and horn. **Figure 2.2** shows a complete stack for fluidsonics, ultrasonics applied to flluids and fluid processing.

2.1.2.3 Transducer

Transducers are resonant half wave units that contain eight piezoelectric ceramic discs clamped between end masses of various metals. The piezoelectric ceramics are polarised, so that they expand and contract in an alternating electric field of typically 1000 V. Thus, they transform the electrical energy to mechanical vibrational energy. They are 90% to 95% efficient, but still a 6 kW unit requires cooling to remove the 600 W of energy lost as heat when operating at full power. **Figure 2.3** shows a transducer without a cover. The eight ceramic discs can clearly be seen with their associated connection wires.

2.1.2.4 Booster horn with integral flange

The flanged booster is a horn with a nodal, isolated non-vibrating central annulus growing out of the nodal ring from the one piece metal cylinder. It is drilled and tapped with a screw thread at both ends and fits between the transducer and the horn (or interstage). It may be a non-magnifying horn or may add gain to the system (**Figure 2.5)**.

Figure 2.1*: Generator cabinet*

Figure 2.2*: Complete 3 kW transducer stack*

Figure 2.3*: Transducer without cover*

Figure 2.4 shows three standard flanged boosters with gains of x1, x1.5 and x2. This factor amplifies the tip amplitude. The flange is used to support the stack and to apply force to the load via the output tip.

***Figure 2.4**: Three boosters*

2.1.2.5 Interstage horn

An interstage horn is primarily used to extend the length of the stack so that the tip, which dissipates the ultrasonic energy can be further away from the supporting flange. Gain can also be introduced as required. It can be any multiple of half wavelengths. Little energy is lost from these horn elements, only 1% or 2%. **Figure 2.5** shows various types of extension horn.

***Figure 2.5**: Interstage horns*

2.1.2.6 Horn

The horn is the essential key to every ultrasonic system as it transfers the vibrational energy to the load or workpiece. It is a one piece, metal half wavelength vibrating device. A good analogy is the tuning fork (see **Figure 2.6**). The vibration is a compressive standing wave. As a resonant unit it stores energy much like a laser cavity. **Figure 2.7** shows the schematic of a simple magnifying single half wavelength horn with a gain of x3. The ends are antinodes - which are low stress points with maximum extension, and the centre is the node - the maximum stress point with zero extension. The optimum step position for the two diameters - the ratio of the masses either side of the node gives the gain factor. For simple cylinders this is the ratio of the diameters squared. Energy is transmitted from the working tip which is profiled for most welding applications. **Figure 2.8** shows various complex and single horns.

Figure 2.6*: Tuning fork*

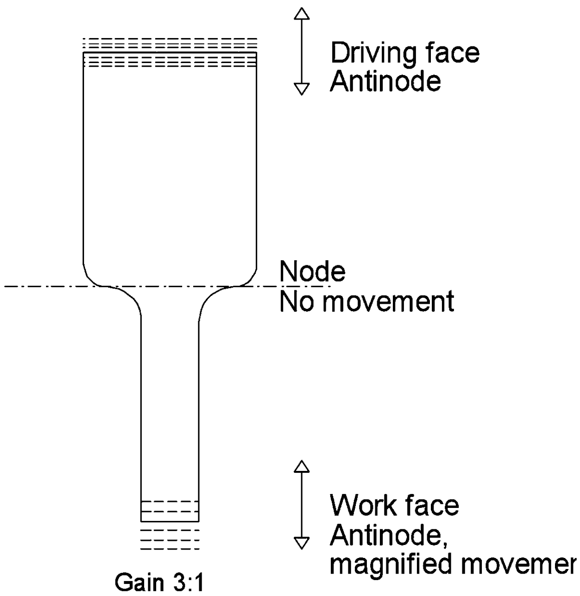

Figure 2.7*: Schematic of a horn*

Figure 2.8*: Complex and simple horns*

2.1.2.7 Studs

Socket grub screws are used to screw each half wavelength resonator or horn tightly together to form the resonant stack. The mechanical vibration must be transferred over each joint. The studs can be seen half inserted in the horns in **Figures 2.5 and 2.8**.

2.1.2.8 Press and jig for welding plastics

The most common application of ultrasonics is for welding thermoplastics. The stack is attached to a pneumatic press, the two components to be welded are placed in a jig in the press and the head is lowered on to the component at a set pressure and the ultrasonics switched on. The plastic melts at the joint, the pressure is held while the plastic cools and solidifies. **Figure 2.9** shows typical press setups including a fluidsonics setup.

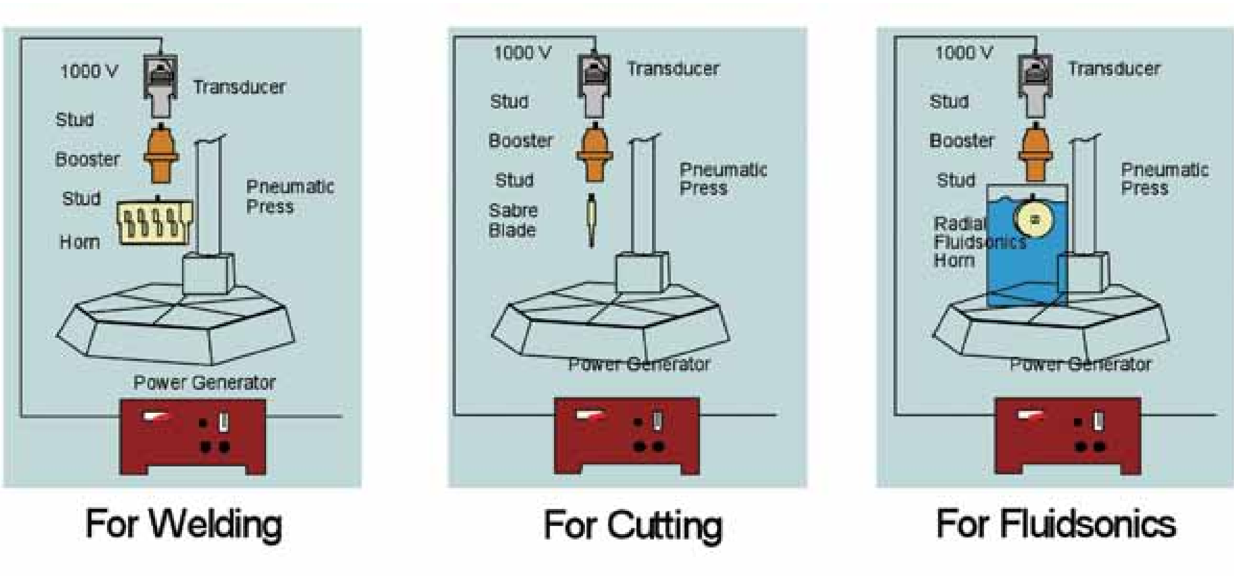

***Figure 2.9**: Press systems*

2.1.3 Operational parameters applied to solids

Operational parameters for a high power welding system are discussed next. Power is delivered on demand from the stack by loading the horn tip via the press pneumatics. The tip motion or amplitude is set by the gain of each element of the stack, with the transducer usually being set at 20 µm peak to peak; with horn and booster gains of 1.5 and 2 typical amplitudes would be 60 µm with a weld time of one to two seconds.

To optimise the energy transfer the tip is profiled to match the component surface, after which the horn is tuned by metal removal to tune to the operational frequency which is usually 20 kHz, just above the level of human hearing. The main commercially used resonant frequency is 20 kHz, as a frequency lower than this requires excessive sound adsorption to deaden the airborne noise level.

Ultrasound is defined as a mechanical vibration above 20 kHz. Power ultrasound is practically limited to about 40 kHz. Low energy ultrasonic scanners operate at 5-10 MHz. Design of the component and the material type is very importance for weld quality.

For energy transfer to the plastic material the system and the load must be impedance matched, much as a radio amplifier and speaker system, or in a car using the correct gear to enable the engine to deliver power. The matching in an ultrasonic system is to select the correct tip amplitude.

2.1.4 Ultrasonics applied to water and fluids

Applying ultrasonics to water opens up a range of new phenomena and effects. Ultrasonics applied to fluids, mainly water for high power, high volume, processing is based on the welding equipment and uses virtually the same shaped bar and block horns. The main change is that the pressure applied is now the hydrodynamic force on the stack applied by the water on the working tip face. The full working face area is a major factor in dissipating energy. Horn amplitude remains a major factor. For the bar horn, the sides also vibrate with reducing amplitude towards the node so that more energy is delivered the deeper the horn is immersed in the fluid. Fully immersed both top and bottom faces deliver energy to the water or the fluid giving the maximum energy available from that horn and amplitude. Fluid density alters the loading and the loading also changes as the density varies with temperature. The temperature must be monitored as must the atmospheric pressure, or applied pressure if a pumped or pressurised system is used.

2.1.5 Effect of Ultrasonics on water and fluids

2.1.5.1 Atomisation of fluids

Water dripped on to a vibrating ultrasonic horn will atomise into fine droplets in a tight bandwidth, as a function of frequency, at horn amplitudes above a threshold level. The narrow bandwidth droplet median size is a function of frequency - at 20 kHz water droplets will be 100 µm, at 1 MHz droplet size is 1 µm. Commercially, solder powder particles are produced at 35 kHz. Droplet velocity is low giving good control.

Cavitation phenomena

The primary phenomena occurring when ultrasonics is applied to water and fluids is a powerful energy release known as cavitation. This is the energy released when unstable oscillating vapour bubbles collapse causing a shock wave and microscopic local instantaneous extreme temperatures and pressures. The power of cavitation was perhaps realised when the metal of a ship's propellers was pitted and eroded sometimes very quickly, so while propeller blade failure in ships was a problem, it was solved by a blade shape design which eliminated the unwanted cavitation, and it was recognised that cavitation might be useful in chemistry and fluid processing. The vibrating ultrasonic horn was found to be a controlled method of creating cavitation in water. **Figure 2.10** shows a schematic of the cavitation process.

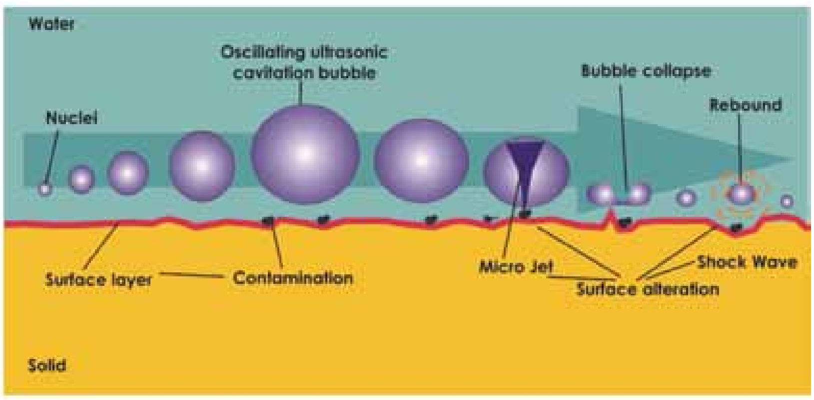

***Figure 2.10**: Cavitation process*

The first commercial applications were with a bath or vessel with external transducers glued to the outside giving a low intensity field used for cleaning. Water could be degassed and the process removed grease, machining swarf and other contaminants.

Using high amplitude probes or horns from plastic welding applications, with high power generators, high intensity fields in the fluids could be achieved. These intense fields proved useful for degassing, de-agglomeration, particle size reduction, enhancing chemical reactions, cell lesions, homogenisation and mixing. These effects also occur in hot molten metals such as aluminium.

With fluid media, unlike energy dissipation into solids where static pressure is increased to increase power drawn, it is the hydrostatic force or pressure of the fluid on the emitting tip or working face, i.e., the end face surface area of the horn and its amplitude, which are important, these are increased to increase the power delivered. As most systems are open to the atmosphere, hydrostatic pressure only changes with pump pressures or fluid density. It is easy to exceed the maximum power available from a given system; care must be taken in the final horn design.

The cavitating field is complex and difficult to measure, also many of its effects within the fluid or slurry are not well understood. The phenomena, which are useful or problematic in the Ultrafibre project are:

1) Unstable bubbles nucleate on particles and in crevices and grow under the oscillating field. When the bubbles collapse they create a shock wave and high temperatures and pressures and they can be used to perform useful effects.

2) Bubbles collapsing near a surface can form a jet through the bubble that impinges on the surface resulting in erosion and rapid movement of the material away from the surface resulting in jet streaming or mixing.

3) The working faces of the horns are eroded by these jet impacts.

4) The intensity or active region falls off rapidly with distance from the horn emitting face. which leads to the radial horn design discussed in **section 2.1.10**.

2.1.6 Batch and through feed processing

For small quantities a batch process can be used but it is difficult to expose the full vessel volume to the same field, thus, most large systems will be through feed. As it is difficult for fluid to flow around the rectangular horns, the FFR radial cell (see **Figure 2.11)** was developed to aid through feed processing. The fluid flows over an inner core area and over an outer circumference, and the devices are axially mounted in a tube so that all the fluid flows within a uniform field. The inner area is convergent, giving a uniform contained field. Each V5 processor has three to five heads separated by an optimum gap giving continuous exposure to the cavitating field. Commercially this is known as the Sonix process.

Figure 2.11*: The FFR radial cell*

2.1.7 Fluid applications

Two applications of fluidsonics that relate to the UltraFibre project are de-aggregation of titanium dioxide (TiO_2) flakes removed from gel permeation chromatography (GPC) gel beads. **Figure 2.12** shows before (top) and after (bottom) the application of ultrasonics. The second application is cell lesion in sewage sludge showing useful work done on organic material. Not quite an application but more a calibration technique, aluminium

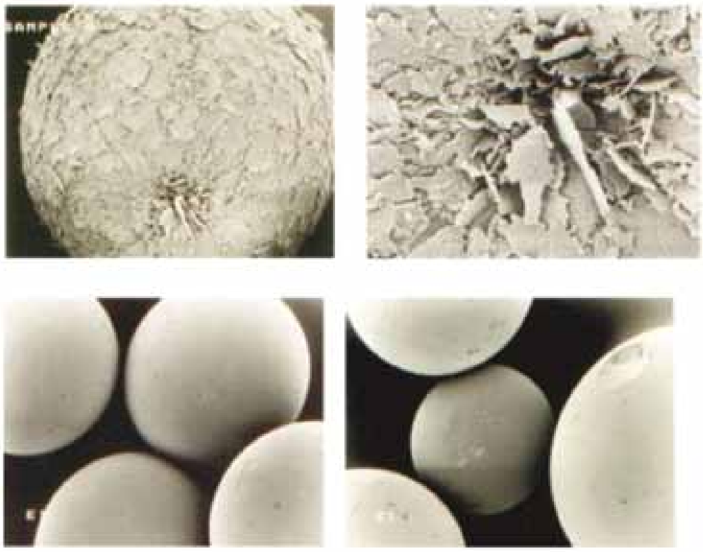

Figure 2.12: *TiO_2 flakes removed from GPC gel beads*

foil is rapidly eroded with pitting, pin holes and larger holes depending on time and intensity or distance from the emitting source.

2.1.8 Bench and scale up equipment

Assessing the previous summary for the hydro acoustic approach required for the UltraFibre project, a three module, 3 kW, 20 kHz generator system was selected for the bench top unit as a versatile power source which could be expanded into the eventual pilot plant unit. A modified V5 processor cell using the FFR radial cell with three heads was also selected. This gives a unit which using a manual feed can be used as a though feed or batch system for laboratory use for these early trials, and as a modular system it can readily be expanded.

2.1.9 Bench top fluidsonics processor Type UF3V5 for the UltraFibre project

2.1.9.1 General design

The aim of this part of the project was to design, build and supply a bench top fluidsonic (ultrasonic) laboratory unit to develop a new fibre processing treatment within the financial and time constraints of the project, and the existing knowledge base of the fibre and its working and handling needs.

To achieve the UltraFibre objectives, the bench top laboratory unit was based on the modular FFR Fluidsonics system. To deliver adequate power for the initial stages and to fully use the generator housing capability, the generator cabinet was built up for three, 3 kW generators (20 kHz). For the first stage, simple on/off controls were fitted. Power is delivered by demand from the stacks.

2.1.10 Transducer/radial cell horn

The three transducer/radial horn stacks (see **Figure 2.13)** are welded one-piece assemblies as this enables the stacks to be fully immersible units with no screw joints. Screw joints immersed in water or fluids cause resonance and running problems as water interferes with the energy transmission.

High power ultrasonics covers a wide range of applications using a great variety of equipment. The previous information attempts to cover briefly, the essentials of ultrasonic theory relevant to the UltraFibre project.

***Figure 2.13**: Transducer / radial horn stack*

2.2 Options for scale-up, outline financial costing and benefits

2.2.1 UltraFibre industrial size ultrasonic plant

The purpose of the pilot plant was to enable processed fibre in adequate volumes to be produced for the other work packages and to provide input data to envisage and design a small industrial plant, which would be fully automated to produce a competitively priced treated fibre. The design concept was to be validated and output and cost elements were to be produced.

Using the pilot plant as a starting point, the industrial scaled-up plant must be fully automated and produce a viable quantity of treated fibre in a shift of 7.5 to 8 hours. Each European country has its own variation of crops and processing needs. Therefore, as an example, one region, in the south-east of the UK, has been chosen as it houses one of the latest state-of-the-art Van Dommele plants manufactured in Belgium.

As it is unlikely that a new add-on process would attract funding as a stand-alone factory and a farm based site would be unsuitable (as UltraFibre is a post process); the obvious site is alongside a modern processing plant, leading to the concept described next.

2.2.2 Version 1 and Version 2 concepts of an industrial scale plant

Pilot plant data using the radial ultrasonics heads leads to the following outputs:

A: a small size, 70 kg a day plant, and

B: a medium size, 210 kg a day plant

The concept allows almost full utilisation of the expensive ultrasonic equipment, by moving heads in sequence to different tanks as shown in **Figure 2.14**, **Figure 2.15** and **Figure 2.16**. The plan was to build a plant alongside a 24 tonnes a day Van Dommele type plant, such as on the HempTec site in the UK (which would cost about €5m to replace). Using a small part of their output and also using their infrastructure, many costs could be sidestepped. One operator would suffice and the fibre would already be unbaled on a conveyor.

Figure 2.14 shows **Version 1** which, is a carousel/robotic concept using four tanks moved to four stations, with the three ultrasonic heads being moved by the robot in and out of the tanks as they are moved around the carousel track. This enables the second robot access to remove the treated fibres with a rotating carding like roller while the water is drained off, filtered and re-cycled, meanwhile the ultrasonic heads process the next tank full of fibre. The next portion of fibres are loaded, wetted and immersed in water in a third tank. The carousel multi-tank system enables all the operations to occur simultaneously. Robot 2 takes the fibres to a washing station (station 5), on the carding roller, then to a take-off roller which transfers the treated, washed fibres to a conveyer which takes the fibres through a drying tunnel (station 6), and on to the plasma coating unit. The fibre is then baled, and wrapped in plastic to retain the plasma coating and avoid loss or damage.

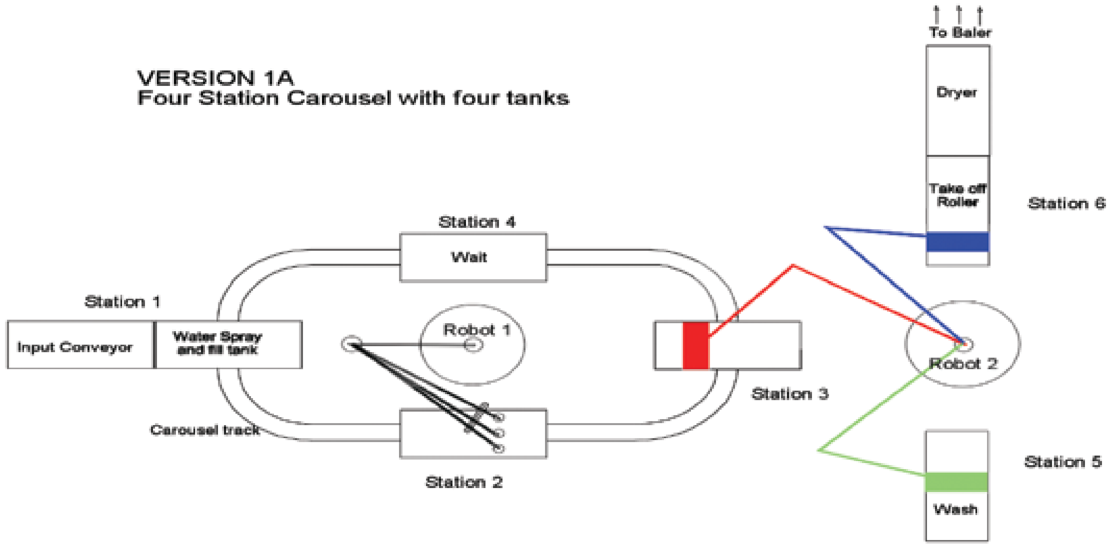

***Figure 2.14**: V1-Carousel, four tanks, two robots, wash station, carding collection roller, dryer*

Figure 2.15 shows **Version 2** of the process. As the concept was developed it became clear that it was not practical to move large tanks of water on a carousel as envisaged, at an economic capital plant cost. Re-examining the required elements at each station, Version 2 was produced using three fixed tanks and was laid out using robots with longer reach and different positions in the layout, which enabled the same process flow to be achieved. Currently the scheme appears to be the most simple and practical so it has been used for the cost estimates in **section 2.2.4**. Version 2 is also easier to scale up to the larger 10 headed higher output of a medium size plant as shown in **Figure 2.16.**

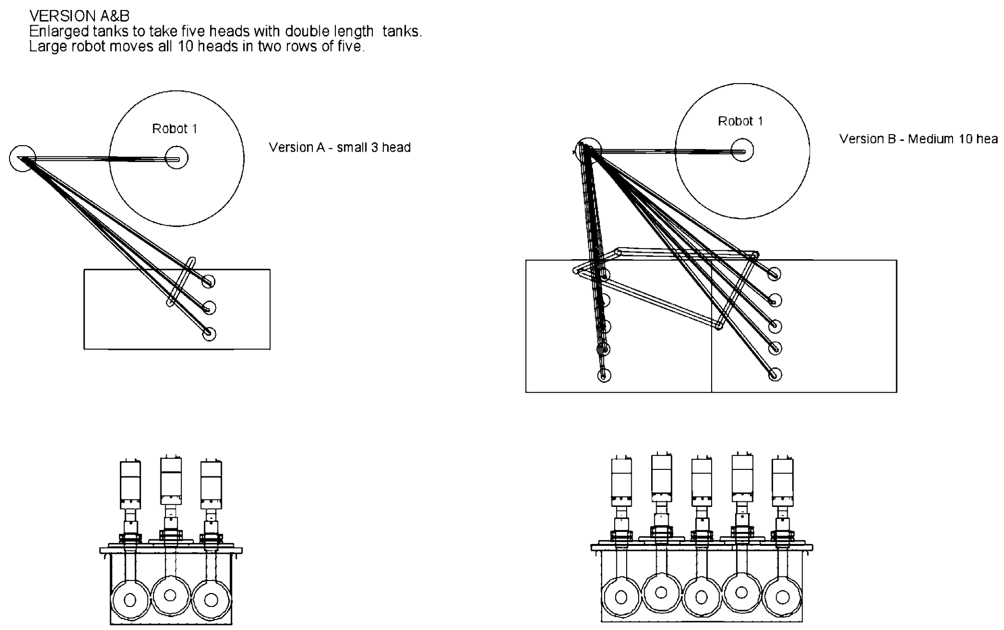

***Figure 2.15**: Heads with potential expansion to 10 heads*

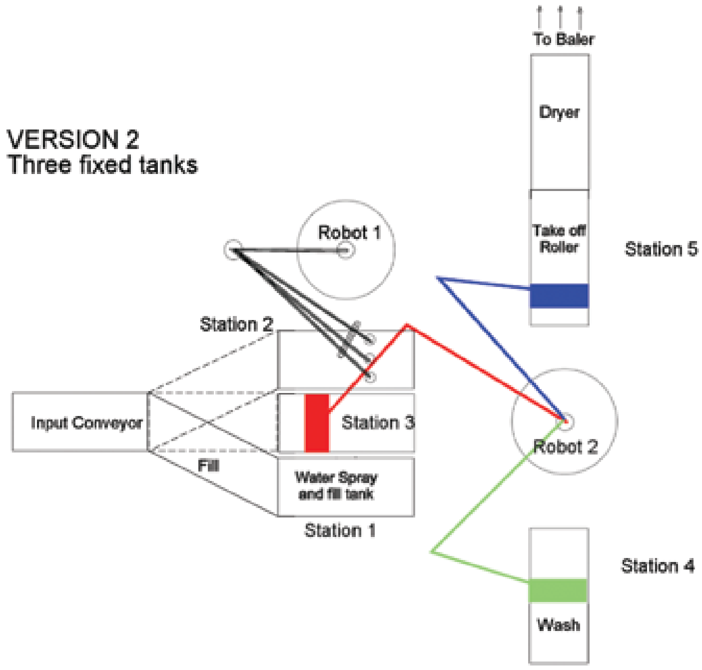

Figure 2.16*: Version 2 with three parallel tanks*

To optimise the dwell time in the processing tank, automated sizing of the fibres is used, two such systems were identified and used. The first was the Sirolan Laserscan system developed by CSIRO (Geelong, Australia) for wool fibres and recalibrated for flax and hemp. The second was the SympaTec (Clausthal-Zellerfeld, Germany) ‘Qic Pic’ laser system. This gives quick feedback to maintain the correct ultrasonic exposure for the optimum elemental fibre production.

2.2.3 The process sequence for the Version 2 industrial plant

A flow chart (see **Figure 2.17**) shows the two processing routes for fibres used in both injection moulding and sheet moulding compound (SMC). Processed straw or scutching, a mechanical beating process produces various quality fibres, shrive or woody part of the stem, dust and other waste fibre.

There are various operations and processes to get from seeds to UltraFibre. Fibres are treated as shown in **Figure 2.14**, where the main inputs and outputs are shown.

Loose fibre is transported on a conveyer from the decortication plant into the tank, and then sprayed with water to wet the fibres as the tank is filled with water. Robot 1 lowers the ultrasonic radial head array (3 or 10 heads), activates the ultrasonic energy and moves the array along the full length of the tank and then repeats this process for three minutes. The movement mixes the fibres and exposes each fibre bundle to the ultrasonic cavitation field. At the end of the cycle the radial horn array is lifted out of the tank by the robotic arm on to the second tank, which is already filled with water and wetted fibre.

The second robot, fitted with a rotating carding type drum with a pick-up wire comb surface is lowered into the tank with the water and treated fibres. The rotating pick-up drum sweeps the length of the tank for about two metres and collects all the treated fibres. The robotic arm then moves to the drying station where there is a take-off roller, which picks the fibres off the pick-up drum and transfers the fibres to the conveyer belt that leads into the hot air drying tunnel. The waste-water is pumped from the tank, filtered and re-used about 10 times and eventually disposed of via the sewage system, this cost is negligible compared to the other costs. No commercial use of the various pectins that glued the elemental fibres together has yet been identified. In total, three tanks are used to enable continuous operation of the expensive ultrasonic equipment. Dried fibres on the conveyor are then fed to the plasma unit for atmospheric plasma coating (for details see **chapter 3**). From the plasma unit the fibres are feed to a baling station.

The sweep speed from the pilot plant system has been optimised to 50 mm per second with a fibre density of 1 kg per 22 litres of water, with an exposure time of three minutes per tank load.

On balance it was concluded that using water with no added chemicals was the most environmentally friendly option and the most cost effective as a slightly long exposure time was cheaper than using and disposing of expensive chemicals. **Figures 2.17**, **2.18 and 2.19** show the essential elements of the pilot plant - the transducer/horn stack, the generator panel and the water tank or vessel. **Figure 2.20** shows the visual effect of the ultrasonic agitation on the water surface with no fibres in the tank.

As water will penetrate the stack screw joints used in the plastic welding equipment, the booster and horns are changed frequently, so a new technique of one piece and welded boosters and horns was developed for

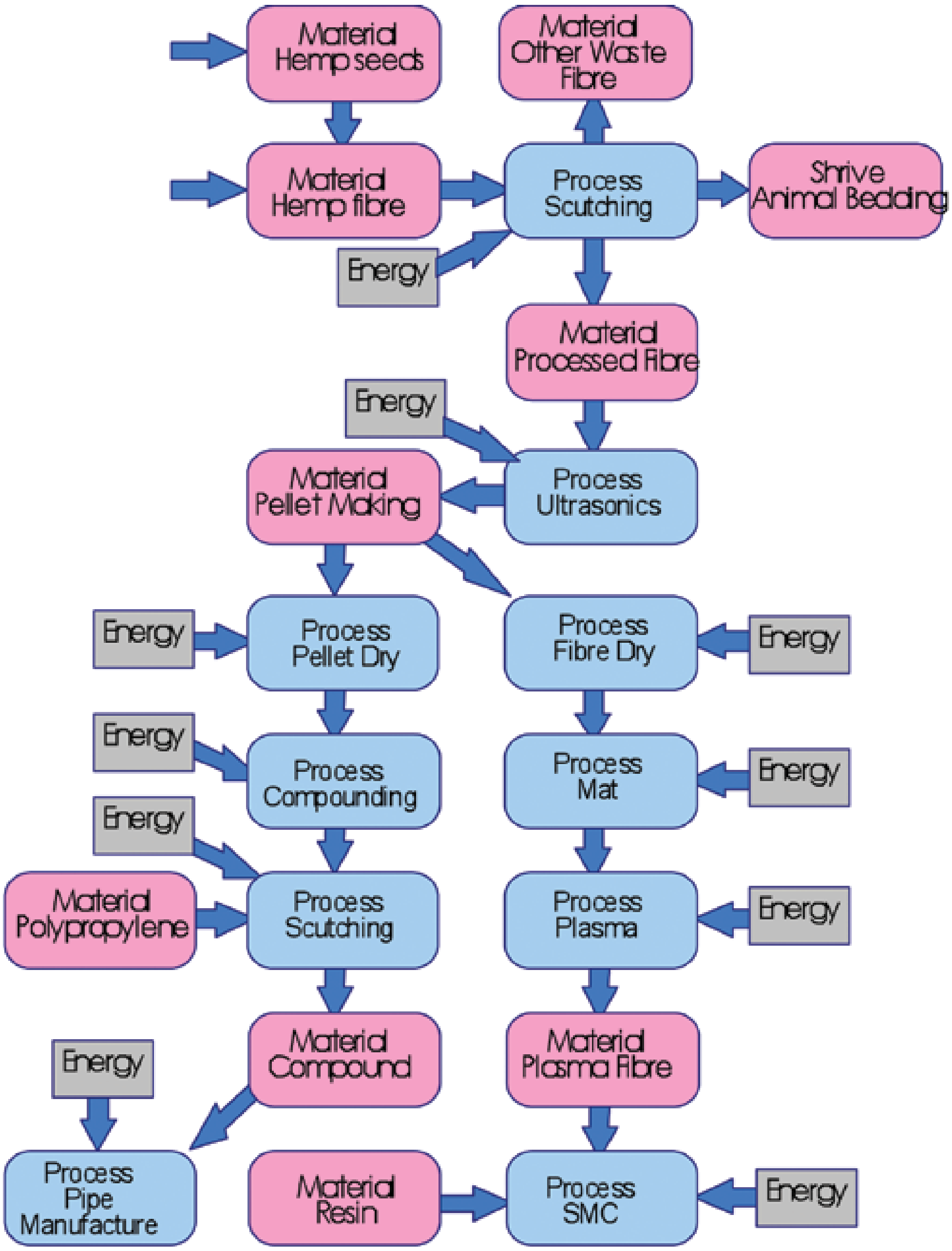

***Figure 2.17**: Schematic outline for the UltraFibre process*

Figure 2.18*: A single 6 kW fan cooled ultrasonic head comprising transducer, booster, extension and radial cell horn*

Figure 2.19*: Three ultrasonic heads in a bath.*
The cross bar moves slowly along the length of the tank and reciprocates sonicating the fibre/water mix. The oscillation stirs the fibres ensuring that all the fibres are sonicated evenly

Figure 2.20*: Agitation of water when the ultrasonics is on.*
The effect of the high power ultrasonics is clearly seen on the water surface with no fibres in the tank

the fluidsonic applications. Welding of titanium is quite difficult and the ultrasonic resonant requirement of joints only at the antinodes makes this a highly specialised application.

2.2.4 Outline financial costings and benefits

Taking the basic outputs from the Version 2 concept of the plant operation the tables given next, list the cost elements of building and running the industrial ultrasonic plant both small and medium size. Costs vary with plant size and mode of operation. Multi-shifts that keep the plant running, significantly reduce the costs of treating the fibre. Firstly the table of potential outputs of an industrial plant is calculated in **Table 2.1**. Allowances are made for starting and stopping the machinery at shift changes and down time for repairs and routine maintenance.

Table 2.1: Outputs: Conservative levels

Amount of fibre produced	Small size plant			Medium size plant		
	1 shift	2 shifts	3 shifts	1 shift	2 shifts	3 shifts
Hour (kg)	12	-	-	36		
Day (8 h) (kg)	70	140	210	210	420	630
Week (kg)	350	700	1050	1050	2100	3,150
Year (tonnes)	16.5	33	50	50	100	150

The machinery elements and costs of Version 2, including the machine builders profit element are given in **Table 2.2** for the small and medium plant sizes. These costs are then converted to cost price per kilo for one, two or three shifts in **Table 2.3**. **Table 2.4** and **Table 2.5** show the maintenance and electrical costs.

Table 2.2: Plant costs for Version 2

Main Items cost of each element. Contained in a full plant	Small-size plant. With 3 ultrasonic FFR Radial Stacks		Medium-size plant. With 10 ultrasonic FFR Radial Stacks
	Euros x1000		Euros x1000
Input conveyer	5		5
4 Tanks 22 l	10	66 l	15
Ultrasonics 4 kW x3	25	4 kW x 10	70
Spray system and water fill	10		10
Robot 1	25		25
Pump and filter system	5		5
Carousel	10		10
Robot 2	25		25
Fixed wash station	10		10
Carding roller	5		5
Take-off roller	5		5
Dryer	10		10
Profit M/c builder	29		39
Total	174		234
Finance costs (5%/5 y)	22		29
Capital Equipment	196		263
Until a full detailed plant is put out to tender prices remain best estimates.			

Table 2.3: Capital equipment – fibre processing cost variation with number of shifts

Plant size	Small	Small	Small	Medium	Medium	Medium
Number of shifts	1	2	3	1	2	3
Plant Cost € x 1000	196			263		
Capacity tonnes x 5 y	80	160	240	240	480	720
V2 plant cost per kg of fibre = €/kg	2.5	1.2	0.8	1.1	0.6	0.4

Maintenance costs are charged at 3% per year of the capital plant costs. As these costs are related to output they are valid for two and three shift working patterns.

So the costs are €0.3 per kg of fibre for the small plant with output of 16 tonnes a year, capital cost of €196,000 and €0.2 per kg for the medium plant with output of 50 tonnes a year, capital cost of €263,000.

Table 2.4: Cost of electrical components

Using electricity costs of €0.2/kW as in Chapter 3	Small plant 3 heads	Medium plant 10 heads
Item	Consumption Estimate in kWh	
Conveyor	0.5	
Robot	0.5	
Ultrasonics	6.0	20
Water pump	0.5	
Carousel	1.0	
Robot 2	0.5	
Water Pump 2	0.5	
Heater	2.0	6.0
Total	12 kWh for 12 kg, i.e., €1.0/kg 28 kWh for 36 kg, i.e., €0.3/kg	

2.2.4.1 Labour

As an add-on plant estimate using one operator at a cost of €25 k/year for 240 days/year for a 70 kg a day small plant costs €1.5/kg and for the 210 kg medium-size plant it would cost €0.5/kg.

2.2.4.2 Water and waste water

The tank takes 22 litres plus 22 litres for washing, 6 litres for spray wetting, giving 50 litres per kg of water to process the fibre.

One m^3 of water costs €1.01. This gives negligible costs of << €0.01/kg even without filtering and re-use compared to other costs. Waste water at 0.3 €/m^3 is also negligible at << €0.003/kg.

2.2.5 Summary

Putting the data from the text and **Tables 2.1, 2.2, 2.3, and 2.4** together, the range of costs of producing processed fibre is estimated in **Table 2.5** The optimum cost is €2.2/kilo in a medium-sized plant operating at capacity.

Some technical barriers to industrial scale-up for ultrasonic technology are as with many new innovations unique to ultrasonics; others are encountered in all civil engineering large-scale plant. Mostly they require government cash support especially when the process is more for environmental reasons rather than for purely economic ones.

Table 2.5: Costs of plant Version 2 A & B

	Costs of Version 2A, small three headed plant / 70 kg / day (€/kg)			Costs of Version 2B, medium 10 Headed / 210 kg / day (€/kg)		
Shifts	1	2	3	1	2	3
Three price options for the purchase of fibre	0.5 or 1.0 or 3.0			0.5 or 1.0 or 3.0		
Electricity	1.0	1.0	1.0	0.8	0.8	0.8
Water	<< 0.01	<< 0.01	<< 0.01	<< 0.01	<< 0.01	<< 0.01
Waste Water	<< 0.003	<< 0.003	<< 0.003	<< 0.003	<< 0.003	<< 0.003
Landfill	<< 0.0003	<< 0.0003	<< 0.0003	<< 0.003	<< 0.003	<< 0.003
Labour	1.5	1.5	1.5	0.5	0.5	0.5
Capital and Interest	2.5	1.2	0.8	1.1	0.6	0.4
Maintenance	0.3	0.3	0.3	0.2	0.2	0.2
12% Mark Up	0.5	0.5	0.5	0.3	0.3	0.3
Processing Totals excluding fibre cost	5.8	4.5	4.1	2.9	2.4	2.2
Totals for different fibre prices added in						
Total €/kg (0.5)	6.3	5.0	5.1	3.2	2.9	2.7
(1.0)	6.8	5.5	5.1	3.7	3.4	3.2
(3.0)	8.8	7.5	7.1	5.7	5.4	5.2

One ultrasonic scale-up problem is that the resonant horn which delivers the power to the water, which then causes the cavitation is limited in size and shape by the nature of the resonant transducers at 20 kHz, the commercial operating frequency. Also the cavitation effect, which focuses the energy into the fibre bundle to split it into elemental fibres, reduces by a square law effect with distance of the fibre from the radiating horn. Tool wear is high on the ultrasonic radial horns that transmit the energy to the water as the cavitation process erodes the horn surface material as well as cleaning and breaking down the fibres into elemental fibres, these costs are reflected in the maintenance charges.

2.2.6 General technical scale-up problems

Logistics of material supply to the processing plant tend to require the processing plant to be built local to the growing area as the fibre source is the bulky stem of the flax and hemp plants. So unprocessed bulky straw plant material has firstly to be stored at the farm for several months until it is wanted for processing and then transported to the processor. As only 25% to 30% of the plant material ends up as useable fibre, transport costs per kilo of straw are high. About 70% of the straw is shrivelled fibres and dust, which are used for animal bedding and fuel briquettes.

2.2.7 Current solutions

The industrial plant has been scaled up using multiples of the 3 to 6 kW ultrasonic system as used in the Sonix 250 kW sewage treatment plant in New Zealand, installed by Purac in 2004 which is probably the largest ultrasonic processing plant in the world. It uses the FFR radial cell horns as described here, with fluid flowing over the inner and outer emitting active surfaces. It is three times as effective as the 2 m long, 50 mm diameter bar horns used in Germany. Surface erosion of the horns causes 10 monthly replacements, which is costly, but which is added into the running costs and no doubt further R&D will reduce the wear and find ways of re-surfacing the horns which currently is not possible. A fully operating plant to run wear trials in, will greatly help such development.

2.3 Results and technical benefits

Fibre supply of flax and hemp for the project was simplified by sourcing all fibre required via Hemptec the UK's largest natural fibre processor and who operate one of the largest and most modern processing plants in Europe. It is relatively easy to ship 50 kg bales of straw and fibre by carrier to Holland and beyond. Fibre was also sourced from flax and hemp growers contracted to De Montfort University in farms local to it in Leicestershire, UK. Fibre characterisation was largely conducted by DLO in Holland. Additionally InControl used two laser based analysis techniques: one at De Montfort University, the Laserscan system and SympaTec's 'Qic Pic' system to look at fibre diameters and fibrillation after ultrasonic processing.

The graph in **Figure 2.21** with six curves shows fibre diameters before and after ultrasonic processing. R1 is the reference fibre, the other curves show the greatly increased count of elemental fibres with a 16 µm diameter after treatment.

The graph in **Figure 2.22** with three curves shows a small elemental fibre peak diameter for flax as 16 µm with large peaks showing the chopped fibre lengths of 2, 4 and 6 mm.

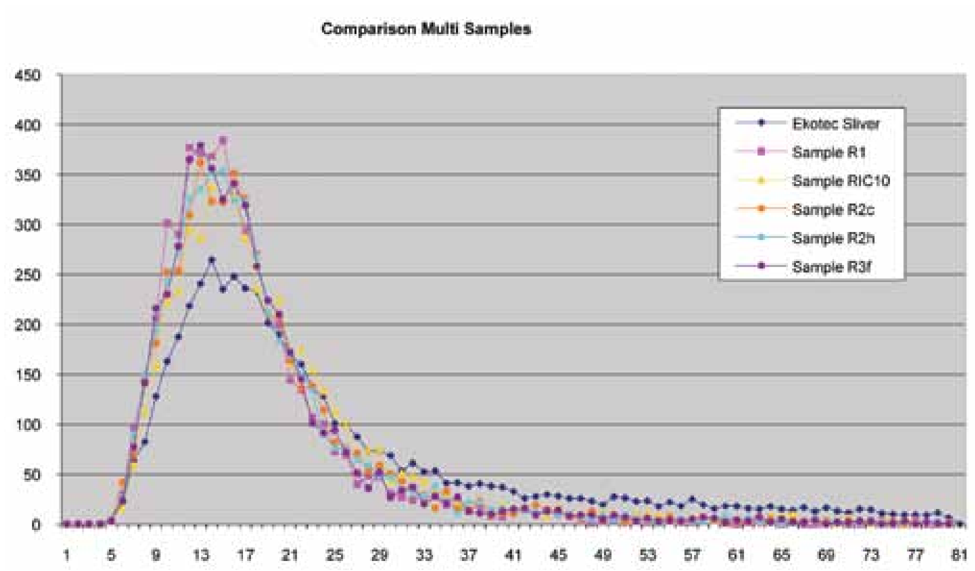

***Figure 2.21**: Treated and untreated flax fibre diameters*

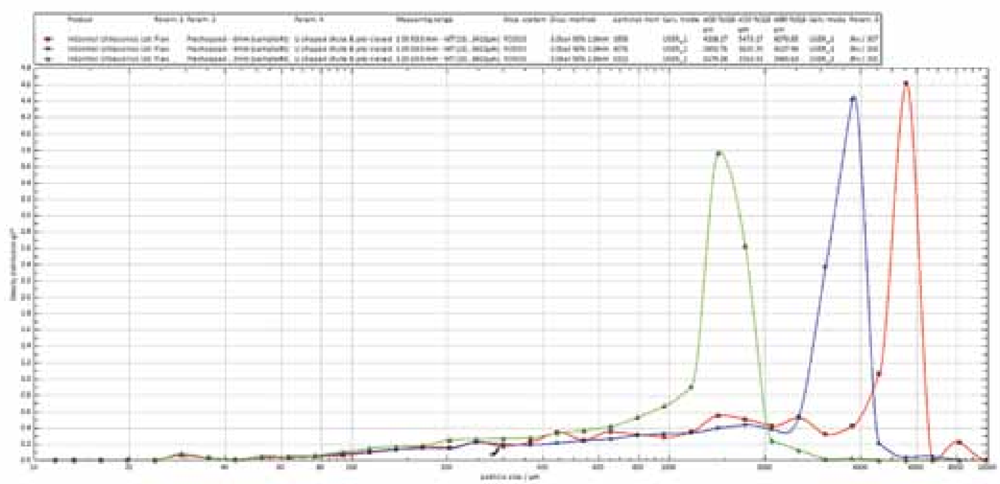

***Figure 2.22**: Fibre diameters for 2 mm (green curve), 4 mm (blue curve) and 6 mm (red curve) chopped flax fibre lengths*

The Sympatec laser system enables a fibre profile to be seen as well as calculating diameter and length as shown in the following three graphs (**Figures 2.23** to **Figure 2.25**).

Commercial barriers to building an industrial plant for a new unproven high technology process are large and can be summarised as discussed in the next sections.

Figure 2.23*: Images of 4 mm chopped flax fibre*

Figure 2.24*: Enlarged Image of the fibre in the box in Figure 2.23*

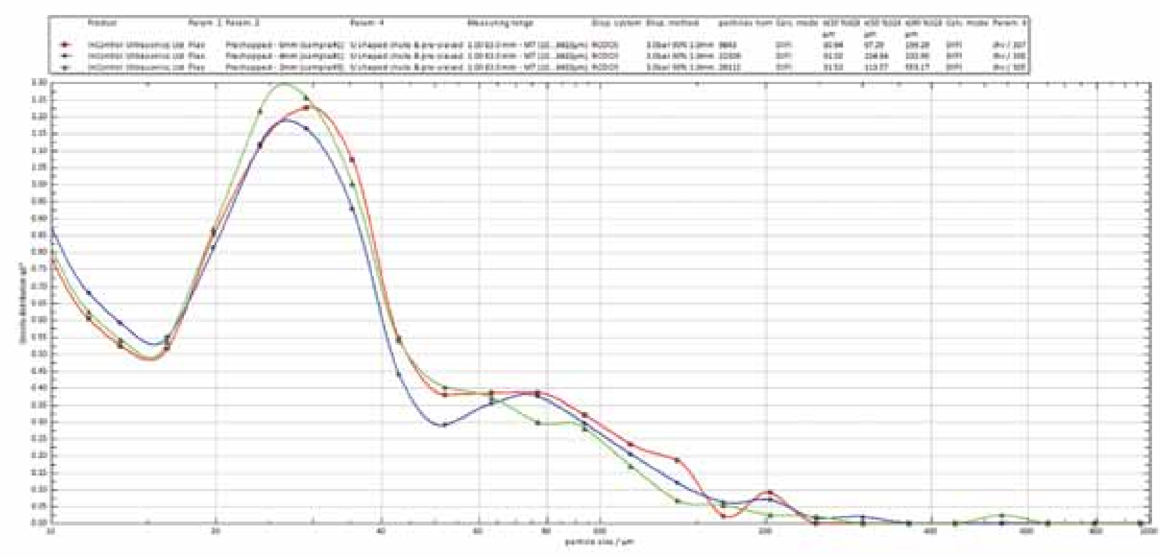

***Figure 2.25**: Diameter of 2 mm (green curve), 4 mm (blue curve) and 6 mm (red curve) chopped flax fibre lengths*

2.3.1 Capital plant expenditure

A large investment of upwards of a quarter of a million Euros is needed to build and launch the ultrasonic process, probably half a million Euros with a start-up sales subsidy. As with any new plant, the product produced while the plant output is ramped up has to be sold at a loss to be competitively priced to sell. The decline of natural fibre production since the 1930 / 1950s with the introduction of man-made fibres will put off investors, especially as the main push is largely government led environmental rather than commercially driven. Fortunately the automotive industry has seen the low density of natural fibre composites giving a weight saving in their vehicles at lower unit costs. This is economically attractive to them and many trials are under way and several interior products are in production. Such composites are also easier to recycle at end-of-life which is an added bonus. The ultrasonic and plasma treated fibres should find a useful high volume 'niche' application in the vehicle market. The fire hazard safety requirements exclude the aerospace market. The media report from 2006 onwards many R&D product developments in the automotive industry, however the gestation period to full production is usually eight to ten years - assured supply is the key to such developments. Automotive just-in-time manufacturing needs a steady flow of product. ***Composites Technology*** [1] reported in 2009 that Lotus showed at the British International Motor show its ECO Elise model with hemp reinforced composite body panels, the double curvature hardtop and the spoiler. It featured an exposed fibre stripe from front to back as a design statement. It should be in production shortly, as accurate details of production are difficult to obtain. Eco-enhancements shaved 32 kg off the 892 kg weight of the Elise a useful 3% to 4% saving which is a large amount in this industry, where savings are usually measured in grams.

2.3.2 Long-term supply of material and markets

Farmers are wary of growing natural fibre crops as the return is low compared to other crops such as oilseed rape; at the present time this is most profitable. In the UK the loss of a government subsidy in 1995 saw the volumes of flax produced decrease.

Hemp in the UK could not be grown legally as it was covered by a blanket ban on the related cannabis plant, marijuana, a class C prohibited drug. The ban was introduced in 1950/1960, which was very convenient for the man-made fibre industry giving them a significant boost, which also stopped the use of flax, which also suffered as water retting the common first processing step was banned by the EU. A special licence was issued during the 1941-1945 period as hemp was grown to replace cotton imports during World War II. In 1993 the UK government were persuaded to re-licence growing hemp in East Anglia and the following year 4,000 acres were planted with a government subsidy of £230 per acre. Hempcore received a large grant in 2004 to build a processing plant to restart the natural fibre industry in the UK.

Currently the market is limited and without a contract to sell their full crop, farmers are reluctant to plant, especially in the UK where the processor to whom they had contracted to sell their crop went into liquidation. They lost a lot of money. It has taken several years for the effect of this to wear off.

2.3.2.1 Variations across Europe

UK grows virtually no flax and hemp was totally banned because of its relationship to drugs. In Ireland flax was once a staple crop to provide fibre for the linen industry. France still grows about 7% of the world crop because the government subsidises it. China grows the most flax at 41% of the world crop, Korea grow 21% and Russia grow 9%. Russia grows a strong variety that the UK used to import for the Royal Navy to use in its cordage and ropes. No one commercialisation route will work across Europe, so this report looks only at the UK route to commercialisation: that of a government subsidised demonstrator plant to prove the process in the market.

2.4 Summary and conclusions

- Sonicating natural fibres cleans the fibre surfaces and reduces the fibre bundles to elemental fibres. This affords a greater surface area for plasma treatment and, therefore, a better adhesion to the polymer matrix is achieved.
- Atmospheric plasma was adapted for fibre use and coated fibre was made into industrial products for testing.
- An industrial scale ultrasonic plant based on the radial horn has been designed and a pilot plant was built that produced treated fibres, which were made into industrial products.
- A route to commercialisation has been identified.
- It is likely that in this current economic climate that large government or EU capital grants will be needed to enable an industrial plant to be built.

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3

Plasma

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3.1 Introduction to technique

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 do not automatically have good interaction with polymers, which is required for optimal material performance. The UltraFibre project has aimed to apply plasma treatment processing for surface modification of flax and hemp fibres in order to obtain improved compatibility and adhesion to polymer matrices. At the same time, treatment should not weaken the fibres, what is often observed after chemical modifications of natural fibres.

Atmospheric pressure plasma (APP), also called Soft Plasma, allows for high throughput processing, unlike the vacuum plasma technology. Soft plasma treatment is supposed to affect only the very surface of a material, maximum about a few nm. Consequently, the bulk of the fibres will remain unaffected and fibre strength will be retained.

In subsequent sections, the following will be addressed:

- Background to the atmospheric pressure plasma technology (**section 3.1.1**)
- Literature survey on existing methods and techniques reported for natural fibre coupling (**section 3.1.2**)
- Considerations related to plasma treatment of natural fibres for use in reinforced polymer composites (**section 3.1.3**)
- Potential fibre-matrix adhesion improvement (**section 3.1.4**)

3.1.1 Background to the atmospheric pressure plasma technology

This section presents a general background to the atmospheric pressure plasma process. The information is a modified copy from www.acxys.com.

3.1.1.1 What is Plasma?

The addition of energy into matter modifies electromagnetic forces binding atoms together. The state of matter evolves from solid to liquid, then from liquid to gas. Adding even more energy dissociates molecular bonds and may lead to ionisation (**Figure 3.1**). Gas molecules are split into charged particles, ions and free electrons. Plasma is often called “the fourth state of matter”.

3.1.1.2 Generating a Plasma

AcXys Technologies’ plasmas are produced by electrical discharge through a gas. Gas is first continuously injected in the plasma generator, then ionised and finally directed towards the surface to be treated (**Figure 3.2**).

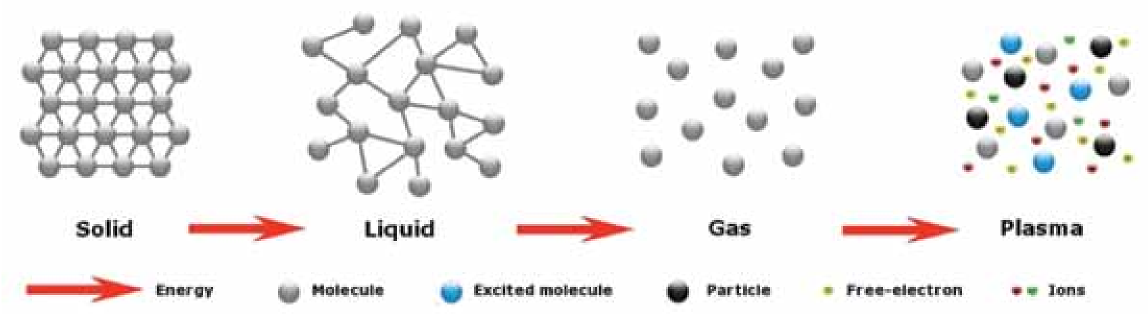

***Figure 3.1**: Positioning of plasma relative to gas*

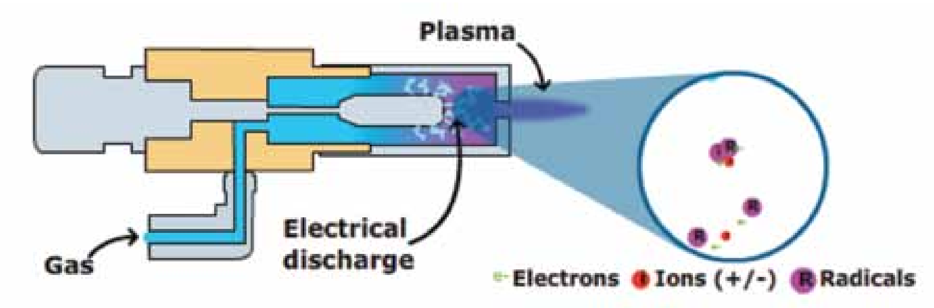

***Figure 3.2**: Schematic representation of plasma generating unit*

Controlling the electrical discharge leads to a low temperature plasma of atmospheric pressure coming out of the source. At high processing speeds, treated materials do not have enough time to increase their surface temperature. For instance, heat-sensitive polymers are treated without damage.

3.1.1.3 Effects on surfaces

Plasma is a continuous supply of highly reactive chemical species used for treating surfaces. Plasma cleans or activates surfaces. Activation is the modification of the composition of a surface, resulting in a change of its surface energy. Surface wettability is drastically increased by grafting polar functions. Consequently, it promotes a stronger adhesion for paint, ink, glue or varnish.

3.1.1.4 Atmospheric pressure plasma systems

APP technology is available in 2 systems: a nozzle type plasma source providing spot like treatment, called ULS system, and a slit type plasma source providing curtain like treatment, called ULD system (**Figure 3.3**).

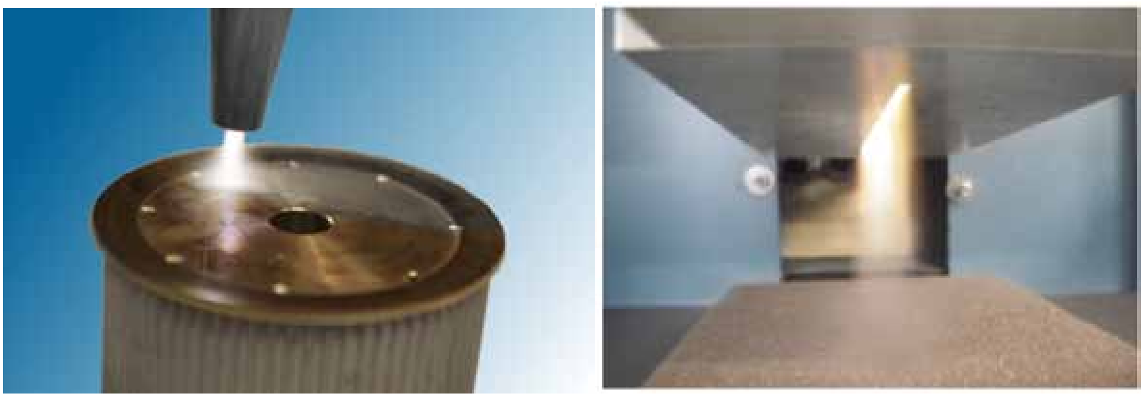

***Figure 3.3**: APP systems: nozzle type plasma source, also called ULS (left), slit type plasma source, also called ULD (right)*

Next, a summary of advantages and limitations of the basic APP technologies available at AcXys is presented:

ULD advantages:

- Large treatment area per unit, seems more suitable for treatment of natural fibres than ULS
- The method operates in 'post-discharge' plasma, which means that rather surface modification than in depth modification of a material is obtained
- Re-use of feed gas possible, up to about factor 4

ULD limitations:

- Lower energy intensity than with ULS, however energy level supposed to be sufficient
- Not known what will be the effective penetration depth through the fibre layer to be treated
- The re-use of feed gas may cause pollution of the plasma unit by small fibre particles
- Plasma flow speed is about 2 m/s, which is much smaller than for ULS

ULS advantages:

- Higher energy intensity than with ULD (not certain whether this is required)
- Higher potential processing speed expected than with ULD (may be of interest for treatment of fibre roving)
- Like for ULD, also the ULS method operates in 'post-discharge' plasma, which means that rather surface modification than in depth modification is obtained

ULS limitations:

- Small treatment area per unit
- Not known what will be the effective penetration depth through the fibre layer to be treated
- No re-use of feed gas
- Plasma flow speed is about 30 m/s, which is very high and may pose a problem for keeping the fibres in place

For reference: Vacuum plasma treatment is a batch process, with low production rates because of time required to apply and release vacuum, and with lower specific energy input levels than with atmospheric plasma treatment.

3.1.2 Literature survey on techniques for natural fibre coupling

To avoid repetition of work, and in order to obtain a benchmark for the development of the APP technology for improved natural fibre-matrix adhesion, Wageningen UR–FBR has performed a literature survey. The project has focussed on thermoplastics (polypropylene, PP, polylactic acid, PLA, polyhydroxy alkanoates, PHA) and thermoset (unsaturated polyester, UP and furan resin) matrices. For the thermoplastics, extrusion compounds and composites based on processing techniques which do not affect fibre structure are addressed separately (see **section 3.1.3**). The patent literature on plasma treatment of natural fibres has been reviewed in order to obtain an indication of the patentability of plasma treatment development for natural fibre-polymer matrix composites.

The results can be summarised as follows:

- *Extrusion compounds based on PP*: Maleic anhydride-grafted polypropylene (MAPP) can increase flexural strength of natural fibre-PP extrusion compounds up to 100% and tensile strength up to 60%. To date, MAPP is the best commercial solution to improve natural fibre-PP adhesion. The stiffness (modulus) of extrusion compounds hardly increases with the use of MAPP

- *Extrusion compounds based on PLA*: A few attempts have been made to improve natural fibre-PLA adhesion in extrusion compounds. Non-renewable methylene diphenyl di-isocyanate (MDI) exhibits the best results, an increase of Elastic (E)-modulus by 20% and tensile strength by 10%. The strength increase however is small compared to the strength of pure PLA

- *Composites based on unsaturated polyester (UP)*: The largest improvement in natural fibre-UP adhesion has been achieved with a UP polymer with a 'more' polar nature, flexural strength and stiffness of unidirectional (UD) kenaf composites increased by 100%. Also 2-hydroxyethyl methacrylate improved mechanical properties of UD kenaf-UP composites by 60-70%. Papers on (low pressure) plasma treatment indicate that an improved adhesion of natural fibres with UP is possible, improvement levels are lower than reported for modified UP resin compositions, however

- *Composites based on bio-based furan resin*: Only a limited number of publications on natural fibre-furan resin composites have been found. Furan resins seem to exhibit fairly good bonding to natural fibres already

- *Composites based on natural fibres that retain their structure in PP composite processing*: Silane modification of natural fibres for improved adhesion in PP composites exhibit a significant positive effect on composite mechanical properties, however, the increase is less than for composites with MAPP as a coupling agent. Plasma modification of natural fibres for improved adhesion in PP composites presented in the found literature are all based on treatment at low pressure and/or in extremely small reactor cells. Plasma treatments have a positive effect on composite mechanical properties; however, the increase is less than for composites with MAPP as a coupling agent. Plasma treatment conditions must be selected carefully as they may largely affect natural fibre tensile strength

- *Composites based on natural fibres that retain their structure in PLA composite processing*: Several researchers have evaluated different kinds of adhesion promoters in natural fibre-PLA composites which showed an increase of composite mechanical performance. The composite strength performance in these studies, however, is lower than for the pure PLA itself. No literature has been found on the use of plasma treatment of natural fibres for use in PLA composites

- *Composites based on natural fibres that retain their structure in PHA composite processing*: PHAs are linear polymers produced by bacterial fermentation. A wide range of different monomers can be combined within this family to give materials with a range of properties. Huge improvement of fibre-PHA modulus has been reported using p-MDI and maleic acid grafter poly(hydroxybutyrate-valerate) (MA-PHBV) coupling agents. Plasma (low pressure) treatment of natural fibres can have a positive effect on fibre-PHA adhesion

- *Patents on plasma treatment of natural fibres for composites*: 3 Patents found relate to 'vacuum' plasma treatment, which has the disadvantage of being limited to batch mode, requiring subsequently an iteration of steps: 1) vacuum application, 2) plasma treatment, 3) increasing pressure to atmospheric conditions, 4) release of the treated sample. For a fourth, Japanese patent, no details could be traced. Also, patents on plasma treatment of natural fibres not intended for use in composites have been reviewed, the majority being on 'vacuum' plasma treatment as well. Only 3 are based on atmospheric plasma treatment: one focussing on paper and cardboard applications, claiming the use of a wide range of gases to modify the materials surface; one describing an apparatus for treatment of solid wood to improve gluing properties; one addressing softening and decontamination of natural fibres

The review of patent and scientific literature suggests that atmospheric pressure plasma technology for treatment of natural fibres for improved adhesion to polymer matrix systems may be patentable.

3.1.3 Considerations related to plasma treatment of natural fibres for use in reinforced polymer composites

During extrusion compounding of natural fibres in thermoplastics, the fibres may be refined to fibres with smaller diameter than the fibres entering the process [1]. This means that during extrusion compounding fresh fibre surface is created. Also during injection moulding, fibres may be refined further. This is certainly the case for bast fibres like flax and hemp in the form in which they are commercially available these days. If such fibre surface is modified prior to extrusion compounding, the freshly created fibre surface during compounding will be an unmodified surface. As a consequence, the fresh fibre surface will not exhibit improved adhesion. Considering that, for instance, flax fibres with a modified surface and having an average diameter of 80 μm are refined during extrusion compounding to fibres with a diameter of 20 μm, then the initial fibre surface is increased by a factor of 4, meaning that only 25% of the fibre surface after extrusion compounding is modified. Surface modification of such bast fibres for extrusion compounding applications will be inefficient. So for extrusion compounding and injection moulding applications, fibres need to be 'fully' refined to elementary plant cell fibres prior to plasma treatment. Elementary plant cell fibres are considered not to refine further during extrusion compounding and injection moulding.

3.1.4 Potential improvement of fibre-matrix adhesion

This section addresses the potential theoretical improvement in composite mechanical performance due to enhanced fibre-matrix adhesion as a result of plasma treatment.

3.1.4.1 PP

MAPP is an effective coupling agent for natural fibre-PP composites (**Figure 3.4**). With the use of MAPP, the mechanical performance of these composites approaches its theoretical maximum [1, 2]. Also, MAPP is commercially available, however it costs about 3,60 €/kg. Plasma surface treatment of natural fibres may have additional value if the plasma processing allows the use of less MAPP while maintaining the same level of composite performance. The costs of plasma treatment should be lower than the savings made by using less MAPP.

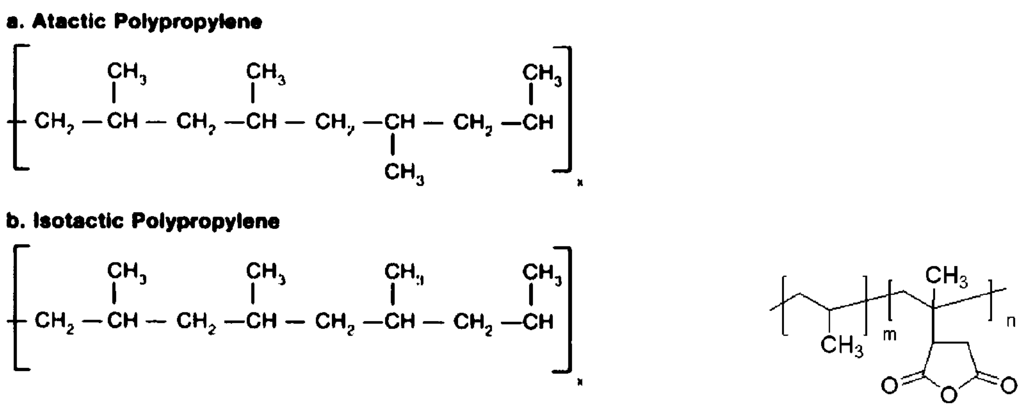

***Figure 3.4**: Structures of PP (atactic and isotactic) and MAPP*

The discussion on natural fibre plasma treatment is different for 2 types of PP composites: extrusion compounds and fibre mat based composites (see **section 3.1.3**). With respect to extrusion compounds, fibres like flax and hemp will need to be plasma treated in the elementary plant cell fibre form. Fibres with elementary plant cell dimensions may be obtained using ultrasonic extraction. In order to get an estimate of economically feasible plasma treatment costs, the following calculations may be performed. Considering a compound with composition natural fibre:PP:MAPP (50:45:5), and assuming a MAPP price of 3.60 €/kg, coupling agent costs are 0.36 €/kg of fibre. If plasma treatment will show a similar coupling effect as MAPP, then plasma treatment is economically feasible if treatment costs are less than 0.36 €/kg of fibre. If plasma treatment allows a reduction of MAPP content by 50%, then plasma treatment is at least economically feasible if treatment costs are less than 0.18 €/kg of fibre.

For fibre mat reinforced PP applications, any kind of natural fibre may be considered. In analogy to the extrusion compound, direct MAPP coupling costs are 0.36 €/kg of fibre for a natural fibre mat composite with composition fibre:PP:MAPP = 50:45:5. However, bearing in mind that the MAPP has to be blended with the PP prior to impregnation of the fibre mat which may cost about 0.25 €/kg of PP/MAPP blend, then the total coupling costs are estimated as 0.61 €/kg of fibre in a 50 wt.% fibre-PP sheet. If plasma treatment allows a reduction of MAPP content by 50%, then plasma treatment is economically feasible if treatment costs are less than 0.30 €/kg of fibre.

3.1.4.2 PLA

A rough calculation exercise, using Kelly-Tyson model for injection moulded composite strength [3], and using tensile strength data of flax fibre-PLA composites [4], and estimating parameters for fibre-matrix adhesion and for fibre orientation in analogy to flax-PP and flax-MAPP composites [1, 2], suggests that a 30% increase in composite tensile strength may be expected if fibre-PLA adhesion can be improved to the level as has been observed for flax-MAPP composites. Techno-economic advantage/disadvantage depends on actual plasma treatment costs and level of natural fibre-PLA adhesion improvement. The chemical structure of PLA is indicated in **Figure 3.5**.

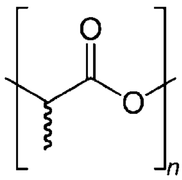

***Figure 3.5**: PLA structure*

3.1.4.3 UP

A rough calculation exercise using the Kelly-Tyson model for composite strength, and using tensile strength data of flax fibre-UP composites [5], and estimating parameters for fibre-matrix adhesion and for fibre orientation in analogy to flax-PP and flax-MAPP composites [2], suggests that a 60% increase in composite tensile strength may be expected if fibre-UP adhesion can be improved to the level as has been observed for flax-MAPP composites. The techno-economic advantage/disadvantage will depend on actual plasma treatment costs and the level of natural fibre-UP adhesion improvement.

The chemical structure of UP is indicated in **Figure 3.6**. In a conventional UP system, the double bond in unsaturated polyester reacts with styrene resulting in a 3D cross-linked structure. The cross-linking is initiated through an exothermic reaction involving an organic peroxide, such as methyl ethyl ketone peroxide (MEKP) (**Figure 3.6** and **Figure 3.7**).

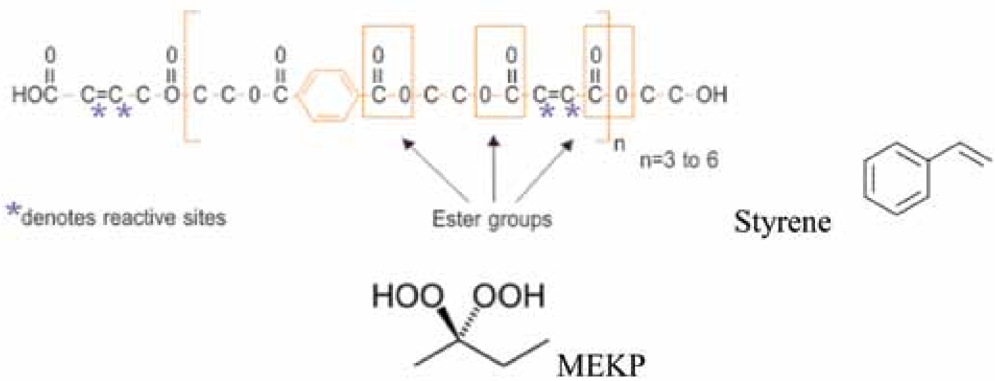

***Figure 3.6**: Structure of unsaturated polyester oligomer, styrene and methyl ethyl ketone peroxide (MEKP)*

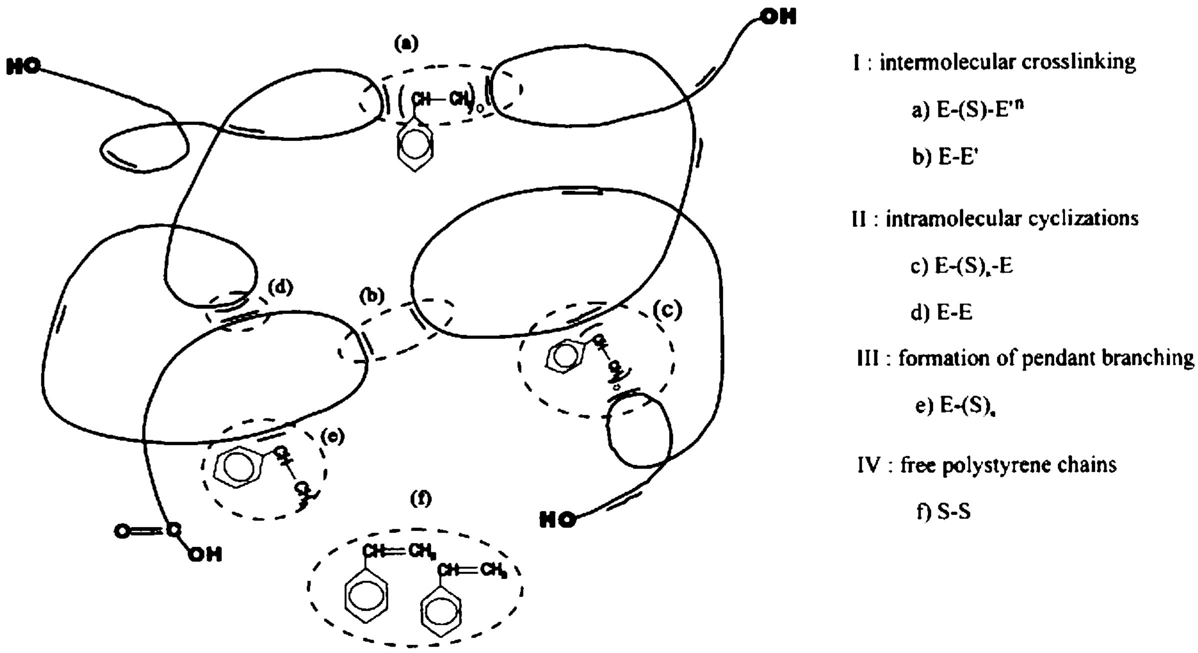

Figure 3.7*: Possibilities for reaction between UP and styrene [6]*

3.1.4.4 Furan resin

Literature sources indicate that good interaction between natural fibres and furan resin is obtained without adhesion promotion. Therefore, no further improvement of fibre-matrix adhesion is expected.

3.2 Results and technical benefits

Results in this section refer to the lab scale APP unit which was manufactured by AcXys for the UltraFibre project. The technology is scalable to industrial size (**section 3.3.1**).

3.2.1 Design of plasma unit for treatment of natural fibres

Fibre reinforced composites are known in different forms, as are the fibres incorporated. Short natural fibres are mostly used in extrusion and injection moulded products, as well as in sheet moulding compounds (SMC). Natural fibre roving is of interest for pultruded composites. Non-wovens may be used in vacuum assisted resin transfer moulded thermoset composite products (VA-RTM), SMCs and natural fibre mat thermoplastic composites (NMT). After consultation with Wageningen UR-FBR, Movevirgo and RAPRA regarding specific requirements, AcXys has designed and manufactured a plasma treatment unit which allows for the treatment of the three forms of natural fibres which are used in different composite processing techniques: non-woven, roving (sliver) and short fibres (**Figure 3.8**). This multi-purpose unit is new in the way that usually plasma treatment units are designed for processing only one form of material. The system used is based on AcXys' atmospheric pressure plasma (APP) technology.

For the UltraFibre project, an APP unit has been constructed based on a 6 cm wide ULD plasma source. At industrial scale, the width of the ULD system may be increased up to 50 cm and a manifold of this width. The UltraFibre unit comprises the following:

- ULD plasma source of 6 cm width
- Belt system which allows for transportation and plasma treatment of fibres (**Figure 3.9**)
- Nitrogen is the main feed gas
- The nitrogen may be doped with a wide range of oxidative or reductive gases, such that plasma of a wide range of chemical compositions can be produced. The reductive and oxidative dopant gases are fed through

separate entrance tubes in order to avoid accidents with reducing and oxidising gases coming together

- The plasma unit is placed in a closed box with exhaust opening to extract resulting gases
- The front end side of the housing and part of the tunnel around the belt has been made transparent to monitor the plasma flame and sample treatment (**Figure 3.10**)
- Fibres grades which can be treated include: non-wovens, sliver (roving) and short natural fibres with a minimum length of 5-10 mm
- The processing rate of the UltraFibre plasma test unit can be varied in the range of 3 to 25 m/min, but it is no problem to construct a system which allows much lower or even higher rates
- The system consumes electric power and uses cooling water

Figure 3.8*: Composites are based on 3 different fibre forms*

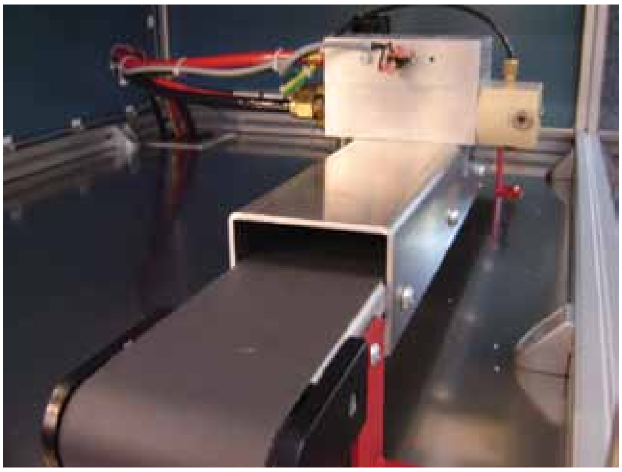

Figure 3.9*: Belt system and ULD plasma source mounted on top*

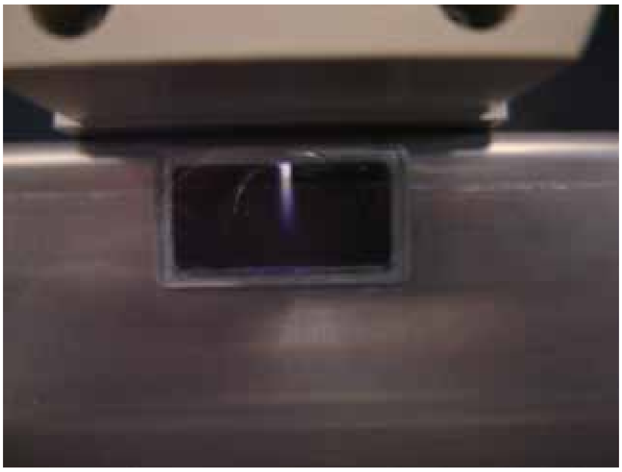

Figure 3.10*: Plasma flame visible through transparent section in tunnel around belt*

3.2.2 Plasma unit operation

3.2.2.1 General procedures and findings

During operation of the plasma unit at Wageningen UR–FBR, the following general procedures and findings may be noted:

- The nitrogen gas was taken from a fixed system of high purity (5.0) N_2 gas. Source of the supply system was a large liquid N_2 tank. A pressure reduction valve was applied to assure an N_2 pressure of about 5.5 bar entering the plasma unit at flowing conditions. Nitrogen flow is adjusted at the plasma unit up to a maximum of 60 l/min

- Dopant gases of high purity are consumed from 40 or 50 l bottles containing compressed gas. Pressure reduction valves to reduce the pressure to about 6 bar were sourced for each individual dopant gas. In order to achieve good mixing of dopant gas and nitrogen, the pressure of the dopant gas has to be slightly higher than the nitrogen pressure

- The dopant gas flow is adjusted at the plasma unit. Maximum gas flow for hydrogen and oxygen are 1.8 and 0.6 l/min, respectively. Other oxidising dopants are fed through the oxygen entrance tube. However, as the flow control is calibrated for O_2, flow control of other gases requires a conversion factor: (the 'oxygen' flow has to be set to 0.353 l/min to obtain a flow of 0.3 l/min of CO_2 or N_2O)

- Power consumption was in the range of 1000 – 1100 W when applying 60 l/min of N_2 plasma and any of the dopant gases and using the belt system. Considering the 6 cm wide ULD source, power consumption is 178 W/cm of ULD source

- The transparent front end side of the housing and part of the tunnel around the belt allow easy monitoring of the plasma flame and process. No effect of the transparent section in the tunnel has been noted

- Natural fibre non-wovens and sliver (roving) are not blown away from the belt when applying plasma at 60 l/min flow using the 6 cm wide ULD source. Even 5-10 mm short fibres, which show at least some kind of entanglements as usually is the case for natural fibres like flax, hemp, kenaf, jute, etc., are not blown away by the plasma flow and stay in place on the belt

- The whole system is placed on wheels to allow simple moving of the system

3.2.2.2 Emissions

The APP technology only uses electricity and feed gases. No waste water is produced, except for cooling water. The APP technology can be considered a clean technology. Emissions mainly depend on the feed gas composition. Generally using compressed air or mixed gases mainly consisting of Nitrogen, related harmfulness of such plasma processing is mainly linked to ozone and nitrogen oxides (NO_x) emissions. Other emissions may be gaseous substances released from the fibre surface during plasma treatment, for instance CO_2, H_2O and potentially methanol. Quantified evaluation of plasma emissions at AcXys shows that ozone emission is less than 0.05 ppm for pure nitrogen feed gas and NO_x could not be detected. These values are within the World Health Organisation (WHO) occupational limitation references. If feed gas contains oxygen, both emission values go up. The level of ozone becomes critical to operators at small amounts of oxygen in the feed gas already. Consequently, extraction is a necessary precaution. To guarantee a minimum extraction flow, a safety system is mounted in the exhaust tube (**Figure 3.11**). NO_x emissions are not overpassing the WHO safety limits, even at high contents of oxygen in the feed gas.

Ozone is a greenhouse gas, however, also very unstable and no legal pressure to reduce ozone production is known.

Considering a 1 m wide ULD plasma unit, operated 225 days/annum, 16 h/day, consuming 10 l/min.cm of N_2 or O_2 doped N_2, the annual NO_x emissions are calculated to be 16.2 – 122 g NO_x based on 0.04 and 0.3 ppm of NO_x. This is similar to NO_x emissions of a car travelling 160 – 1200 km at an average emission of 0.1 g/km. This calculation shows that NO_x emissions of such an industrial scale plasma unit are relatively small.

Figure 3.11*: Safety module in the exhaust tube of the plasma unit*

3.2.3 Experimental results

3.2.3.1 Plasma treatment of natural fibres

Before extensively investigating the effect of plasma on fibre surface modification and fibre-matrix adhesion, experimental plasma trials were performed at Wageningen UR–FBR to obtain information on:

- The potential of the APP technology to modify the chemical composition of natural fibre surfaces
- The effect of storage conditions on the durability of the modification

Flax sliver was sourced from Ekotex (Poland) and plasma treated for about 20 s using a first selection of feed gases based on AcXys' experience: N_2, N_2 + 0.5% CO_2 and N_2 + 0.5% N_2O. A water droplet test indicates that even the hydrophobicity of flax fibre surfaces can be changed (**Figure 3.12**). A more detailed analysis of surface modification was obtained using x-ray photoelectron spectroscopy (XPS).

Figure 3.12*: Water absorption increases after plasma treatment (right) compared to untreated reference (left)*

The results show that:

- The plasma treatment causes a large change in carbon, oxygen and nitrogen element composition at the fibre surface, depending on feed gas composition (**Table 3.1**). The analysis was performed 2.5 weeks after the plasma treatment, indicating that the surface modification has a durable character

- AcXys' experience shows that aluminium protects the surface modification achieved with plasma treatment. Therefore, part of the pure N_2 treated flax fibres were wrapped in aluminium foil before putting in a plastic bag. Surface analysis results are ambiguous: change of nitrogen content is less, but change of oxygen content is larger compared to the sample not wrapped in aluminium. Overall this suggests a slight protective effect by the aluminium wrap

- Fibres needed to be dried prior to XPS analysis. Therefore, the effect of drying temperature was evaluated (105 °C at atmospheric pressure versus 50 °C at low vacuum). XPS results show that part of the surface modification is lost after storage at too high temperature

Table 3.1: 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 plasma (no aluminium)	12.2	73.8	11.6
Flax, N_2+CO_2 plasma	36.7	50.4	6.7
Flax, N_2+CO_2 plasma (105 °C)	31.8	61.5	5.5
Flax, N_2+N_2O plasma	41.9	52.2	2.1

3.2.3.2 Plasma treatment of natural fibres for injection moulding

In order to avoid fibre refining during extrusion compounding and injection moulding (see **section 3.1.3**), fibres were refined prior to plasma treatment using a Shirley trash separator (**Figure 3.13**). An indication of the refining effect is presented in **Figure 3.14**. The focus is on hemp fibre, because this is of more interest to the partners in the project, but also flax fibres were evaluated. Flax was sliver from Ekotex (Poland) and hemp was tow grade from Hemp Technology (UK).

***Figure 3.13**: Shirley trash separator*

Refined fibres were made into mats having a width of about 6 cm (width of tunnel around the belt) and a length of about 25 cm (dimension suitable for manual handling to feed to the plasma unit). Thorough plasma treatment was applied at both sides using an effective treatment speed of 0.48 m/min, and maximum nitrogen flow of 60 l/min. In order to introduce a variety of chemical groups onto the fibre surface, a range of feed gas compositions were applied. Feed gas compositions for the plasma trials were based on AcXys' experience:

N_2, N_2 + 0.5% O_2, N_2 + 0.5% CO_2, N_2 + 1% H_2, N_2 + 0.5% N_2O

***Figure 3.14**: Shirley refined flax sliver: unrefined fibre (left), fine fibre (top right) and small amount of coarse fibre (bottom right)*

Fibres were analysed in detail and the results show that:

- The effect of plasma treatment on fibre surface elemental composition is similar for flax and hemp
- Surface modification can be influenced by selecting feed gas composition. Depending on dopant gas (O_2, CO_2, N_2O), oxygen and/or nitrogen content at the fibre surface may be increased. H_2 appears to have basically no effect on fibre surface elemental composition (**Table 3.2**)
- Increasing production rate by a factor of 3 (treatment speed of 1.45 m/min) reduces the relative surface modification by a factor of 3
- Durability of plasma treatment is not infinite. 52 Days after plasma treatment the fibre surface modification is reduced to about 30% compared to after 4 days
- The fibre surface morphology was analysed using SEM and did not show any change due to APP treatment, so no advantage or disadvantage related to mechanical interaction with polymers is to be expected
- The fibre tensile strength is retained after plasma treatment (**Figure 3.15**), and as a consequence the reinforcing potential of the fibres
- The plasma treated fibres can be directly processed in composites

Table 3.2: Elemental composition (%) of untreated and plasma treated hemp and flax fibre surface (upper few nm) using XPS

	Oxygen	Carbon	Nitrogen
Hemp, untreated	21.4	76.0	1.5
Hemp, N_2 plasma	21.3	73.6	4.5
Hemp, N_2 + O_2 plasma	26.0	71.5	1.6
Hemp, N_2 + CO_2 plasma	29.2	67.3	2.6
Hemp, N_2 + H_2 plasma	20.5	77.3	1.5
Hemp, N_2 + N_2O plasma	30.7	66.4	1.6
Flax, untreated	15.6	82.8	0.9
Flax, N_2 plasma	11.2	84.9	3.2
Flax, N_2 plasma (after 52 days)	14.2	84.0	1.5
Flax, N_2 plasma (at 3x higher speed)	12.9	83.9	1.6

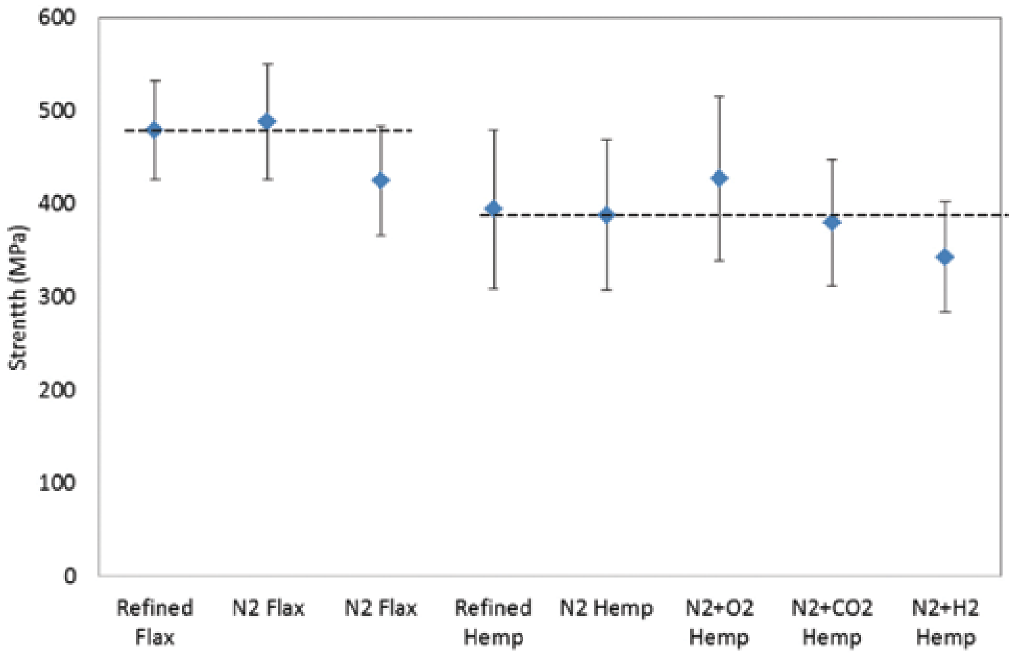

Figure 3.15*: Collective fibre tensile strength of Shirley refined and plasma treated and untreated flax and hemp fibres. Dashed lines representing level of untreated fibres*

It is confirmed that APP is a useful technology to modify natural fibre surface chemical composition without affecting the strength and therefore the reinforcing potential of the fibres.

An attempt was made to obtain more particular information regarding the chemical groups present at the fibre surface. XPS narrow carbon scans may be fitted assuming that only particular groups are present, (C-C, C=O, O-C=O, *etc…*). Due to many groups being potentially present even in untreated natural fibres, it appeared that a unique fit could not be determined. Results were even confusing when only focussing on the major constituent groups. Consequently, a simple steering parameter to enhance fibre-matrix adhesion could not be derived from XPS. Therefore, the actual value of the surface modification needs to be derived from the fibre reinforcing performance in polymer composites, which will be addressed in the next sections.

3.2.3.3 PP composites based on plasma treated fibres

At Wageningen UR–FBR, plasma treated hemp and flax fibres and untreated reference fibres were compounded in PP matrix and injection moulded into test specimens. Fibre content in the composites was 30 wt.%. Reference composites were produced and evaluated in duplicate, in order to have reliable values for reference composite performance, as these values determine the relative effect of the pre-treatments.

The flexural strength gives a good indication of fibre-matrix adhesion, while showing the composite mechanical performance at the same time. Therefore, this method was selected to analyse the effect of plasma treatment on composite performance. Specimens were conditions at 20 °C and 50% RH for about 1 week or more prior to further analysis. Scanning electron microscopy (SEM) was performed in order to better understand the mechanical performance results.

As a result of plasma treatment of flax fibres, flax-PP composite flexural strength increases by 23%, close to the 29% improvement by using 1% MAPP (**Figure 3.16**). Improved fibre-matrix adhesion is confirmed by SEM (not shown). N_2 treated flax-1% MAPP performs similar to untreated flax-3% MAPP, so about 1.5 wt.% MAPP can be saved.

In order to study the effect of processing rate on efficiency of the plasma treatment, a flax sample was plasma treated at a higher speed: 1.45 m/min versus 0.48 m/min for trials described previously. At the increased plasma treatment speed, only 8% composite strength improvement was observed, indicating that effective plasma treatment requires a minimal treatment time.

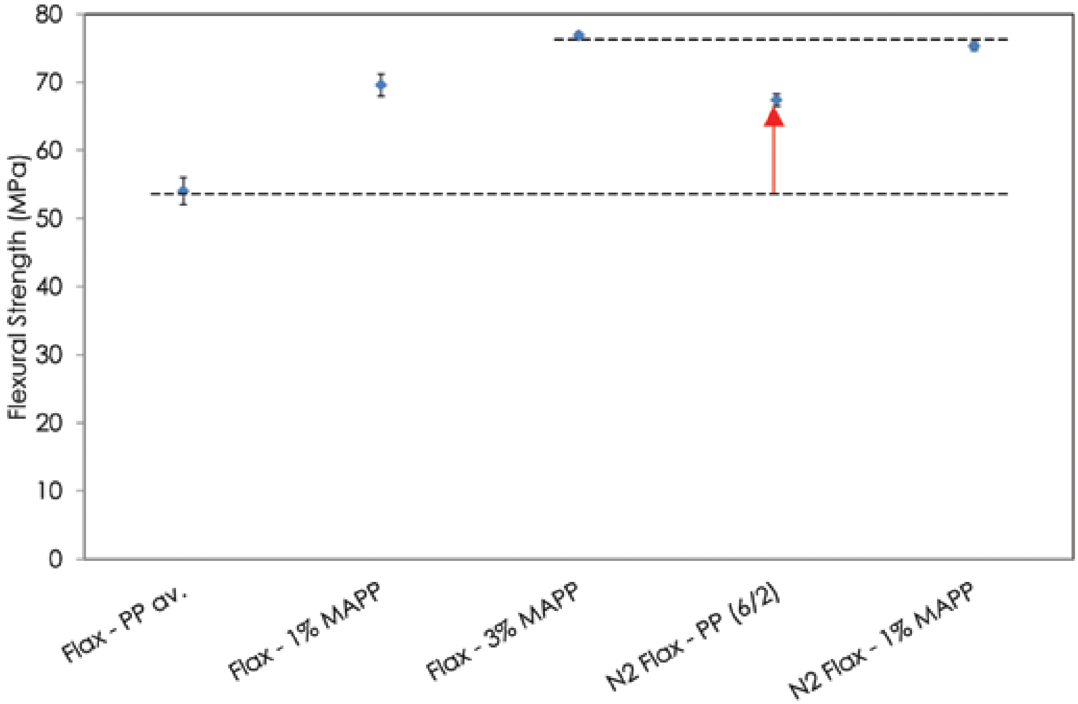

***Figure 3.16**: Flexural strength of (refined) flax-PP composites: effect of plasma treatment and MAPP. Dashed lines represent levels of untreated flax-PP and untreated flax-PP/3% MAPP*

In order to study the durability of the plasma treatment, a plasma treated flax sample was stored in aluminium foil for 4 months prior to compounding in PP. The composite exhibited a 12% flexural strength increase compared to the untreated reference. This indicates that the effectiveness of the plasma treatment slowly deteriorates with time.

For hemp-PP composites, no improved strength performance was observed for a range of plasma feed gas compositions (**Figure 3.17**). Hemp fibres appear to refine during compounding, thus creating fresh untreated fibre surface, whereas flax fibres do not refine (**Figure 3.18**). This may (partly) explain why hemp-PP composite strength does not improve after plasma treatment, whereas flax composite strength does improve.

A further reason for the absence of improved adhesion may be the waxy substances on hemp fibres (**Figure 3.19**), which hinders adhesion between the load bearing cellulose backbone of the natural fibre and the polymer. The hemp fibres used so far were unretted hemp fibres, and it was suggested that (partly) retted hemp may contain less waxy substances on the fibre surface, thus allowing better adhesion between the fibre and the matrix. However, no such effect was found (**Figure 3.20**).

On the other hand, hemp-PP flexural modulus increases by 11-22%, similar to and more than achieved by using 1 or 3% MAPP (**Figure 3.21**). 1 and 3% MAPP show 8 and 11% increase in modulus, respectively. The usual solution to increase modulus, however, is using higher content of fibres.

3.2.3.4 PLA composites based on plasma treated fibres

Plasma treated hemp and flax fibres and untreated reference fibres were compounded in a PLA matrix and injection moulded into test specimens. Fibre content in the composite was 30 wt.%. Reference composites were produced and evaluated in duplicate, in order to have reliable values for reference composite performance, as these values determine the relative effect of the plasma treatments.

Trends for hemp-PLA composites seem opposite to what has been found for PP composites. Hemp-PLA flexural modulus does not improve after plasma treatment, whereas flexural strength increases by 20-24% for N_2, N_2 + 0.5% O_2, and N_2 + 0.5% CO_2 (**Figure 3.22**). Using H_2 as a dopant gas has no effect on composite strength. The untreated hemp-PLA composite has been produced and analysed in duplicate to make sure

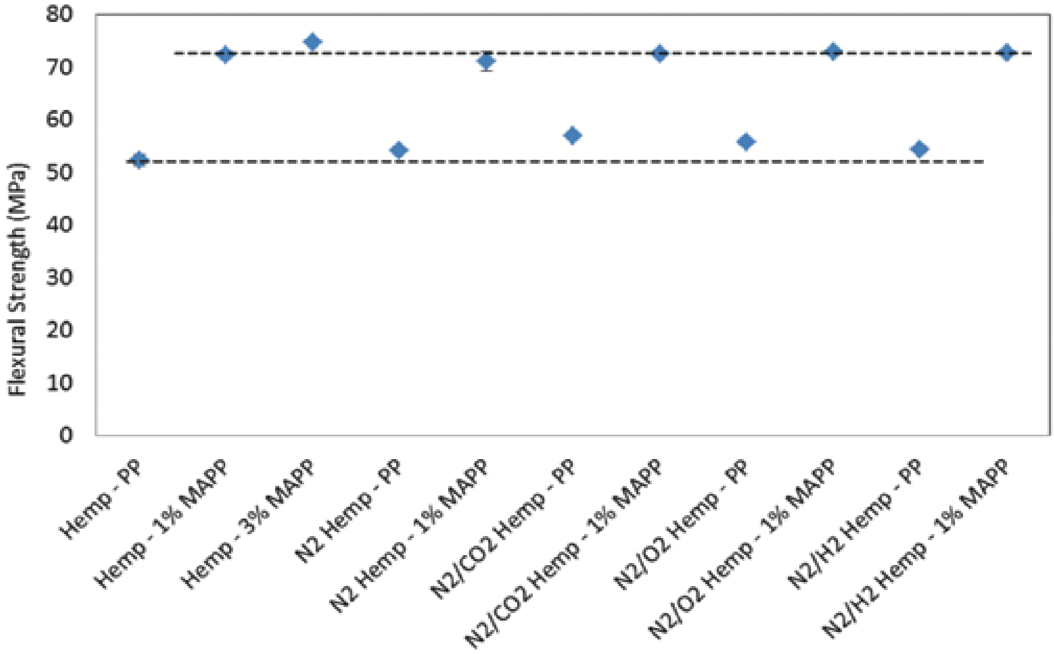

***Figure 3.17**: Flexural strength of hemp-PP composites: effect of plasma treatment and MAPP. Dashed lines represent levels of untreated hemp-PP composites and hemp-PP/1% MAPP*

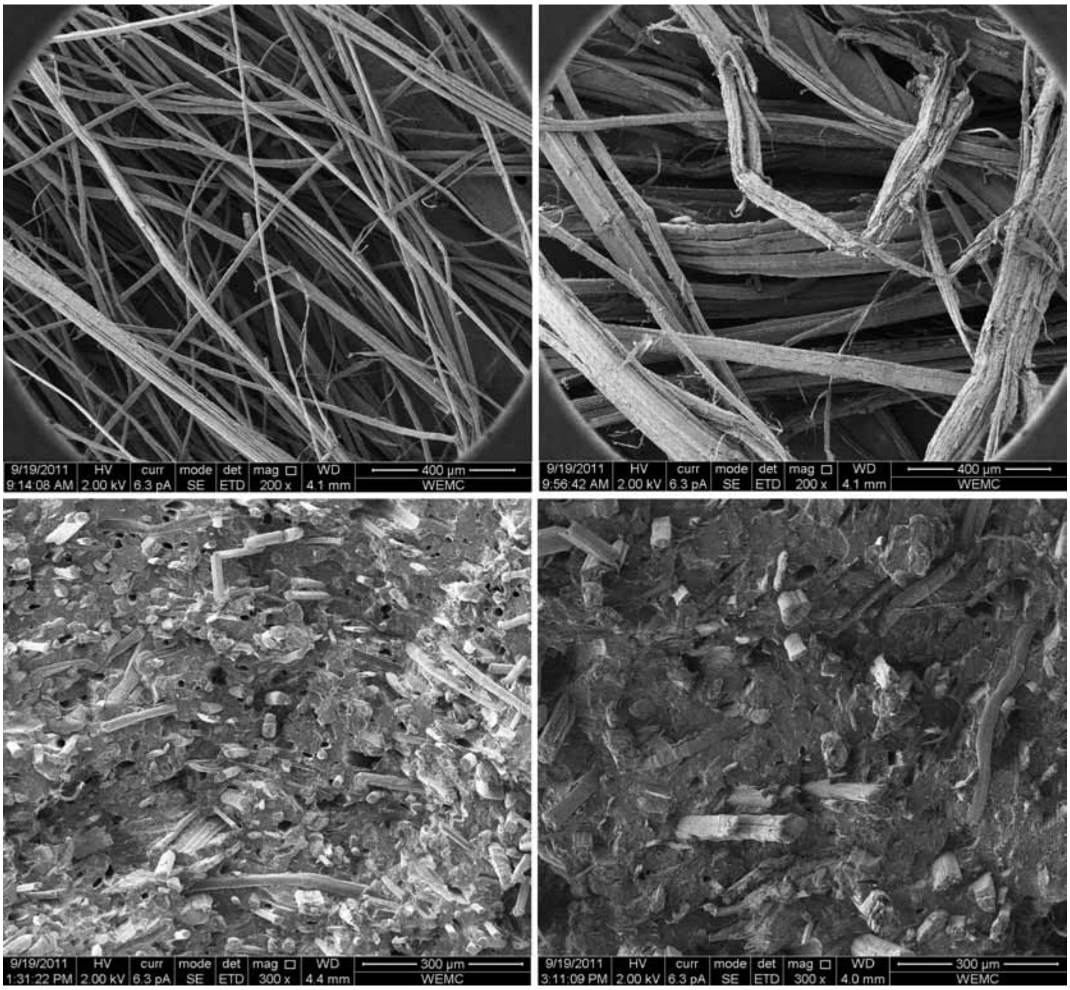

***Figure 3.18**: SEM pictures of Shirley refined flax (left) and hemp (right) fibres (top) and fracture surfaces of their composites (bottom)*

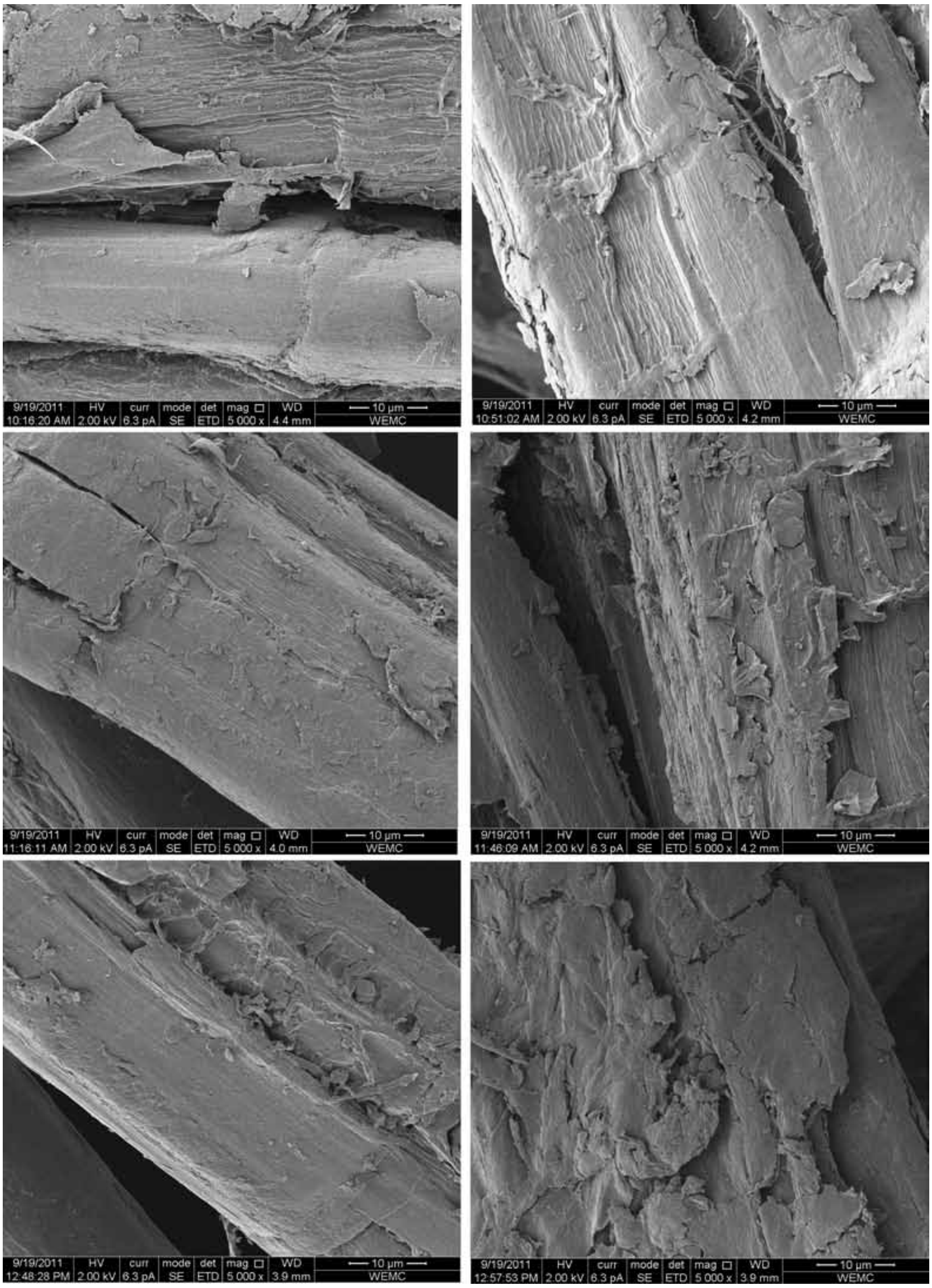

Figure 3.19: *SEM pictures of untreated and N_2, $N_2 + O_2$, $N_2 + CO_2$, $N_2 + H_2$, $N_2 + N_2O$ plasma treated hemp fibres (going from upper left corner to lower right corner)*

that the reference values have a solid base. SEM analysis (not presented) does not present any explanation for mechanical performance observations. So far, no explanation has been found for the difference of performance of hemp-PP and hemp-PLA composites.

For flax-PLA composites, the applied plasma treatment has no significant improving effect on flexural strength, possibly as a result of the high level of strength performance of flax-PLA already.

3.2.3.5 UP composites based on plasma treated fibres

In this project, sheet moulding compound (SMC) type of composite was selected for evaluation of the effect of APP treatment on UP based composite performance. Since fibres do not refine during SMC processing, fibres may be plasma treated as received, as no fresh (untreated) surface will be created during further processing.

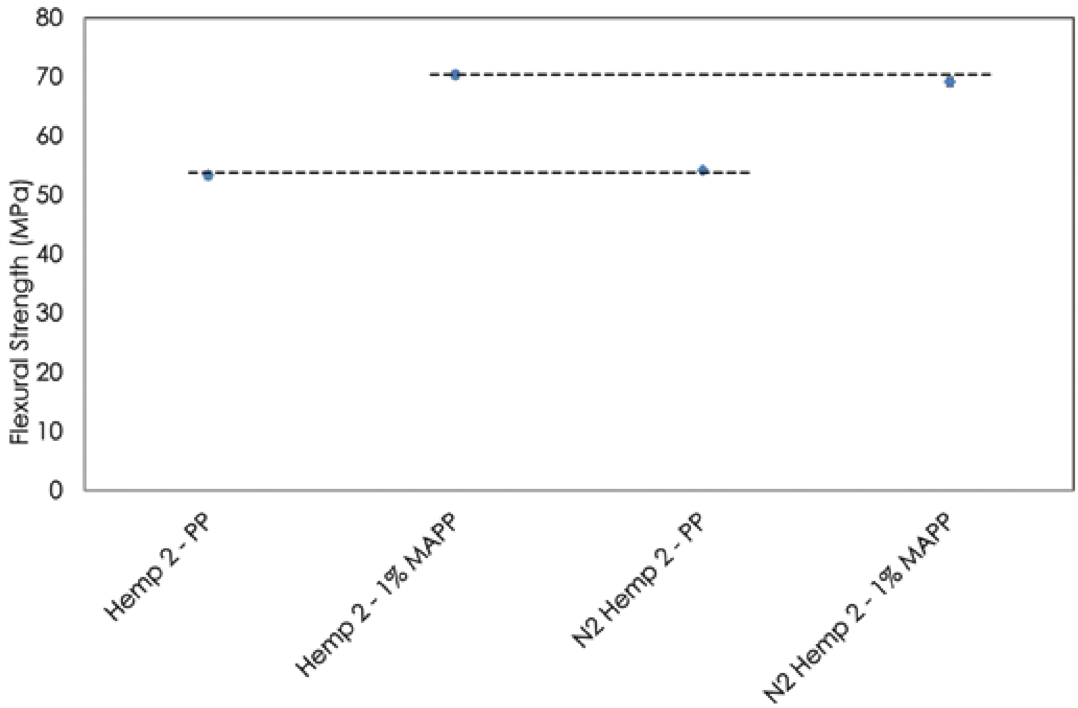

Figure 3.20: *Flexural strength of (partly) retted hemp-PP composites: effect of plasma treatment and MAPP. Dashed lines represent levels of untreated hemp-PP composites and hemp-PP/1% MAPP*

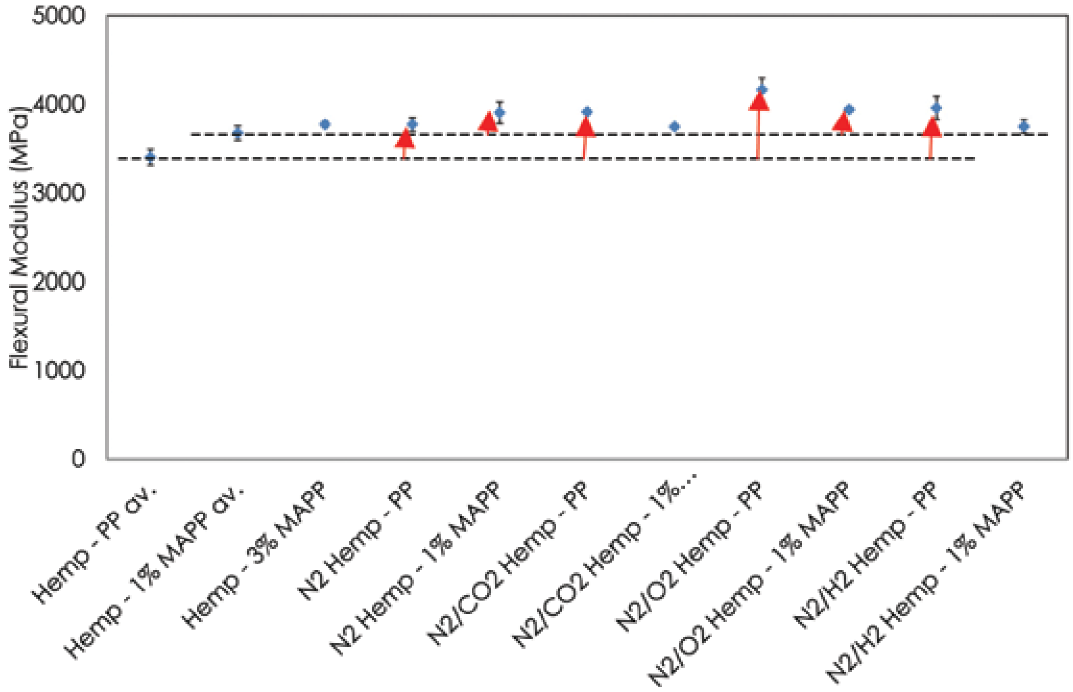

Figure 3.21: *Flexural modulus of hemp-PP composites: effect of plasma treatment and MAPP. Dashed lines represent levels of untreated hemp-PP composites and hemp-PP/1% MAPP*

Natural fibres contain typically about 10% of moisture at regular environmental conditions. Previous research has shown that the moisture present in natural fibres limits adhesion between fibres and unsaturated polyester (UP). Therefore, fibres were dried in an oven at 105 °C and cooled in a desiccator for 30 min prior to plasma treatment. Fibre samples are kept dry as much as possible during further storage and transportation until moulding by placing in a closed plastic bucket containing pre-dried silica gel.

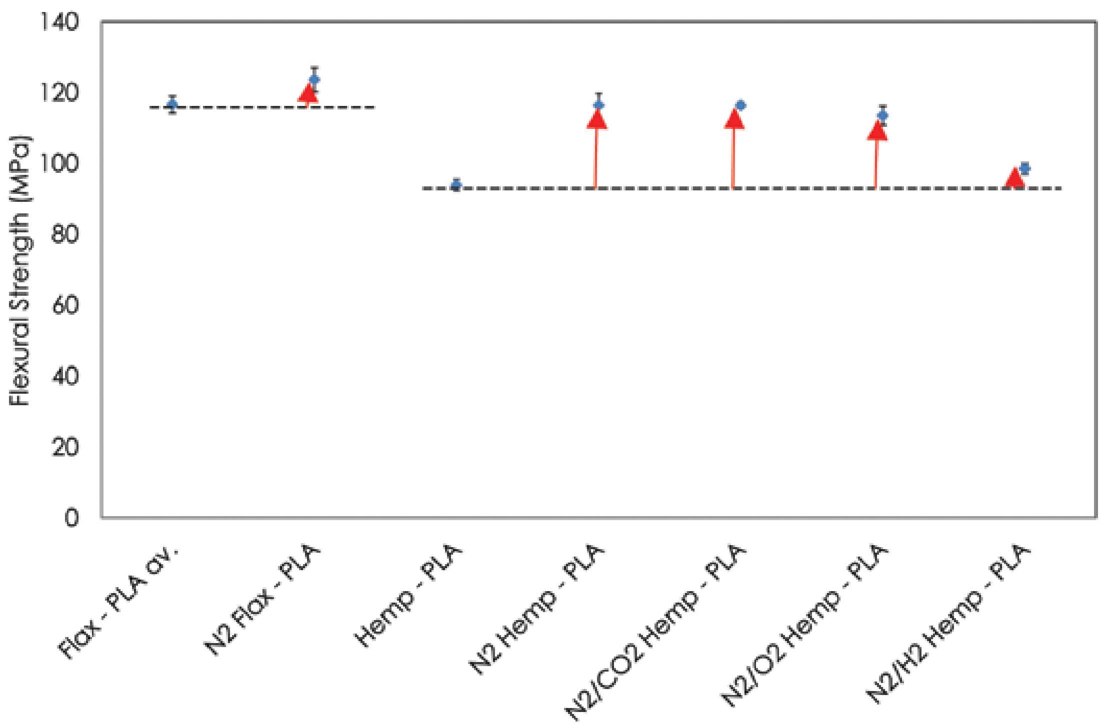

***Figure 3.22**: Effect of plasma treatment on flexural strength of (refined) flax and hemp-PLA composites. Dashed lines represent levels of untreated fibre PLA composites*

The procedure followed at Wageningen UR–FBR for making SMC samples based on plasma treated fibres comprised the following:

- Overnight drying of fibre samples in an oven at 105 °C
- Cooling the fibre samples in a desiccator for 1 h
- Placing the fibre samples in a closed plastic bucket containing pre-dried silica gel during transportation to the plasma unit and further transportation and storage
- Plasma treatment of fibre samples as in **section 3.2.3.2**, except that no fibre refining step was included, and except that O_2 dopant concentration was 0.1% instead of 0.5%
- Preparing 2 layers of resin paste onto release films and impregnating fibre non-woven samples from 2 sides with resin paste using fluted rollers (**Figure 3.23**). Fibre samples were impregnated with resin paste within 30 minutes after plasma treatment
- Maturing the resin paste in the SMC samples under a 10 kg weight, in a closed plastic bucket containing pre-dried silica gel, for 1 or 2 nights
- Consolidating the SMC samples in a PHI hot press at 140 °C for 3 minutes using a flat mould (**Figure 3.24**, manufactured by Movevirgo), to allow cutting of suitable test specimens

In order to adequately evaluate the effect of plasma treatment on SMC composite performance, the following was performed to determine optimised fibre-UP composition and moulding conditions:

- A range of hemp fibre contents was evaluated, 17.5 – 35 wt.% fibre in the UP composite. Hemp grade used was a needle punched mat sourced from Hemp Technology. Composite flexural strength significantly increased up to 25 wt.% fibre. At higher fibre content, flexural strength slightly increased further

- Using additives to improve resin flow and fibre wetting (BYK-W 996 to reduce UP resin viscosity and BYK-P 9065 to improve natural fibre-matrix wetting/adhesion) did not result in improved SMC composite performance. The absence of positive results may be related with the moment of mixing the additives: BYK brochures suggest that the additives have to be mixed with the resin prior to mixing with the $CaCO_3$ filler for effect, whereas in this project only ready formulated resin paste could be obtained

- Increasing moulding temperature to 160 °C, thus obtaining a lower initial resin viscosity and consequently better resin flow, did not result in improved composite performance

- Because glass fibre based SMCs contain typically about 25 wt.% glass fibre, this fibre content was used to evaluate the effect of plasma on UP based composites. To obtain composites containing about 25 wt.% fibre, 3 layers of hemp were required to make a composite plaque of about 3.8 mm thickness for testing. Moulding conditions selected were 140 °C for 3 minutes

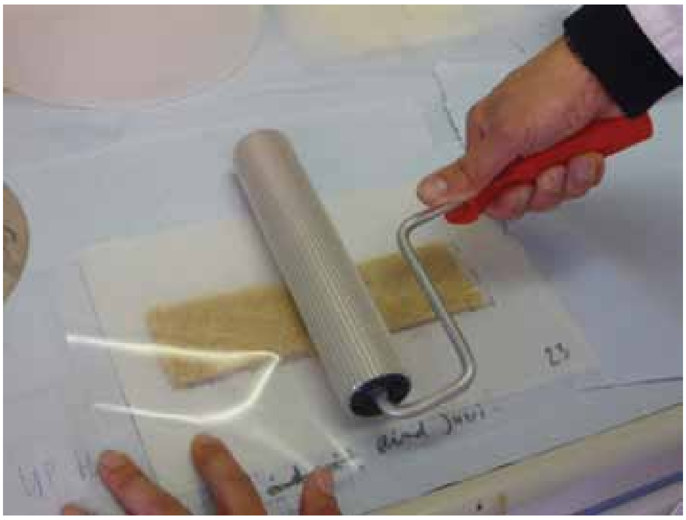

Figure 3.23: *Impregnating fibre non-woven with resin*

Figure 3.24: *Specially designed mould for making SMC test specimens, fixed in hot press*

SMC composites are based on a formulation containing UP resin, low shrink additives, $CaCO_3$ filler, additives for wetting and mould release agent, MgO paste and fibres. Because of the complex effects of all these ingredients, it was decided to source a standard resin paste formulation from MoveVirgo's SMC supplier, which needed just to be mixed with the MgO thickener and applied onto the projects natural fibres prior to SMC composite moulding. The resin paste formulation thickens over time, however, and as a consequence has a limited life time. Therefore, each batch of fresh resin paste was used only for about 2 months maximum after supply. To further minimise the effect of resin paste ageing, a reference of untreated hemp fibre based SMC has been included for each series of trials.

UP hemp fibre composite flexural strength increases by 20% for N_2 + CO_2 plasma treatments see **Table 3.3**. Also, improved strain at maximum stress of 26% confirms improved fibre-matrix adhesion. N_2 + N_2O plasma resulted in a 15% increase in composite flexural strength. Flexural modulus hardly increases, as may be expected for long fibre composites.

N_2 + H_2 feed gas, which was evaluated in a separate series, did not have a positive effect on composite flexural strength, like N_2, and for N_2 + O_2 a small 5% increase was found. Combining results from **Table 3.2** and **Table 3.3**, it may be suggested that the improved composite strength performance of hemp-UP composites is related to an increase of oxygen content at the fibre surface.

SEM has been applied in order to better understand the results. Images of fracture surfaces of untreated and plasma treated hemp-UP composites have been presented in **Figure 3.25**. Fibre pull out length seems to be shorter for the for N_2 + CO_2 plasma treated hemp fibre composite than for the untreated fibre composite, suggesting better fibre-matrix adhesion after N_2 + CO_2 plasma treatment. Keeping in mind that a tight enclosure of fibres by UP matrix means a good interaction between the fibres and the matrix which tends to shrink upon curing, it may be noted that SEM images for both composites show good fibre-matrix adhesion as well as poor (gaps between fibres and matrix, **Figure 3.25**). However, poor bonding predominates in the untreated hemp fibre SMC, and good bonding predominates in the N_2 + CO_2 plasma treated hemp fibre composite.

Table 3.3: Properties of hemp fibre SMC composites: Effect of plasma

Code	Plasma	Fibre Content	Density	Flexural Strength		Flexural Modulus		Strain at Max. Stress	
		(wt%)	(g/cm³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-27	-	23.6%	1.56	54.3	3.9	7.65	0.41	1.38	0.18
SMC-20	N_2	23.8%	1.47	54.3	3.9	7.54	0.35	1.57	0.18
SMC-21	N_2+0.1% O_2	24.5%	1.49	57.2	4.7	7.61	0.58	1.53	0.14
SMC-22	N_2+0.5% CO_2	25.4%	1.51	76.9	3.5	8.12	0.29	1.74	0.13
SMC-23	N_2+0.5% N_2O	26.4%	1.44	74.1	3.6	7.91	0.45	1.76	0.15

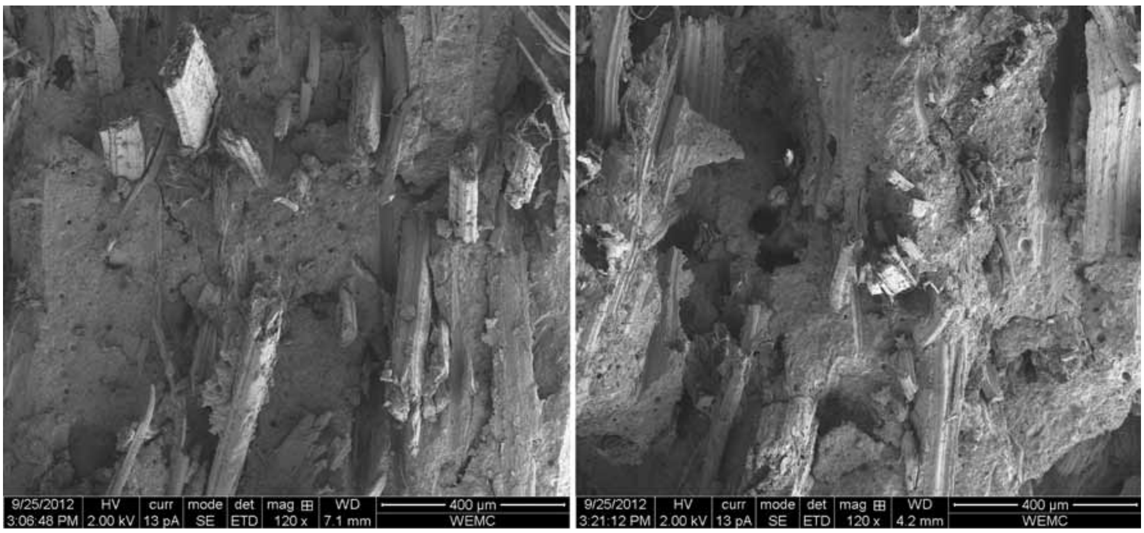

***Figure 3.25**: SEM pictures of fracture surfaces of UP composites based on untreated (left) and N_2 + CO_2 plasma treated (right) hemp fibres*

In order to study the effect of processing rate on efficiency of the plasma treatment for coupling to UP resin, hemp samples were plasma treated at higher speeds: 1.45 and 2.9 m/min versus 0.48 m/min for trials described previously. At increased plasma treatment speed, no composite strength improvement is observed, however, indicating that effective plasma treatment requires a minimal treatment time.

The effectiveness of the plasma treatment on fibre-matrix adhesion may be limited due to fibre surface contaminants which are not firmly bonded to the fibre (**section 3.2.3.3** and **Figure 3.19**). Ultrasonic (US) treatment is supposed to clean fibre surfaces, and as a consequence improved fibre-matrix interaction may be expected. US treated fibres were supplied by RAPRA and non-woven mats were manually prepared and processed into SMC composites as performed for other SMCs discussed so far. **Table 3.4** shows the US treated hemp-UP composite performance relative to the untreated hemp-UP composite. It appears that US treatment results in a 14% higher composite flexural strength. From SEM images (not shown) it must be concluded, however, that the strength improvement is not due to fibre refining or surface cleaning: US treated and untreated fibres appear to exhibit similar fibre diameter range, surface morphology (cleanness) and fibre pull out length. Plasma treatment does not exhibit further increase of composite strength, probably due to limited effectiveness as a result of too high treatment speed of 1.45 m/min.

Table 3.4: Properties of hemp fibre SMC composites: Effect of ultrasonic treatment

Code	Plasma	Fibre Content	Density	Flexural Strength		Flexural Modulus		Strain at Max. Stress	
		(wt%)	(g/cm³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-31	-	25.8%	1.56	77.8	3.5	7.79	0.32	1.91	0.15
SMC-36 (Ultrasonic)	-	27.8%	1.55	88.9	10.7	8.55	0.35	2.06	0.23
SMC-37 (Ultrasonic)	N_2+0.5% CO_2 (2/2)	27.7%	1.65	90.0	9.4	8.55	0.50	1.94	0.23

In order to get an impression of fibre impregnation and composite performance for very fine fibres, steam exploded flax (supplied by Wageningen UR–FBR) has been evaluated. The steam exploded flax basically consists of 100% elementary plant cell fibres having a diameter in the range 10-25 micron, whereas hemp tow fibres have a diameter in the range of 40-150 micron (**Figure 3.26**).

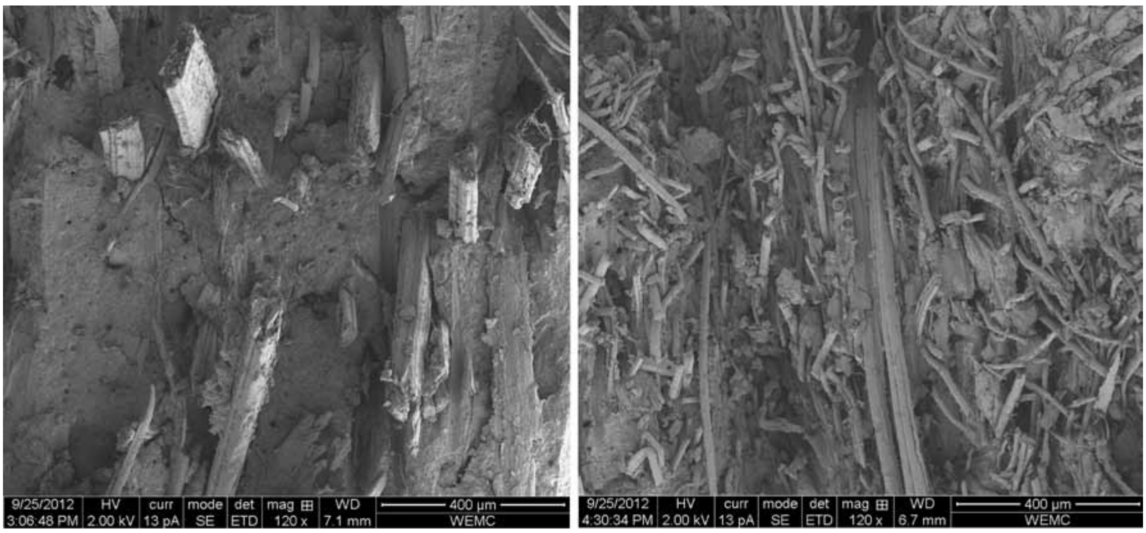

***Figure 3.26**: SEM pictures of fracture surfaces of UP composites based on untreated hemp (left) and steam exploded flax fibres (right)*

SMC composite based on steam exploded flax appears to be somewhat stronger than hemp based composites (**Table 3.5**). However, flax results are shadowed by poor fibre impregnation of the central part (30 – 50%) of the composite (**Figure 3.27**, left image). Poor impregnation may be caused by resistance to resin flow which is likely higher for the fine steam exploded flax fibres than for the coarse hemp tow fibres.

Unfortunately, no untreated flax reference was included in the SMC series including the N_2 plasma treatment. As a result of ageing of the resin paste as explained previously, the resin content in the central part of the composite (**Figure 3.27**, right image) is even lower than for the untreated fibre composite. The lower resin content tends to reduce composite performance. Still, the best 2 specimens show a strength improvement of 12% up to 101 MPa relative to the untreated flax composite where on average the better resin flow was obtained. Resin flow appears critical for very fine fibres like steam exploded flax fibres. For the more coarse hemp fibres, resin flow does not appear to be a limiting factor.

Table 3.5: Properties of (steam exploded) flax fibre SMC composites

Code	Plasma	Fibre Content	Density	Flexural Strength		Flexural Modulus		Strain at Max. Stress	
		(wt%)	(g/cm³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-7	-	28.2%	1.59	89.8	2.1	9.12	0.60	1.88	0.12
SMC-24	N_2	26.9%	1.40	82.8	18.3	8.99	1.68	1.67	0.26
SMC-24 (2 best)	N_2			100.5	3.5	9.86	0.78	1.67	0.26

***Figure 3.27**: SMC specimens based on steam exploded flax fibre, the central section of the composite showing incomplete fibre impregnation. SMC-7 (left), SMC-24 (right)*

Comparison to glass fibre based SMC

Glass fibre based SMC (commercial grade) was provided by Movevirgo, moulded by Wageningen UR–FBR, and cut to test specimens, all in analogy to the natural fibre based SMC composites. Comparison of mechanical performance of the natural fibre based SMCs and this commercial grade glass fibre based SMC shows the following (**Table 3.6**):

- For hemp, ultrasonic treatment followed by N_2 + CO_2 plasma treatment appears to give the best performance, reaching the same level for flexural modulus as commercial grade glass fibre based SMC and 73% of its flexural strength

- N_2 plasma treated steam exploded flax based SMC reaches 82% of the flexural strength of glass-SMC and 115% of its flexural modulus, even if the central part of the fibres in the SMC was not well impregnated

Table 3.6: Comparison of hemp, flax and glass fibre SMC composite properties

Code	Fibre Grade (Pre-treatment)	Fibre Content	Density	Flexural Strength		Flexural Modulus		Strain at Max. Stress	
		(wt%)	(g/cm³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-5	Hemp (-)	26.1%	1.61	83.1	3.0	7.74	0.26	1.99	0.16
SMC-7	Flax (-)	28.2%	1.59	89.8	2.1	9.12	0.6	1.88	0.12
SMC-37	Hemp (Ultrasonics, CO_2 plasma)	27.7%	1.65	90.0	9.4	8.55	0.5	1.94	0.23
SMC-24	Flax (N_2 plasma)	26.9%	1.40	100.5	3.5	9.86	0.78	1.67	0.26
G-1	Glass (-)	25.0%	1.70	122.8	12.9	8.55	0.48	2.61	0.34

3.2.3.6 Use of additional coupling agents

In order to improve the effectiveness/efficiency of plasma treatment for improved natural fibre-UP adhesion, the use of chemical reactants has been considered. The idea is that bi-active chemical agents may react with the plasma activated fibre surface on one end and with UP on the other end. Discussions with specialists in organic chemistry at Wageningen UR–FBR have delivered the following potential routes.

Ethylene oxide (EO) or propylene oxide (PO)

Hydroxyl groups of natural fibres are at least secondary or even tertiary OH groups, which limits their reactivity. EO and PO easily polymerise on even tertiary OH functionalities, and result in primary OH groups, which are protruding from the fibre surface, so having good accessibility and reactivity. Such OH group can react with carboxyl group of fumaric acid end capped UP pre-polymer.

A negative aspect to this route is that EO and PO are carcinogens, otherwise highly toxic and highly flammable. Therefore, this option is not elaborated further for modification of natural fibre surfaces.

Silane coupling agents

Trimethoxy- or triethoxy-silane coupling agents are extensively used in glass fibre sizing chemistry, e.g., gamma-metharcylpropyl-trimethoxysilane. The silane moiety easily reacts with glass fibre. For condensation onto natural fibres, reaction temperature should be above 90 °C [7]. The vinyl group can react with UP polymers, forming a chemical bond between the fibre and the matrix.

So far, a large amount of research on silane coupling agents for natural fibre reinforced composite purposes was published; however, very limited success regarding composite strength improvement was reported. Therefore this route is not selected for trials in this project.

Glycidyl Methacrylate (GMA)

This compound (2,3-epoxypropyl-methacrylate) contains 2 functional groups: an epoxy and a vinyl functionality. The epoxy moiety easily reacts with amine groups (NH_2), which can be introduced onto the fibres by plasma treatment. The vinyl moiety can react with UP polymers, forming a chemical bond between the fibre and the matrix.

Papers on coupling of GMA to carrier materials are based on different processing techniques: solution methods, melt processing or low pressure plasma. No coupling in atmospheric gas phase is found. Still, the epoxide group of GMA is expected to be reactive to NH_2 groups at temperatures below the GMA flashpoint (83 °C). The presence of O_2 would suppress polymerisation.

Though more harmful than the silane coupling agents, this chemical compound is expected to give potentially good coupling performance for plasma treated natural fibre reinforced UP composites.

Literature shows research on coupling of GMA onto:

PTFE sheets using low pressure (vacuum) plasma pre-activation and polymerisation for improved adhesion to polyimide (PI): method, potential reaction scheme, XPS and FTIR analysis, manifold improved peel adhesion strength [8].

- Si(100) wafers using low pressure plasma for improved adhesion to PI: method, potential reaction schemes and kinetics [9]

- Hemp and cellulose fibres using a solution method and PP, PS, EVA polymers using melt blending method for improved composite mechanical properties: proposed reaction schemes, little/no effect on strength of composite [10]
- PTFE sheets using GMA and low pressure plasma for linking amine and hydroxyl groups which would allow bonding of bio-compatible components: method, potential reaction schemes and FTIR analysis [11]

The majority of the papers focus on low pressure plasma or on using solvent systems to apply the GMA coupling agent. In general, research papers on modification of natural fibre surfaces and on applying coupling agents onto natural fibres are mainly based on solution methods [12, 13, 14].

Experimental trials using combined plasma treatment and GMA

The UltraFibre project focussed on atmospheric plasma and it was attempted to directly apply the coupling agent to the plasma activated fibres. After plasma treatment, fibres were directly (within 5 minutes) placed in an oven of 75 °C for a certain period of time, together with a beaker of about 50 cm^2 containing GMA (**Figure 3.28**). The plasma processing speed is selected relatively high (2.9 m/min) because the idea behind using a coupling agent is to reduce plasma treatment costs by increasing production rate. The temperature of the oven is selected to achieve highest possible GMA vapour pressure while certainly staying below the flash point of 83 °C. For safety reasons, the oven was placed in a hood.

Application of GMA results in a flexural strength increase of 6–8% (**Table 3.7**), however, it appears that this improvement is independent of plasma treatment or not. The limited performance of GMA in these trials may be related to GMA not being bonded well to the fibre or not effectively reacting with the UP resin.

***Figure 3.28**: Set-up for applying GMA onto plasma treated hemp non-woven*

Table 3.7: Properties of hemp fibre SMC composites: Effect of additional coupling agent

Code	Plasma + GMA time	Fibre Content	Density	Flexural Strength		Flexural Modulus		Strain at Max. Stress	
		(wt%)	(g/cm³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-40	-	26.3%	1.61	83.1	3.0	7.74	0.26	1.99	0.16
SMC-41	N_2 + 1% H_2 (6.2)	27.0%	1.59	89.8	2.1	9.12	0.6	1.88	0.12
SMC-42	N_2+1% H_2 (1/2) + 60 min GMA	27.4%	1.65	90.0	9.4	8.55	0.5	1.94	0.23
SMC-43	N_2+1% H_2 (1/2) + 10 min GMA	26.4%	1.40	100.5	3.5	9.86	0.78	1.67	0.26
SMC-44	N_2 (1/2) + 60 min GMA	26.4%	1.70	122.8	12.9	8.55	0.48	2.61	0.34
SMC-45	85 min GMA	28.1%							

3.2.4 Technical benefits

Research at Wageningen UR–FBR and AcXys has shown that the chemical composition of natural fibre surfaces can be significantly modified by applying APP technology. The actual modification depends on the plasma feed gas composition. In other words, the chemical composition of the fibre surface can be steered by selecting the feed gas composition. At the same time, hemp and flax fibre strength is not significantly affected for any plasma treatment applied. This means that the reinforcing potential of the fibres is kept intact.

AcXys has developed and produced a scalable atmospheric pressure plasma process, also called SoftPlasma, which allows treatment of natural fibres in different forms: short natural fibres which are mostly used in extrusion and injection moulded products, as well as in sheet moulding compounds (SMC), natural fibre roving (sliver) being of interest for pultruded composites, and non-wovens which may be used in vacuum assisted resin transfer moulded thermoset composite products (VA-RTM), SMCs and natural fibre mat thermoplastic composites (NMT).

Surface modification resulting from plasma treatment appears effective for several months. Under evaluated conditions, however, plasma treatment needs to be thorough in order to obtain significantly improved adhesion to matrices. Particular plasma treatments result in improved composites flexural strength, which is a good indication of fibre-matrix adhesion, while showing the composite mechanical performance at the same time. Flexural strength improvement found was 20-24% for hemp-PLA, 23% for flax-PP and 20% for hemp-UP composites. A 20% increase in flexural strength would allow a 10% thinner (=10% less material cost) product, having the same strength performance under loading. Consequently, APP technology may increase the application window of natural fibre composites.

The flexural strength improvement after plasma treatment for flax-PP is similar to that achieved with commercially applied MAPP. It is estimated that using plasma treated flax; about half of the 3 wt.% of MAPP typically applied in 30 wt.% fibre-PP composites may be saved.

The increase in hemp-PLA composite performance due to atmospheric plasma treatment is similar to or exceeding improvements found in literature (**section 3.1.2**) for composites based on chemically treated fibres.

In a comparison with commercial glass fibre based SMC, N_2 plasma treated steam exploded flax based SMC reaches 82% of the flexural strength of glass-SMC and 115% of its flexural modulus, even if the central part of the fibres in the SMC was not well impregnated due to limited resin flow. The natural fibre reinforced SMC composite performance will certainly benefit from improved resin flow.

Natural fibres are known for poor impact performance. Charpy impact strength is not significantly affected by any plasma treatment applied, for neither PP, nor PLA, nor UP based composites. Natural fibre based composites can only be used in applications which are not critical for impact performance.

Effective plasma treatment requires that fibres do not refine during further processing. For extrusion compounds, like PP and PLA based composites, this means that fibres need to be refined prior to plasma treatment. It appears that flax fibres can be sufficiently refined using a Shirley trash separator, and hemp fibres not. A Shirley trash separator is a lab scale version of a kind of carding drum which can be scaled up to industrial scale.

Plasma treated natural fibres may retain their surface modification best when wrapped in aluminium foil. Best way to store plasma treated samples would be in vacuum, however, this would affect the fibre-fibre interaction in such a way that successful further processing into composites is largely hindered.

Plasma treatment is a dry and clean process. The most critical emissions, being ozone and NO_x, may need to be extracted to protect operators, depending on concentration of oxidising dopant to the feed gas. Once in air, ozone quickly decomposes and there are no legal regulations. The annual NO_x emissions of an industrial scale plasma unit are calculated to be in the range of a car travelling 160 – 1200 km, which is considered a small emission for the production of 250 tonnes of treated fibre.

3.3 Options for scale-up, outline financial costing and benefits

3.3.1 Scaling up

3.3.3.1 Plasma treatments

Pilot scale trials at a partner of AcXys in France have shown that the APP technology works well for natural fibre non-wovens at a processing width of 25 cm (**Figure 3.29**). Hemp fibre mats of 25 cm wide and 30 m long were unrolled on a paper belt without further fixation and plasma treated at 2 sides. Plasma treatment parameters were:

- 250 L/min of N_2 at 3 bar. 1.25 L/min of CO_2 at 3.9 bar ('O_2 flow' was set to 1.47 L/min taking into account the required conversion factor)
- 2800 W power = 112 W/cm (178 W/cm for lab scale trials at DLO-FBR)
- Paper belt speed is 0.5 m/min
- Samples treated at both sides
- Oxygen content in the plasma room is 0.4 – 1.2%
- Distance between the ULD and the fibre mat is 3-4 mm
- Gloves were used to handle the fibre material

Figure 3.29*: Pilot scale plasma unit of 25 cm wide (left), treatment of natural fibre non-woven (right)*

At an industrial scale, the width of the ULD system may be increased up to 50 cm and a manifold of this width. Herewith, the APP has proven to be a scalable technology for modification of hemp and flax fibre surface chemical composition while maintaining fibre strength. This allows production of natural fibre reinforced polymer composites with improved fibre-matrix adhesion and consequently improved mechanical performance.

The modification of the fibre surface appears to deteriorate with time (**section 3.2.3.3**). Consequently, shelf life of plasma treated fibres is limited. Based on AcXys' experience, surface modification is best retained when the treated material is packed in aluminium foil. The best way to store plasma treated samples would be in a vacuum, however, this would destroy the non-woven structure to such extent that successful further processing into SMCs will not be possible anymore. It is not clear so far at which party in the supply chain the plasma technology may be best installed:

- The fibre producer will benefit from economy of scales
- The composite manufacturer will be able to keep time between plasma treatment and composite manufacturing shortest

3.3.3.2 SMC sheet manufacturing

Pilot scale SMC sheet production was performed at a partner of Movevirgo in the UK. Thin layers of resin paste were applied on both sides of the hemp non-woven and covered with a thin PE film for ease of handling. Resin:fibre ratio aimed at was 3:1. The amount of resin paste on the hemp fibre mats seemed very low (**Figure 3.30**). Nevertheless, the ratio of resin:hemp was about 3:1 for the 500 g/m^2 hemp mats.

***Figure 3.30**: Protecting film released from SMC sheet, showing distribution of resin paste on hemp mat*

SMC sheet costs are still significantly (about 60%) larger for natural fibre mat based SMCs than for commercial glass fibre based SMC sheet. The way to decrease natural fibre SMC cost is by higher production volumes and ideally by the ability to generate short natural fibres rather than having to use the a form of mat.

3.3.3.3 Industrial moulding: Electrical joint connector

Movevirgo has produced several series of electrical joint connectors (EJC, **Figure 3.31**) based on flax and hemp fibre based SMC sheets. Initial trials showed the importance of mould filling degree. Two needle punched hemp based SMC sheets were impregnated with UP resin paste by Movevirgo and placed in the mould, overlapping in the middle section, thus resulting in a product with 1 and 2 SMC layers on top, respectively, each layer having a fibre content of about 10 wt.%. As the distance between the mould halves is the same for 1 and 2 layers on top, the actual difference between the 1 and 2 layer sections is a factor of 2 difference in fibre content. Test specimens were cut from the flat areas of the EJCs and evaluated for flexural performance, coded MV-2 and MV-3, respectively (**Table 3.8**). These results confirm lab scale trials at Wageningen UR–FBR: composite performance increases with fibre content. It may be concluded that, although variation of glass fibre SMC flexural strength is very high, the average strength of the hemp based SMC MV-3 is similar to that of the commercial glass fibre based MV-7. Further, it may be concluded that the performance of the best industrially moulded EJCs exceeds the best lab scale moulded SMCs, which is due to better moulding and resulting in low void content.

Previous research has shown that the moisture present in natural fibres, typically about 10%, limits adhesion between fibres and unsaturated polyester. At lab scale processing, fibres could be easily dried and stored at dry conditions until final SMC moulding. For the pilot scale trials, fibres were not dried as equipment was not adapted to keep fibres dry. Keeping fibres dry at industrial scale requires some modifications of the processing equipment, and may result in better composite performance than achieved in the present pilot scale trials.

***Figure 3.31**: Electrical joint connector, moulded by Movevirgo*

Table 3.8: Flexural properties of test specimens cut from industrially moulded SMC composite product

Code	Fibre grade	Flexural strength		Flexural modulus		Strain at max Strength	
		(MPa)	StDev	(GPa)	StDev	(%)	StDev
MV-2	1 layer needle punched hemp	49.5	11.7	5.72	0.08	1.68	0.58
MV-3	2 layers needle punched hemp	112.8	12.1	5.43	0.91	3.39	0.09
MV-5	PLA thermobonded hemp	75.3	9.3	7.52	0.43	1.53	0.31
MV-7	Commercial glass fibre SMC	116.3	71	9.5	2.18	1.97	0.98

As needle punched mats show a low level of stretching during 3D moulding, cutting and placing of SMC sheets in the mould is very critical for obtaining a homogeneously reinforced product. Otherwise, the fibre mat will be easily torn apart, leaving areas poor of fibres and rich in resin. Also, poor flow of natural fibre mats could mean that high shear forces are resulting in pinch off areas of a mould, and consequently may cause mould deterioration. Consequently, it is important that the fibres flow with the resin during moulding.

As needle punching restricts stretching of a fibre web too much, it was decided to evaluate a just air laid fibre web without needle punching. These non-bonded, non-woven reinforcement materials have proved to be delicate in their makeup which, although helping the wet through of the resin paste, causes issues in the preparation of the materials for running on the SMC machine. If this type of material were to be selected a powered supply roller option would need to be considered as the material is not strong enough to allow it to be drawn off the roll during the production process without tearing and breaking. In particular also during moulding the non-bonded mats required careful handling.

An alternative would be to use chopped fibres, but investigations to date have shown that, due to the nature of the fibre, consistent fibre length and a clean cut are difficult to achieve consistently.

Further, it is expected that a thermobonded hemp non-wovens might exhibit better ‘fibre flow’ during SMC moulding than needle punched non-wovens. Therefore, Movevirgo has sourced a PLA thermobonded hemp fibre non-woven from Advance Non-Woven (Denmark). With the PLA thermobonded mat, SMC cutting and placing appears more forgiving: due to its almost elastic property it is easier for the mat to stretch into all areas of the mould cavity. Whereas glass fibre filled SMC can actually ‘flow’ due to the use of short length fibres, the thermobonded hemp mat rather ‘moves’ inside the mould cavity. Herewith, thermobonded natural fibre based SMCs show enough stretch to be industrially moulded.

The sourced thermobonded hemp mat, however, appeared to exhibit a rather uneven fibre distribution, which may lead to weak areas in the moulded product. Indeed, the performance of composites based on pilot scale plasma treatment and SMC production only shows about 65% of glass fibre SMC flexural strength and about 80% of glass fibre SMC modulus (**Table 3.8**). These relative differences correspond very well with lab scale trials which have shown that the flexural strength of PLA thermobonded hemp based SMCs is 30% lower than for the needle punched hemp non-wovens. It may be concluded that optimal natural fibre based SMC composites:

- Contain high enough fibre content, at least > 20%
- Show sufficient fibre stretch/flow
- Require that the negative parameter in the PLA thermobonded hemp non-woven will be identified and eliminated, parameters may be inhomogeneous fibre distribution causing fibre poor/resin rich areas or the PLA itself

The pilot scale plasma treatments appeared to have limited positive effect on SMC composite performance. This was considered due to the inhomogeneous fibre distribution, causing weak spots acting as the weakest link in the composite. A second series based on ultrasonically treated fibres showed limited effect of plasma due to low fibre content, being 14–19%. Heat deflection temperature (HDT), however, increased after plasma treatment, up to 40%. HDT of the best performing hemp based SMC was 190 °C, close to the value for glass based SMC which was > 200 °C.

Mass balance analysis indicated that the hemp based SMCs lost up to 8% by weight during moulding, versus 1–2% for glass fibre based SMC. The weight loss is attributed to evaporation of styrene mainly. As styrene is the reactive solvent of the UP resin and a human toxic component, measures should be taken to reduce evaporation of styrene. Adequately closing moulds and extraction hoods are required.

Several composite products showed warping after moulding, both at lab scale as well as after industrial moulding, although, not all composites showed warping. The origin of the warping is not clear so far and requires further investigation. Warping of flat SMC composite plaques seems to correlate with fibre content: warping decreases with increasing fibre content (**Figure 3.32**), although variation in warping is very high.

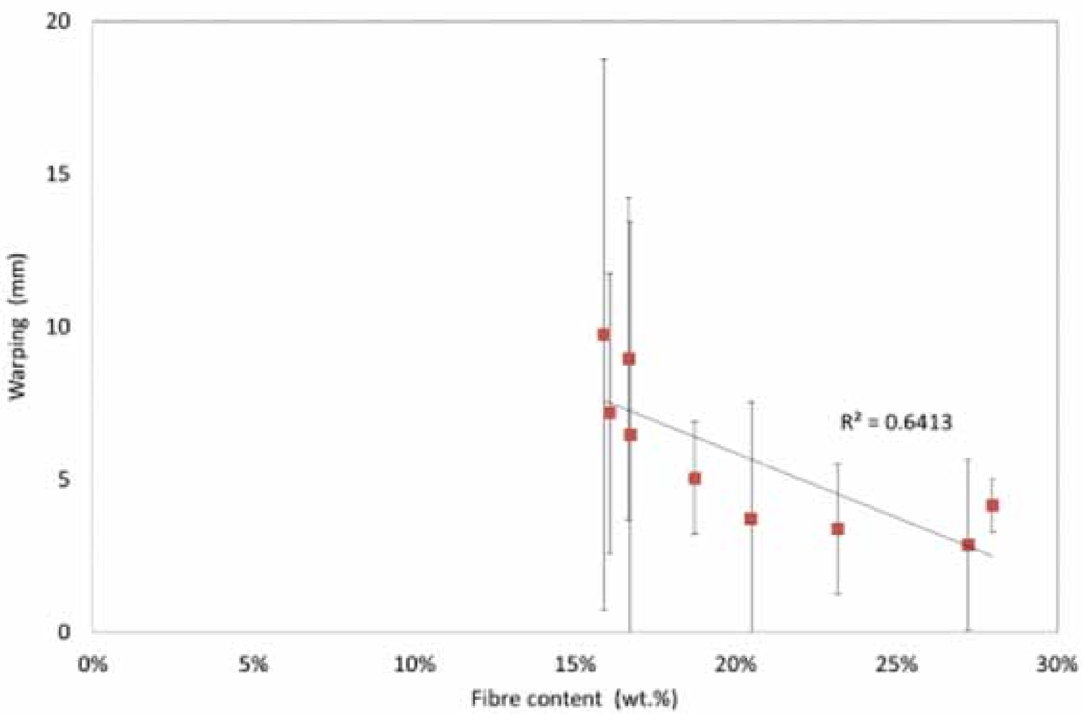

***Figure 3.32**: Warping of SMC composite plaques versus fibre content*

3.3.2 Economic calculations

The cost analysis of the plasma treatment of natural fibres for reinforced composites is based on the following assumptions:

- Expected cost of 100 cm ULD system is in the range € 80.000 – 150.000. € 100.000 is supposed to be a good estimate
- Depreciation time of 5 years is a typical period, no interest is calculated
- 40 working hours per week, 45 weeks per year
- Gas consumption of 60 l/min as used for current lab trials, which equals 10 l/min per 1 cm of ULD. Prices as paid by Wageningen UR–FBR for liquid N_2 in tank and dopant gases in bottles:
  - N_2: 10 l_{gas}/min.cm at 646 l_{gas}/l_{liquid} at 0.156 €/l_{liquid}
  - O_2: 0.05 l_{gas}/min.cm at 798 l_{gas}/l_{liquid} at 1.95 €/l_{liquid}
  - CO_2: 0.05 l_{gas}/min.cm at 513 l_{gas}/l_{liquid} at 1.18 €/l_{liquid}
  - N_2O: 0.05 l_{gas}/min.cm at 664 l_{gas}/l_{liquid} at 2.68 €/l_{liquid}
  - H_2: 0.1 l_{gas}/min.cm at 788 l_{gas}/l_{liquid} at 0.94 €/l_{liquid}
- Maintenance costs are in the range of 2-4% of total investment/year. 3% is a good average estimate
- Non-woven weight of 170 and 500 g/m^2 for flax and hemp as for lab and pilot scale trials for UP composites as performed in this project, or 1000 g/m^2 as estimated upper limits. Hemp m^2-weight was higher than for flax because of the coarser nature of the hemp fibres
- Plasma treatment at both sides
- Processing speed of 0.48 m/min as for current lab trials, or 10 m/min as an estimated upper limit
- 0.2 operator at 15 €/h to operate the machine (Machine should require human assistance mainly when starting a new batch, which can be a roll of non-woven)
- Power consumption of 1065 kW for a 6 cm wide ULD plasma source including the belt system = 178 W/cm ULD at 0.22 €/kWh

Natural fibre-UP composites

Plasma treatment costs as a function of processing rate and fibre mat weight, and based on the previous assumptions are presented in **Figure 3.33**. Since there is no regular commercial coupling agent available for UP matrix composites (coupling agent is usually applied in the sizing of glass fibres), cost savings could be made due to a possible decrease of material amount required to obtain the same level of mechanical performance. Assuming a flexural strength improvement of 20% as found for plasma treated hemp-UP composites, about 10% thinner product is required to provide the strength level of untreated hemp-UP composite. Assuming hemp-UP SMC sheet costs of about 3 €/kg, cost savings are 0.30 €/kg of composite or 1.2 €/kg of fibre for a 25 wt.% fibre composite. Translation of plasma processing parameters successfully applied in this study to industrial scale production shows a cost level which is higher than the savings made by requiring 10% less material to achieve the same level of flexural strength (**Figure 3.33**). Breakeven will be achieved if the effective treatment speed for hemp mats (500 g/m^2) can be increased to about 2 m/min, while providing the same adhesion and strength improvement.

The plasma processing may be optimised in terms of production hours/day (from 8 to 16 h) and gas consumption (AcXys' gas 'recycling technology' allows a gas consumption reduction from 60 to 15 l/min if the recycled gas can be filtered free of fibre/dust particles). At these conditions, breakeven will be achieved at a treatment speed of about 1 m/min (**Figure 3.34**). In order to make plasma treatment a cost effective technology to improve natural fibre composite performance, processing speed needs to be increased by a factor of 2-10 compared to rates applied in this study, while providing the same adhesion and strength improvement.

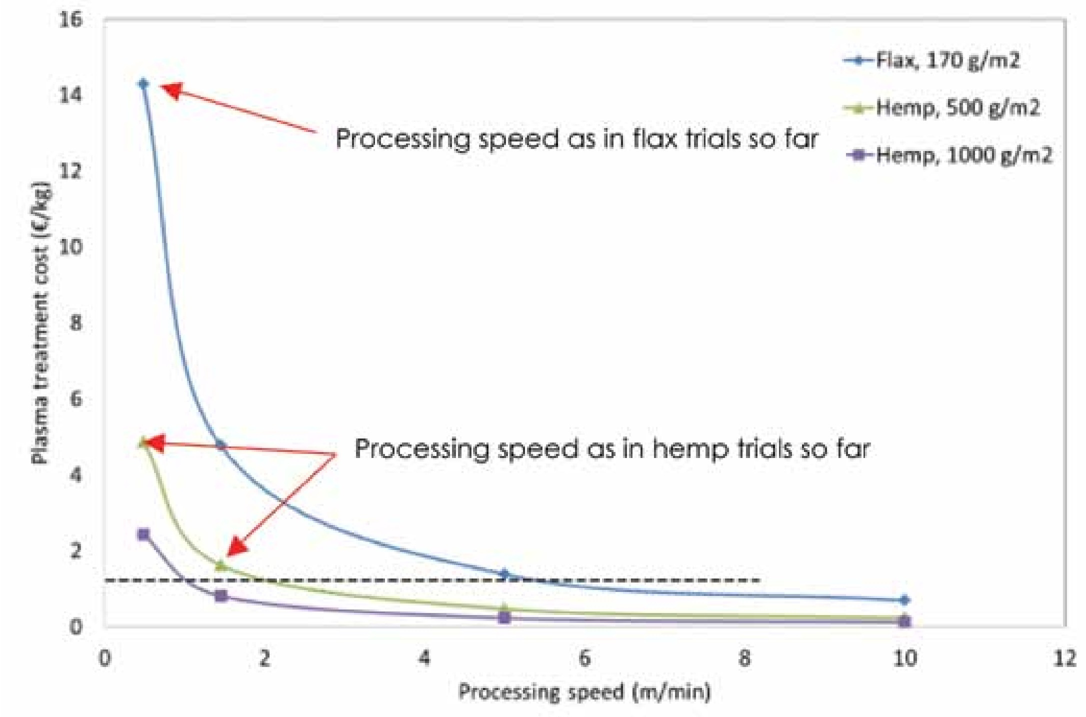

***Figure 3.33**: Plasma treatment cost per kg of fibre based on assumptions summarised previously. Dashed line represents cost savings level for hemp-UP SMC with 20% improvement of strength*

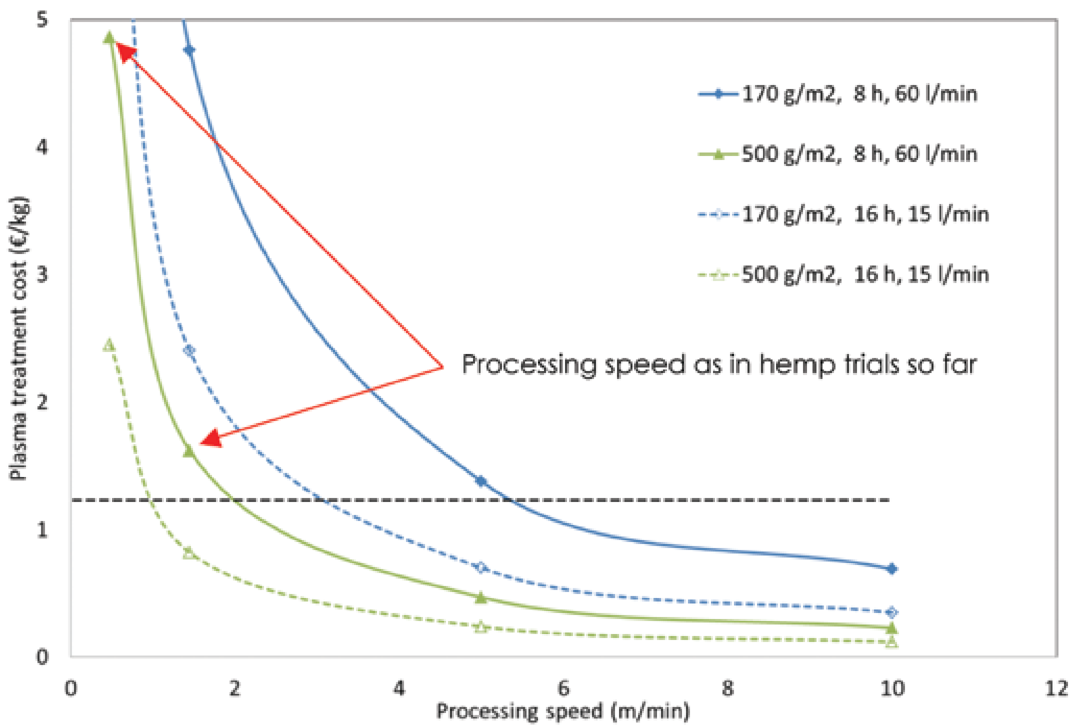

***Figure 3.34**: Plasma treatment cost when operating 16 h/day and using gas flow of 15 l/min. Dashed line represents material cost savings level for hemp-UP SMC with 20% improvement of flexural strength*

Suggestions to improve plasma treatment effectiveness and efficiency by applying reactive couple agents have addressed in **section 3.2.3.6**.

Natural fibre-PP

Assuming plasma treatment conferring a saving potential of 1.5% of the 3% MAPP in a 30 wt.% natural fibre-PP composite, and MAPP cost of 4 €/kg, cost savings would be 0.30 €/kg of fibre for a 30 wt.% fibre composite. The techno-economic analysis suggests that, at present conditions, the costs of effective plasma treatment of refined fibres for PP based injection moulding compounds will be significantly higher than costs for using commercial MAPP coupling agent.

Natural fibre-PLA

Since no commercial coupling agent is available for UP based natural fibre reinforced composites, plasma treatment may be an option. Cost savings can be made due to a possible decrease of material amount used to obtain the same level of mechanical performance. Assuming a flexural strength improvement of 20-24% as found for hemp-PLA compounds, about 10% thinner product is required to provide the strength level of untreated hemp-PLA composite. Assuming hemp-PLA composite costs 3 €/kg, cost savings are 0.3 €/kg of composite or 1 €/kg of fibre for a 30 wt.% fibre composite. Most probably, costs savings will be higher because the estimated cost/kg of PLA composite is low and thinner products would allow shorter cycle times. For natural fibre mat reinforced PLA composites (PLA based NMTs), the economic calculations will be similar to those presented previously for the UP based composites: breakeven will be achieved at slightly higher processing rates as the savings level is slightly lower for PLA.

For injection compounds, cost level is more negative due to lower fibre mat weight (refined fibre mats are more lofty and effective plasma treatment allows lower m^2-weight) and refining costs.

3.4 Summary and conclusions

Research at Wageningen UR–FBR and AcXys has shown that the chemical composition of natural fibre surfaces can be significantly modified by applying atmospheric pressure plasma (APP) technology. The actual modification depends on the plasma feed gas composition. In other words, the modification of chemical composition of the fibre surface can be steered by selecting the feed gas composition. Even natural fibre surfaces with a hydrophobic character have been obtained. At the same time, hemp and flax fibre strength is not significantly affected for any plasma treatment applied. This means that the reinforcing potential of the fibres is kept intact.

AcXys has developed and produced a scalable APP process, which allows treatment of natural fibres in different forms: short natural fibres which are mostly used in extrusion and injection moulded products, as well as in sheet moulding compounds (SMC), natural fibre roving (sliver) being of interest for pultruded composites, and non-wovens which may be used in vacuum assisted resin transfer moulded thermoset composite products (VA-RTM), SMCs and natural fibre mat thermoplastic composites (NMT). The APP technology can be easily scaled up to widths of 50 cm and a manifold of this width in order to allow high volume processing, as will be required for mass production composite applications. In contrast, low vacuum plasma treatment technology is a batch process.

Particular plasma treatments result in improved composites flexural strength, which is a good indication of fibre-matrix adhesion, while showing the composite mechanical performance at the same time. Flexural strength improvement found was 20-24% for hemp-PLA composites, 23% for flax-PP composites and 20% for hemp-UP based SMC composites. A 20% increase in flexural strength would allow a 10% thinner product (=10% less material cost), having the same strength performance under loading. Consequently, APP technology may increase the application window of natural fibre composites.

In order to meet customers demand for greener materials and products, composite resins with bio-based content are being developed and marketed. Some ‘green resins’ however, contain no more than about 10 wt.% of bio-based components. The use of natural fibres may substantially add to the bio-based content of SMC composites. Pilot scale trials making an SMC based electrical joint connector at Movevirgo show that the average strength of a hemp based SMC is very close (97%) to that of a commercial glass fibre based SMC, although variation of glass fibre SMC flexural strength was very high. Lab scale trials showed that flax based SMC may outperform glass fibre SMC flexural stiffness by 15%.

Natural fibres contain typically about 10% of moisture at regular environmental conditions. Previous research has shown that this moisture limits adhesion between fibres and unsaturated polyester. For the pilot scale trials, fibres were not dried as equipment was not adapted to keep fibres dry. Keeping fibres dry at industrial scale requires some modifications of the processing equipment, and may result in better composite performance than achieved in the present pilot scale trials.

Needle punched mats exhibit a low level of stretching during industrial moulding, which triggers tearing apart of the mat, causing inhomogeneous composites with areas poor of fibres and rich in resin. Thermobonded hemp mats appear to be elastic enough to stretch into all areas of the 3D SMC mould cavity, making SMC cutting and placing rather forgiving, more than needle punched mats do. The PLA thermobonded hemp mats used in this project, however, exhibited rather uneven fibre distribution, which results in inhomogeneous composites with relatively poor performance. A homogeneous fibre mat is required to make natural fibres an interesting alternative for UP based SMC composites.

Effective plasma treatment requires that fibres do not refine during further processing. For thermoplastic extrusion compounds, like PP and PLA based composites, this means that fibres need to be refined prior to plasma treatment. It appears that flax fibres can be sufficiently refined using a Shirley trash separator, whereas hemp fibres cannot. A Shirley trash separator is a lab scale version of a kind of carding drum which can be scaled up to industrial scale.

The modification of the fibre surface appears to deteriorate slowly with time proceeding, meaning that the shelf life of plasma treated fibres is limited. The best way to retain surface modification is packing the material in aluminium foil. It is not clear so far at which party in the supply chain the plasma technology may be best installed:

- The fibre producer will benefit from economy of scales
- The composite manufacturer will be able to keep time between plasma treatment and composite manufacturing shortest

Plasma treated natural fibres may retain their surface modification best when wrapped in aluminium foil. Best way to store plasma treated samples would be in vacuum, however, this would affect the fibre-fibre interaction in such a way that successful further processing into composites is largely hindered.

Plasma treatment is a dry and clean process. The most critical emissions, being ozone and NO_x, may need to be extracted to protect operators, depending on concentration of oxidising dopant to the feed gas. Once in air, ozone quickly decomposes and there are no legal regulations. The annual NO_x emissions of an industrial scale plasma unit are calculated to be in the range of a car travelling 160 – 1200 km, which is considered a small emission for the production of 250 tonnes of treated fibre.

The techno-economic evaluation indicates that the APP technology will be economically feasible if the processing speed can be increased by a factor of 2–10 compared to rates applied in this study for UP, PLA and PP composites, while providing the same adhesion and strength improvement. Most interesting composites are those based on coarse fibre mats like unsaturated polyester based SMCs and natural fibre mat thermoplastic composites (NMTs).

In order to further improve the effectiveness/efficiency of plasma treatment for improved natural fibre-UP adhesion, the use of chemical reactants has been considered. A bi-active chemical agent may react with the plasma activated fibre surface on one end and with the polymer matrix on the other end. Discussions with specialists in organic chemistry at Wageningen UR–FBR have delivered a route based on Glycidyl methacrylate for the UP based SMCs. First results show that effective processing conditions have not been established so far.

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4

Processing

4.1 Overview of processing options for fibres

This chapter describes the best practice for extrusion compounding, using natural fibres treated by the UltraFibre process. The objectives of the UltraFibre project were:

1) To produce compound formulations for use in the production of sustainable composites,

2) To evaluate the performance and processing characteristics of the natural fibres produced with the UltraFibre process using laboratory scale and pilot plant processing equipment,

3) To develop an extruder rig to allow for effective homogenisation of the fibre with the matrix,

4) To produce pilot plant scale quantities of the compound, and

5) To carry out industrial scale validation of the composite materials

In the past decade, industry has shown a keen interest in the fact that natural fibres, such as flax and hemp can be an excellent renewable and sustainable substitute for glass fibres as reinforcement in thermoplastic and thermoset composite materials. Natural fibres have good intrinsic mechanical properties, a low density compared to glass fibres as well as a lower price. Research publications nearly all show a composite stiffness for flax and hemp fibre reinforced composites close to or even higher than that of commercial glass mat reinforced thermoplastic composites and thermoset sheet moulding compound (SMC) [1, 2, 3]. However, in most cases, the strength of the natural fibre composites, was low compared to the strength of the glass fibre reinforced composites [2, 4]. This is basically due to the composite-like structure of natural fibres [5]; they are not generally single filaments as most man-made fibres are but they can have several physical forms, which depend on the degree of fibre isolation. The physical form of the natural fibres should be taken into account when evaluating natural fibre-based composites.

The physical form of the flax and hemp fibres present in the composite materials ranges from fibre bundles to elementary fibres, or to even further opened-up shapes (**Figure 4.1**). The mechanical properties of these different fibre forms differ strongly. Flax and hemp fibre bundles are obtained after the first isolation processes called breaking and scutching. These fibre bundles have an acceptable price-performance ratio and are often commercially used in natural fibre mat thermoplastic (NMT) and thermoset composites. Their lateral strength is rather poor compared with their axial strength, mainly due to the weak pectin bonds between the so-called ‘technical fibres’. The really strong fibres are the elementary fibres, which have an average tensile strength up to 1500 MPa.

The combination of cellulose content per weight unit of a natural fibre source and their fibre form largely determines the amount of reinforcement obtained with the extrusion compounded composite granules. For example, cellulose-rich flax bast fibres, which can also be further opened-up to give relatively thin elementary fibres, can have a dramatically different reinforcing effect on the thermoplastic matrix compared with softwood powder. The latter has a lower cellulose content and a lower aspect ratio. As a result wood flower will act more like a filler in extrusion compounded granules, whereas flax and hemp fibres will act more like a true reinforcing agent.

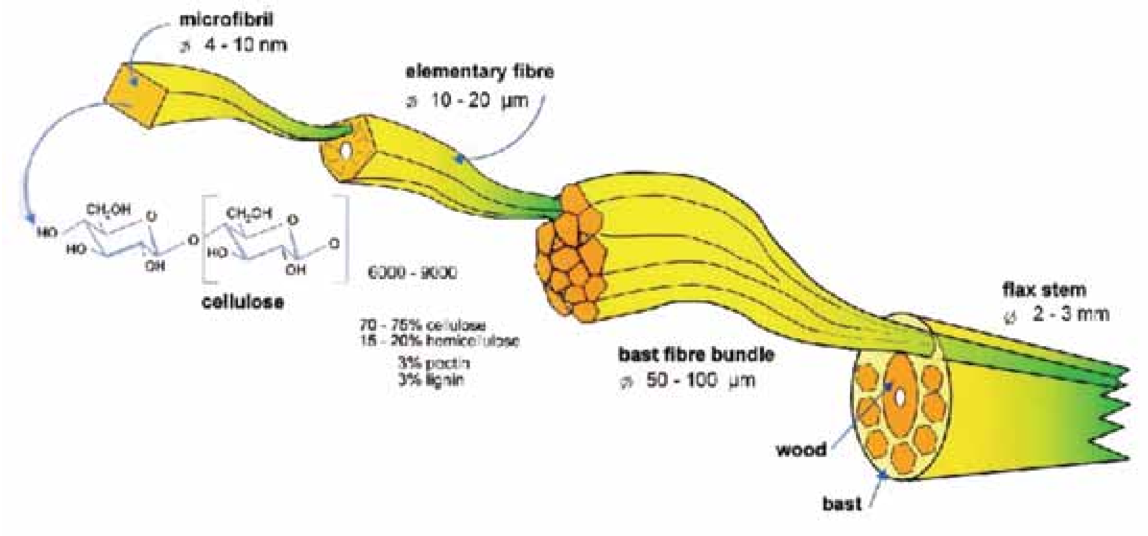

***Figure 4.1**: Flax fibre structure*

These intrinsic natural fibre properties should be taken into account when designing a process and product route, which is an alternative to the traditional (for example chalk) filled or glass fibre reinforced composite materials. To technically compete with the properties of glass fibre reinforced extrusion compounded granules, it is essential to pay as much attention to the fibre-matrix dispersion as to its distribution. The latter determines to what extent fibres are homogeneously mixed into the matrix, the former determines the form/aspect ratio or in other words: the extent to which the natural fibre is opened-up to a smaller fibre dimension. By using the right extrusion compounding technology, bast fibres – such as flax and hemp - can be both homogeneously mixed through the thermoplastic matrix, and opened up to elementary fibres, which have the preferred high aspect ratio. The resulting mechanical properties of the compounded granules are such that they can compete with glass fibre reinforced thermoplastics.

4.2 Results and technical benefits

4.2.1 Introduction

Using extrusion compounding, the UltraFibre project aimed to apply ultrasound and plasma treatment processing for surface modification of flax and hemp fibres, to obtain improved compatibility and adhesion to polymer matrices. At the same time, the treatment should not weaken the fibres, which is often observed after chemical modifications of natural fibres. The goal was to achieve a 25% increase in mechanical properties compared with the untreated fibres.

In close co-operation with Smithers Rapra (SR) and with technical input from GreenGran and ICMA (Milan, Italy), regarding specific fibre form requirements, InControl Ultrasonics has designed and manufactured an ultrasound fibre treatment (USF) unit. It allows for the treatment of several forms of natural fibres, which are used in different composite processing techniques.

In order to focus on finding the right fibre form and the resulting fibre/polymer property requirements for future commercial applications, a specific target product was first defined: surfboard fittings. Based on the currently used polymer materials the products' requirements were determined in terms of mechanical performance, mainly its required stiffness and strength.

Several formulations were produced in laboratory, pilot and industrial extrusion compounding machinery, using polypropylene (PP) and untreated natural fibres. Their properties were measured and as such set as reference levels for USF/polymer compounds.

4.2.2 From end product requirements to laboratory scale reference compounds

Now that surfboard fittings had been defined as a specific target product (see **Figure 4.2**), the products' requirements were determined in terms of mechanical performance, mainly its required stiffness and strength.

***Figure 4.2**: Surfboard fittings - the first specific target product*

The requirements of the specific target product – based on the material properties of polyamide – were defined as:

- Flexural modulus: 1,600 MPa
- Flexural strength: 65 MPa
- Izod notched impact: 70 kJ/m^2
- Tensile strength: 50 MPa

Two formulations were produced industrially: PP with 30 or 40 wt.% fibre. Their properties were also measured and as such set as reference levels for future UltraFibre treated fibre/polymer compounds. These properties are:

For PP with 30 wt.% natural fibres:

- Charpy unnotched impact: 22 kJ/m^2
- Flexural modulus: 3,038 MPa
- Flexural strength: 71 MPa

For PP with 40 wt.% natural fibres:

- Charpy unnotched impact: 18 kJ/m^2
- Flexural modulus: 4,080 MPa
- Flexural strength: 79 MPa
- Tensile strength: 47 MPa

Several laboratory mixing devices were evaluated for their suitability for the specific tasks, including the minimixer, the Hampden internal mixer and a 21 mm Rondol twin-screw extruder.

Materials: it has been decided to start with flax bast fibres for making the natural fibre composites reference material.

With both compounding methods, i.e., batch kneader and laboratory extruder, loose fibres were used first, for two reasons:

- Fibre pelletising requires a substantial amount of fibres, which for the UltraFibre-treated fibres were not available at that stage
- Fibre pelletising might negatively influence the effect of the UltraFibre-treatments, due to the severe mechanical forces being put upon the fibres during pelletising

Gravimetric feeding of untreated chopped flax fibres without modification on the laboratory extruder turned out to be difficult. The fibres are fluffy by nature, causing blockages at the feeder, which also made it difficult to feed the fibres through at higher fibre contents. The maximum level of chopped flax fibres was found to be 30 wt.%.

Industrially produced pre-pelletised fibres did not show these limitations. Here fibres with a content up to 50 wt.% were fed through the extruder without any problems. To anticipate this, a laboratory scale pellet-mill for preparing fibre pellets was used (**Figure 4.3**).

***Figure 4.3**: Turning loose fibres to fibre pellets by using a pellet mill*

Due to its scaling capabilities, extrusion compounding was selected as the mixing method. **Figure 4.4** shows a schematic drawing of the reference laboratory scale compounding process. PP granules are being fed upstream in the co-rotating twin-screw extruder, which is pre-heated at 195 °C. Further downstream, fibre-pellets were mixed with the melted PP by using a side-feeder. In the final stage, PP and fibres are homogeneously mixed, by fibre-matrix dispersive and distributive action. This combination ensures optimum fibre distribution with the maximum achievable fibre length-to-diameter (aspect) ratio.

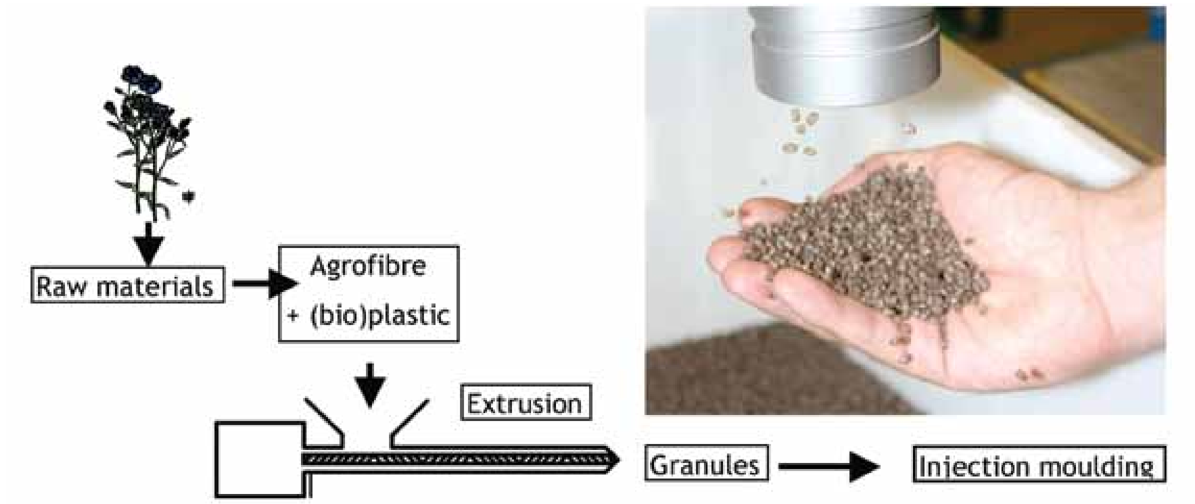

***Figure 4.4**: Schematic drawing of the compounding process*

At first it turned out to be difficult to produce laboratory scale untreated fibre pellets having the equivalent properties needed for industrial compounding. This appeared not a problem with the fibre, but rather an intrinsic problem with the machine. Rather than producing soft pellets the fibres were 'crushed' into powder. In addition, cutting 6 mm fibres into smaller sizes, created bridging problems when feeding it into the extruder, because of its more fluffy nature.

It was demonstrated in practice, by using reference fibres for laboratory extrusion compounding, that, for sufficient upscaling, fibres are being fed as 'bast fibre bundles' (diameter 50-100 μm) and need to have the minimum possible fibre length ~ 2-4 mm prior to feeding. However, feeding trials using hemp technical fibres, of length ~ 2-4 mm, were unsuccessful. Even with the small fibre length, in fact, the smallest length commercially available, fibres were still too fluffy, which caused continuous feeding problems and bridging problems at the feeder's entrance.

The solution was found by changing the pelletising conditions using the 2-4 mm hemp fibres. Now soft reference hemp fibre pellets were produced, which were successfully fed in to the 21 mm Rondol extruder.

Compounding quality was further improved by selecting the right combination of screw configuration ***versus*** PP melt flow. The latter was created by using mixing screw elements, transportation screw elements which vary in screw speed, and by selection of a medium melt flow PP. **Figure 4.5**, shows the schematic drawing of the optimum screw configuration for compounding at the laboratory scale.

The screw configuration as shown in **Figure 4.5** turned out to be successful, both for feeding the pellets and for making homogeneously distributed fibre/polymer compounds.

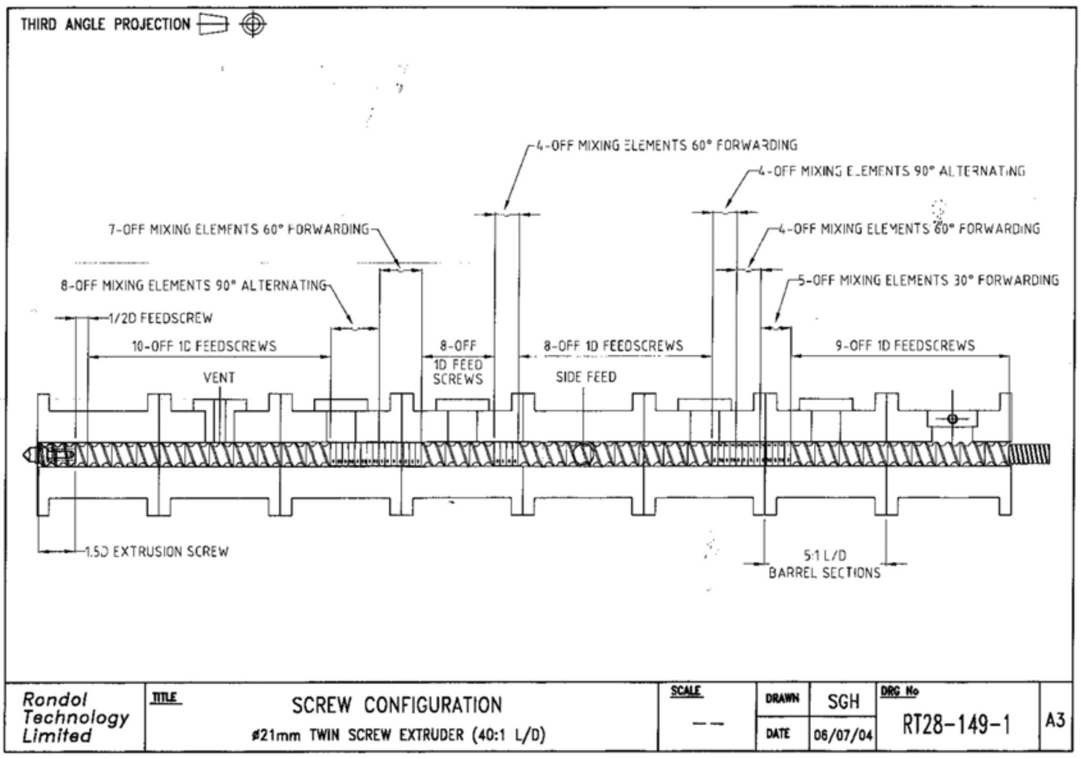

***Figure 4.5**: Schematic drawing of the compounding screw configuration*

4.2.3 From laboratory scale reference compounds to UltraFibre treated compounds

Although flax had been used as the initial fibre source, the consortium decided to include – and in time change to – hemp as the fibre source for scaling up. In the interim, both fibre sources were used for securing a proper benchmark transition. Due to the limited availability of both ultrasound and plasma treated fibres, all compounds were first produced by using batch kneaders. This is an efficient way: (1) to reduce material used, and (2) to screen many different compound compositions. Also, the properties of compounded compositions are representative for continuous extrusion compounding.

The following series of compounds were compounded and injection moulded using the Haake batch kneader:

- 30% of Shirley treated flax in 70% PP (575P)
- 30% of Shirley treated flax in 1% MAPP (G3015) + 69% PP
- 30% of Shirley treated flax in 3% MAPP + 67% PP
- 30% of N_2 Shirley treated flax in 70% PP
- 30% of N_2 Shirley treated flax in 1% MAPP + 69% PP
- 30% of Shirley treated hemp in 70% PP
- 30% of Shirley treated hemp in 1% MAPP + 69% PP
- 30% of Shirley treated hemp in 3% MAPP + 67% PP
- 30% of N_2 + Shirley treated hemp in 70% PP
- 30% of N_2 + O_2 + Shirley treated hemp in 70% PP
- 30% of N_2 + O_2 + Shirley treated hemp in 1% MAPP + 69% PP
- 30% of N_2 + CO_2 + Shirley treated hemp in 70% PP
- 30% of N_2 + CO_2 + Shirley treated hemp in 1% MAPP + 69% PP
- 30% of Shirley treated hemp in 70% polylactic acid (PLA)
- 30% of N_2 + O_2 + Shirley treated hemp in PLA
- 30% of N_2 + CO_2 + Shirley treated hemp in PLA
- 30% untreated fibres in 3% MAPP + 67% PP
- 30% Shirley/ultrasound treated fibres in 3% MAPP + 67% PP

Results for the composites' mechanical properties – see **Chapter 3** for further details – revealed that plasma treatment of flax fibres does increase the PP composite strength significantly, whereas plasma treatment of hemp fibres does not increase the PP composite strength. This is explained by the fact that plasma treatment on flax was effectively performed at the surface of clean elementary fibres. In contrast, the hemp fibres were partly unrefined prior to plasma treatment; compounding of the treated hemp further opens up the fibre bundles, which exposes a large area of non-plasma treated fibre surface.

Even though plasma treatment gives a technical advantage when treating clean elementary fibres – and suggesting potential cost advantages by reducing the amount of coupling agent for composite compounding – it turned out not to be the route to follow for scaling up the extrusion compounding; its rationale is explained next.

When scaling up the minimum fibre throughput needed is increased. The fibre feeding units require that the fibres are packed densely in order to meet the minimum throughputs and to prevent bridging problems in the feeders. The following fibre shapes were evaluated:

- Reference hemp elementary fibres
- Reference hemp technical fibres, length ~ 10 mm
- Reference hemp technical fibres, length ~ 2-4 mm

Feeding trials failed for both hemp elementary fibres and for hemp technical fibres, length ~ 10 mm. Both fibre sources were too fluffy, which caused bridging problems at the feeder's entrance. Also, the throughput was too low for proper compounding.

The technological feeding requirements for scaling up create a dilemma when considering the form of the successfully plasma treated fibres. Plasma treatment only worked effectively on elementary fibres, of thin layers, whereas extrusion compounding required technical fibres of 2-4 mm length, or for higher densities such as fibre pellets. Plasma treatment is ineffective after fibre pelletising. Because fibres in pellet form are needed, the fibres should be plasma treated prior to pelletising. In doing so the 'surface-activating' effect of the plasma treatment is largely/completely cancelled by the high mechanical forces being put upon the fibres during pelletising. In other words: plasma treated fibres are not surface-activated anymore after pelletising. The dilemma was discussed with all parties involved. It was decided to use plasma treatment specifically for non-woven mats, to produce NMT and SMC composites. For extrusion compounding, only ultrasound treated fibres were further evaluated for their composite performance.

4.2.4 Scale up UltraFibre-treated PP compounding

Previous fibre feeding issues had been tackled at Smithers Rapra by using soft fibre pellets instead. For technology transfer to ICMA it was essential that fibre feeding issues – especially bridging problems – would not occur. Having screw diameters of a similar size at ICMA and taking into account that 6 mm diameter pellets worked at Smithers Rapra, it was decided to have pellets of a maximum 5 mm diameter produced by an external manufacturer. As a result bridging issues during the pellets' feeding at ICMA did not occur.

A series of PP/hemp compound batches were produced using ICMA's co-rotating twin-screw extruder. The same quality raw materials – PP homopolymer, MAPP coupling agent and hemp bast-fibre having 10% woody particles - as used at Smithers Rapra were used. The same applies for the compounds' composition. Three critical processing parameters were varied in order to verify their influence on the resulting composites' properties:

- Screw configuration → SR's screw ***versus*** ICMA proprietary screw for making wood plastic composites (WPC)
- Screw speed → from 100 rpm to 150 rpm
- Compounds' throughput → from 10 kg/h to 15 kg/h. Smaller and larger throughputs resulted in continuity problems and were not used further

The six different batches, including their processing parameters are listed in **Table 4.1**.

Table 4.1 Compounds' batches with varying processing parameters

Batch name	Screw type	Screw speed (rpm)	Throughput (kg/h)
1-24	SR	100	10
1-25	ICMA	100	10
2-24	SR	150	10
2-25	ICMA	150	10
3-24	SR	150	15
3-25	ICMA	150	15

Figure 4.6 shows the typical compounding conditions for melt temperature, barrel set temperatures, torque and pressure.

***Figure 4.6**: Typical compounding conditions*

Figure 4.7 shows a typical compounding line. A dry blend of PP and MAPP is fed upstream, whereas hemp fibre pellets are fed downstream, in the melted mass. The resulting compound leaves the extruder as melted strands, which were quench-cooled in a waterbath and then granulated.

(a) (b)

***Figure 4.7**: A typical compounding line: (a) overview and (b) strand granulation detail*

All six compounding conditions resulted in homogeneous compounds. When the compounds were examined by the naked eye, the fibres/pellets were well distributed in the polymeric matrix.

Next, the six batches were shipped to CESAP (Verdellino/Zingonia, Italy). There, they were predried, injection moulded, conditioned to bypass the effect of post-crystallisation and their material properties were measured.

Figure 4.8 summarises the material properties of the six batches.

CON IL PATROCINIO DI: UNIONPLAST, ASSOCOMAPLAST,
UNIONE INDUSTRIALI DI BERGAMO,
TORINO, TREVISO E VARESE,
APILOMBARDA, ASSOCIAZIONE E
UNIONE ARTIGIANI DI BERGAMO

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ULTRAFIBRE TESTS

SPECIMENS INJECTION MOULDED

Test	Tensile strenght at break	Tensile strain at break	Flexural elastic modulus	Charpy notched impact strenght	*Heat deflection temperature HDT	Flammability UL 94 V
Standard	ISO 527-1-2 (5 mm/min)	ISO 527-1-2 (5 mm/min)	ISO 178 (2 mm/min)	179-1	ISO 75-1-2 (1.80 MPa)	UL 94 V (1.6 mm)
Unit	MPa	%	MPa	KJ/m²	°C	Class
PP raw mat.	29.0	830	1150	2.40	60	N.C
1-24	34.7	3.5	2470	4.25	89	N.C.
1-25	36.0	3.3	2560	4.17	94	N.C.
2-24	38.3	3.6	2590	3.89	99	N.C.
2-25	35.7	3.5	2620	4.11	101	N.C.
3-24	34.6	3.5	2600	4.20	89	N.C.
3-25	36.0	3.8	2600	3.86	96	N.C.

* the HDT tests carried out on the six samples with fibers have shown results with a high variability (also more than 10°C among the specimens tested, at least four for each sample), because of this the values of temperature indicated are to be considered approximate.

In the tensile test for the sample PP raw material is indicated the yield strength instead of the break strength (the samples with fibers don't yield).

In the UL 94 test the specimens of all the samples burn completely after the first application of the flame, so they are not classified according to UL 94 V (V0, V1, V2).

SPECIMENS INJECTION MOULDED AND CONDITIONED IN WATER FOR 24 H AT 23°C

Test	Tensile strenght at break	Tensile strain at break	Flexural elastic modulus	Charpy notched impact strenght
Standard	ISO 527-1-2 (5 mm/min)	ISO 527-1-2 (5 mm/min)	ISO 178 (2 mm/min)	179-1
Unit	MPa	%	MPa	KJ/m²
1-24	32.4	2.8	2490	4.03
1-25	32.3	2.9	2530	4.10
2-24	35.2	3.1	2610	4.00
2-25	33.4	2.9	2500	4.40
3-24	33.2	3.0	2400	4.08
3-25	34.8	3.2	2430	3.98

***Figure 4.8**: Test results for the compound's material properties*

Although **Figure 4.8** shows small differences in individual mechanical properties – such as stiffness, strength and impact strength – in general, it confirms that both screw configurations give compounds of a similar quality.

For scaled up trails at ICMA, using ultrasound treated hemp fibre pellets, it was decided to use the screw based on the configuration, which was designed at SR. **Figure 4.9** shows it a schematic drawing of the screw configuration used. **Table 4.2** gives the different compounding parameters.

Table 4.2: Compounds' batches with varying processing parameters

Batch name	Screw type	Screw speed (rpm)	Throughput (kg/h)
4	SR	100	10
5	SR	150	10
6	SR	150	15

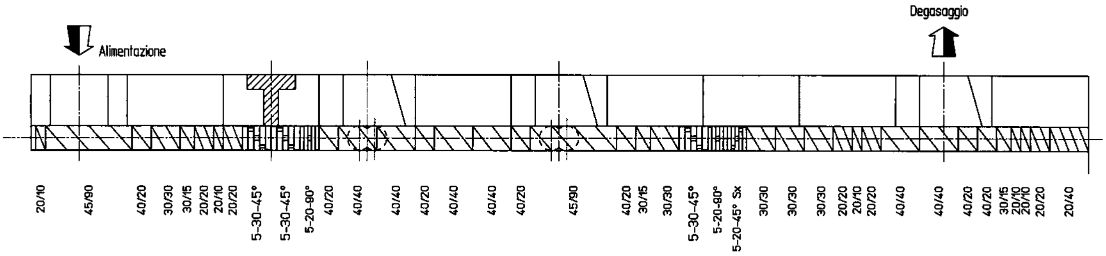

Figure 4.9: *Schematic drawing of the scaled up compounding screw configuration*

CON IL PATROCINIO DI: UNIONPLAST, ASSOCOMAPLAST, UNIONE INDUSTRIALI DI BERGAMO, TORINO, TREVISO E VARESE, APILOMBARDA, ASSOCIAZIONE E UNIONE ARTIGIANI DI BERGAMO

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ULTRAFIBRE TESTS CARRIED OUT BY CESAP

BATCHES WITH ULTRASOUND TREATED HEMP FIBERS (IN A PP MATRIX)

SPECIMENS INJECTION MOULDED

Test	Tensile strenght at break	Tensile strain at break	Flexural elastic modulus	Charpy notched impact strenght	Heat deflection temperature HDT	Flammability UL 94 V
Standard	ISO 527-1-2 (5 mm/min)	ISO 527-1-2 (5 mm/min)	ISO 178 (2 mm/min)	179-1/1eA	ISO 75-1-2 (1.80 MPa)	UL 94 V (1.6 mm)
Unit	MPa	%	MPa	KJ/m^2	°C	Class
Batch 4	37.8	3.6	3000	4.13	117	N.C
Batch 5	38.4	4.2	2990	3.88	117	N.C.
Batch 6	37.9	3.5	2900	3.81	118	N.C.

The HDT tests have showned results undoubtedly more repetitive respect the ones concerning the samples with fibers not treated (the values indicated are the average of three results).

The standards, specimens, test conditions and instruments used for obtaining the results summarized in the table are exactly the same of the tests already carried out on six batches with hemp fibers not treated.

As in the previous tests in the UL 94 test the specimens of all the samples burn completely after the first application of the flame, so they are not classified according to UL 94 V (V0, V1, V2).

Figure 4.10: *Test results for the ultrasound treated fibre compounds material properties*

Figure 4.10 summarises the material properties of the remaining batches. It was demonstrated that the mechanical properties of the hemp fibres were improved after the ultrasound treatment. Stiffness had increased from 2,600 MPa to 3,000 MPa, which is an increase of 15%; the strength remains in the same order of magnitude. The thermal performance was improved remarkably, showing a heat deflection temperature increase from 99 °C to 118 °C, which is an increase of 19%.

It was concluded that technology transfer was successfully executed and up scaled hemp fibre pellets result in a compound of similar quality when compared with the compounds produced at the laboratory scale.

4.2.5 Demonstrator products from scaled up UltraFibre-treated PP compounds

Using the best performing compounding conditions, pilot scale volumes of granules were produced for injection moulding of demonstrator products. Injection moulding was actually performed on two compound grades: (1) commercial reference granules' grade from GreenGran and (2) best performing ultrasound treated hemp/PP compound.

Figure 4.11*: Injection moulding machine for production of surfboard fins*

Figure 4.11 shows the injection moulding trials being carried out. For both grades, moulding went smoothly, where the mould was completely filled after only five shots, as shown in **Figure 4.12**. From there a series of surfboard fins were produced from both grades. Both grades resulted in a constant quality of moulded product. **Figure 4.13** demonstrates a typical example of a surfboard fin made from PP and ultrasound treated hemp.

A series of moulded fins, included a reference, were tested at Wageningen UR-FBR for their mechanical performance and comparison with the same measurements (performed at CESAP) on the materials' test bars, directly made from the granules. The results of the mechanical properties of the moulded fins are shown in **Table 4.3**.

Table 4.3: Mechanical properties of the moulded surfboard fins

Property	Ultrasound treated hemp sample	Reference sample
Flexural strength (MPa)	67.7	76.4
Flexural modulus (GPa)	3.46	3.56
Strain at maximum stress (%)	3.70	4.47
Strain at break (%)	3.78	4.67
Charpy impact (kJ/m^2)	18.0	24.3

Figure 4.12: *Filling up the mould and continuous production of surfboard fins*

Figure 4.13: *Typical injection moulding surfboard fin made from the best performing ultrasound treated hemp/PP compound*

4.3 Conclusions

Based on the compounding research on laboratory, pilot and industrial machines, for evaluating the effect of UltraFibre treatment on flax and hemp on the resulting composite properties, the following conclusions are drawn:

- Plasma treatment of flax fibres does increase the composite strength significantly, whereas plasma treatment on hemp fibres does not increase the composite strength
- Even though plasma treatment gives a technical advantage when treating clean elementary fibres – and there is a suggestion that there would be potential cost advantages by reducing the amount of coupling agent for composite compounding – it appears not to be the route to follow for scaling up the extrusion compounding. Most of its activated surface is lost during compounding where fibres are virtually all opened up to become elementary fibres

- Plasma treated fibres are further used for making compression moulded composites
- Untreated hemp fibres of a minimum length create feeding problems for extrusion compounding
- Using ultrasound treated fibres improves the feeding problem
- Technology transfer was successfully executed and scaled-up hemp fibre pellets result in similar compound quality compared with the laboratory scale situation
- During compounding all the fibres were homogeneously distributed in the PP matrix. This applies for both reference and ultrasound treated hemp samples
- The little spread in mechanical properties, based on sample taking of different fins made from the same grade – less than 5% for all values – confirms that during compounding all the fibres are homogeneously distributed in the PP matrix. This applies for both reference and ultrasound treated hemp samples
- Comparing the mechanical properties of the ultrasound treated moulded products with the material properties of the laboratory scale reference, it demonstrated that the stiffness of the moulded product increased by 17%
- Comparing the mechanical properties of the ultrasound treated moulded products with the polyamide reference material properties, it demonstrates that both the stiffness and strength of the ultrasound treated moulded products are better than what is required. Over 3 GPa ***versus*** the required 1.6 GPa for flexural stiffness, and over 67 MPa ***versus*** the required 65 MPa for flexural strength. Impact strength properties were lower than what was required, based on comparison with the polyamide material properties, but impact tests on the moulded polyamide reference need to be done to show to what extent this might become a problem or not
- The small spread in mechanical properties, based on sample taking from different fins made from the same grade – less than 5% for all values – confirms that during compounding all fibres are homogeneously distributed in the PP matrix. This applies for both the reference and ultrasound treated hemp sample
- Comparing the mechanical properties of the ultrasound treated moulded products with the material properties of the laboratory scale test bars, it demonstrated that the stiffness of the moulded produced is about 500 MPa higher – an increase of 17%
- The surfboard fin made from ultrasound treated hemp sample has slightly lower values for stiffness, strength and impact strength values than its commercial (GreenGran) counterpart

Deriving from this, as the most important conclusion, ultrasound treated hemp/PP compounds have successfully demonstrated – from a technical and technological point of view – that they are an alternative to the commercially available natural fibre composites.

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5

Life Cycle Assement and Case Studies

Abstract

A life cycle analysis of the UltraFibre product manufacturing operations was carried out.

It was found that replacing Nylon-6,6 with UltraFibre Hemp/polypropylene (PP) composite in an injection moulded surf-board skeg led to a significant reduction in environmental impacts. The UltraFibre skeg could also be produced at a reduced manufacturing cost.

An environmental impact comparison between a glass fibre reinforced and hemp fibre reinforced electrical joint connector was made. It was found that the largest contribution came from the unsaturated polyester resin and that very little difference was seen between the glass and hemp fibre components.

5.1 Introduction

A detailed life cycle analysis of the UltraFibre hydro-acoustic fibre treatment, Soft Plasma, composite conversion and product manufacturing operations was carried out. The methodology used was that outlined in ISO 14040/14044; SimaPro software was used to facilitate this LCA. Database information was supplemented by data provided by the consortium partners and data generated in the scale-up production trials carried out in this project. The LCA served both as a characterisation tool for the process, and was a means of quantifying the process such that areas where process optimisation could make the largest environmental savings were accurately identified. This information was fed back to the RTD development and scale-up activities such that effective process optimisations were realised.

In this study, the cradle-to-gate life cycle of UltraFibre processes was investigated. Where possible, data is collected from partners from their specific processes. Some data is used from the Ecoinvent database. The Ecoinvent database was selected to provide background data to estimate quantities of inputs and outputs for different unit processes within the system. This database is used extensively by LCA practitioners over Europe and a strong effort has been made to facilitate the transparency of the data presented in the database, especially in terms of assumptions regarding allocation and material transportation. Other databases are available to use in the software and provide similar data sets for use. A flow chart for the UltraFibre system boundaries is shown in **Figure 5.1**.

Two case studies were evaluated and published as a part of the dissemination activities of the project. These centred around two commercial products on partner MoveVirgo's portfolio list; a surf-board skeg, shown in **Figure 5.2** and an electrical joint connector (EJC), shown in **Figure 5.3**. These two products allowed an accurate assessment of both the fibre reinforced thermoplastic composite sector (Skeg) and the fibre reinforced thermosetting resin sector (EJC). See www.ultrafibre.org for the publications.

5.1.1 Surf-board skeg

Surfing is viewed as an eco-friendly sport due to the use of wind and wave energy to generate the power needed to promote the ability for the surfboard to be used. However, the surfboard and its component fittings are,

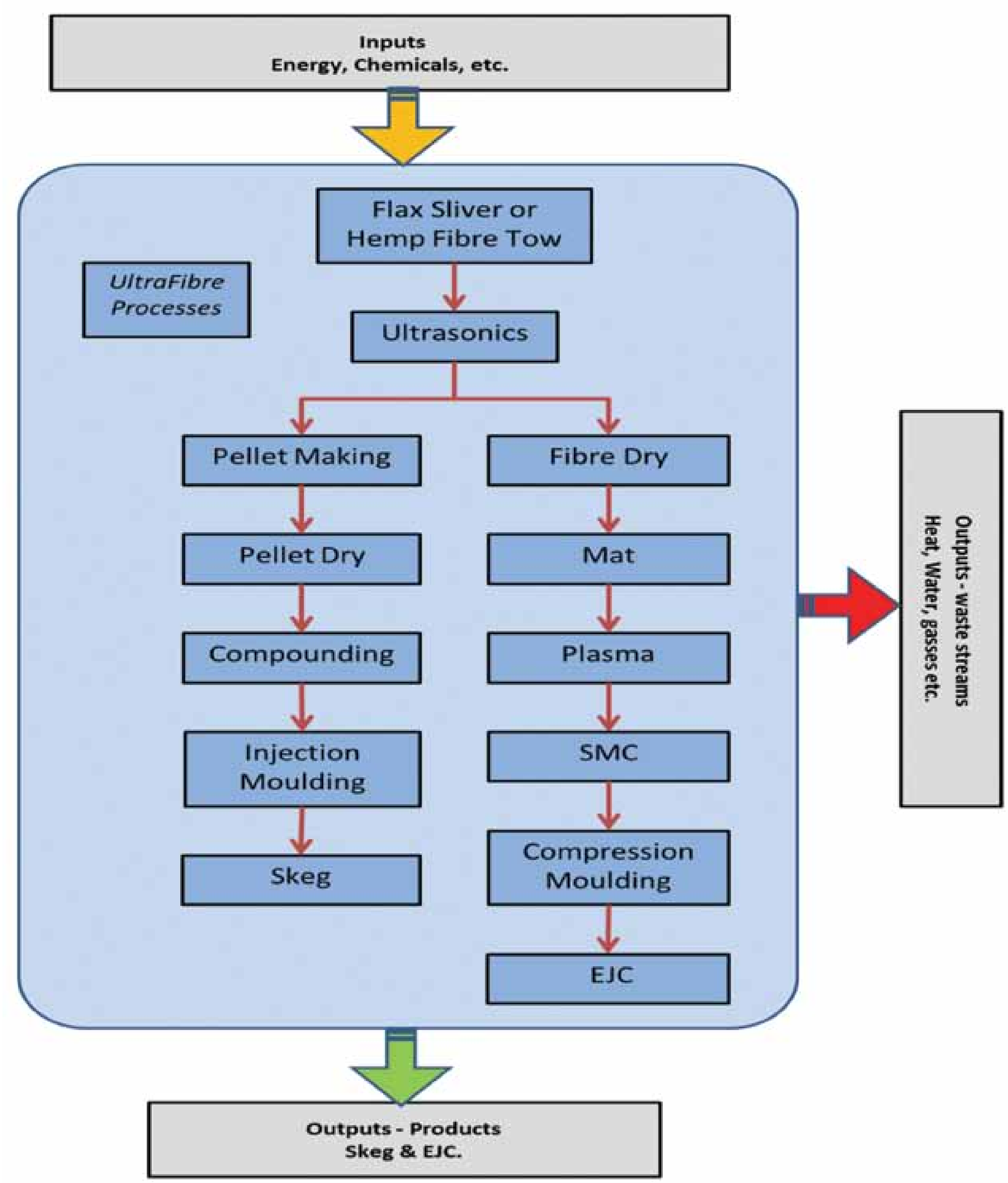

***Figure 5.1**: Flow chart for the UltraFibre system boundaries*

more often than not, produced from man-made, oil based products and chemicals which are unsustainable. These products can prove difficult to dispose of effectively at their end of life. The surfboard skeg and bolts produced using ultrasonically treated hemp fibres, will go quite some way to reducing the environmental impact of these items. Reductions in thermoplastic content are 30%, with an increase in material flexural strength and flexural modulus properties, see **Table 5.1**. Currently the surfboard range using the skeg shown on the left have a high recyclability level due to the use of foam based materials that can be re-used, shredded or added to virgin polymer to create surfboards again. Applying the use of the treated hemp fibres does not increase the recyclability of the material greatly, but it does reduce the levels of oil based compounds that would normally be needed to produce the component material.

Figure 5.2*: Left, Nylon-6,6 skeg and right, UltraFibre Hemp (30%)/PP skeg*

5.1.2 Electrical Joint Connector

These EJCs, as shown in **Figure 5.3**, are used to enable the joining of spur type connections to a main electrical feed cable. The connection can be made and the joint then sealed with a potting compound which prevents the ingress of dirt, moisture etc. Current options feature the use of vacuum thermo formed plastics, or phenolic based materials. These reflect the different product application requirements governed by local regulations. The current product is a glass fibre reinforced unsaturated polyester (UP) composite. The UltraFibre project replaced the glass fibre with UltraFibre hemp fibre using the same UP resin formulation.

Figure 5.3*: Photograph of an electrical joint connector*

Various types of hemp mat were produced; sonicated and non-sonicated, for a plasma treatment scale-up trial, see **chapter 3** for details. The fibre mats were impregnated with the UP resin forming a sheet moulding compound (SMC), which was then compression moulded for testing and EJC production. See **chapter 5.3.2** for results.

The sonicated hemp which was plasma functionalised and impregnated with UP resin to form an SMC, offers product users a genuine chance to reduce their environmental impact by reducing reliance on man-made, oil based products. Although there is still a polyester resin content, the bulk of the moulded volume is taken up by the hemp material. Optimal performance of fibre reinforced composites requires good adhesion between the fibre and the polymer matrix. Natural fibres like hemp and flax do not automatically have good interaction with UP polymer resins. The aim here was to improve the fibre-matrix interfacial adhesion by activating the natural fibre surface by applying atmospheric plasma, see **chapter 3** for details.

5.2 Life cycle assessment method and terms

The International Organization for Standardisation (ISO 14 040-44:2006) provide detailed guidelines for conducting LCA, which includes the following:

- ISO 14040 International Standards. Environmental management – Life cycle assessment – Principles and framework; International Organisation for Standardisation: Geneva, Switzerland, 2006
- ISO 14044 International Standards. Environmental management – Life cycle assessment – Requirements and guidelines; International Organisation for Standardisation: Geneva, Switzerland, 2006

The ISO 14040/14044:2006 guidelines are prescriptive in providing a methodological framework to LCA. The assessment should include a goal and scope definition, inventory analysis, impact assessment and interpretation. The following flow chart, **Figure 5.4**, demonstrates the sequence of events.

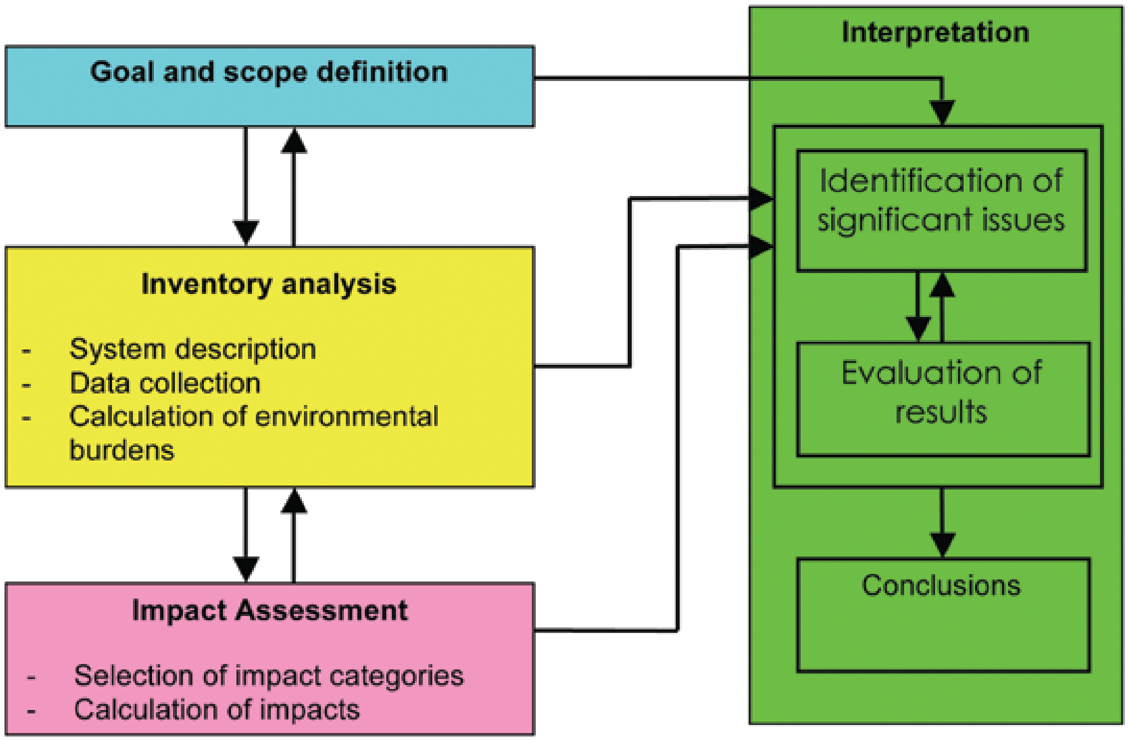

***Figure 5.4**: LCA framework*

Impact Assessment is a technical, quantitative and/or qualitative process to characterise and assess the effects of the environmental burdens identified in the inventory. An LCA consists of 4 steps:

- **Classification:** all substances are sorted into classes according to the effect they have on the environment
- **Characterisation:** all the substances are multiplied by a factor, which reflects their relative contribution to the environmental impact
- **Normalisation:** the quantified impact is compared to a certain reference value, for example the average environmental impact of a European citizen in one year
- **Weighting:** different value choices are given to impact categories to generate a single score

The approaches used to conduct the Impact Assessment are known as the **Problem Oriented Approach** or **midpoint impact category** and the **Damage Oriented Approach** or **endpoint impact category**.

5.2.1 The problem-oriented method (mid points)

In midpoint impact method "CML 2 Baseline 2000", the data in the inventory were aggregated according to relative contributions made to the following surveyable environmental concerns:

- Depletion of abiotic resources

This impact category is concerned with protection of human welfare, human health and ecosystem health. This impact category indictor is related to extraction of minerals and fossil fuels due to inputs in the system. The Abiotic Depletion Factor (ADF) is determined for each extraction of minerals and fossil fuels (kg antimony equivalents/kg extraction) based on concentration reserves and rate of de-accumulation. The geographic scope of this indicator is at a global scale.

- Climate change

Climate change can result in adverse effects upon ecosystem health, human health and material welfare. Climate change is related to emissions of greenhouse gases to air. The characterisation model as developed by the Intergovernmental Panel on Climate Change (IPCC) is selected for development of SimaPro Database Manual Methods library 10 characterisation factors. Factors are expressed as Global Warming Potential for time horizon 100 years (GWP100), in kg carbon dioxide/kg emission. The geographic scope of this indicator is at a global scale. Some Characterisation factors were added from the IPCC 2001 GWP 100a method: Methane, bromodifluoro-, Halon 1201, Methane, dichlorofluoro-, HCFC-21, and Methane, iodotrifluoro-.

- Stratospheric ozone depletion

Because of stratospheric ozone depletion, a larger fraction of UV-B radiation reaches the earth surface. This can have harmful effects upon human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles and on materials. This category is output-related and at global scale. The characterisation model is developed by the World Meteorological Organisation (WMO) and defines ozone depletion potential of different gasses (kg CFC-11 equivalent/kg emission). The geographic scope of this indicator is at a global scale. The time span is infinity.

- Human toxicity

This category concerns effects of toxic substances on the human environment. Health risks of exposure in the working environment are not included. Characterisation factors, Human Toxicity Potentials (HTP), are calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. For each toxic substance HTP's are expressed as 1,4-dichlorobenzene equivalents/kg emission. The geographic scope of this indicator determines on the fate of a substance and can vary between local and global scale.

- Fresh-water aquatic eco-toxicity

This category indicator refers to the impact on fresh water ecosystems, as a result of emissions of toxic substances to air, water and soil. Eco-toxicity Potential (FAETP) is calculated with USES-LCA, describing fate, exposure and effects of toxic substances. The time horizon is infinite. Characterisation factors are expressed as 1, 4-dichlorobenzene equivalents/kg emission. The indicator applies at global/continental/regional and local scale.

- Marine eco-toxicity

Marine eco-toxicity refers to impacts of toxic substances on marine ecosystems (see description fresh water toxicity).

- Terrestrial eco-toxicity

This category refers to impacts of toxic substances on terrestrial ecosystems (see description fresh water toxicity).

- Photo-oxidant formation

Photo-oxidant formation is the formation of reactive substances (mainly ozone) which are injurious to human health and ecosystems and which also may damage crops. This problem is also indicated with "summer smog". Winter smog is outside the scope of this category. Photochemical Ozone Creation Potential (POCP) for emission of substances to air is calculated with the UNECE Trajectory model (including fate), and expressed in kg ethylene equivalents/kg emission. The time span is 5 days and the geographical scale varies between local and continental scale.

- Acidification

Acidifying substances cause a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials (buildings). Acidification Potentials (AP) for emissions to air is calculated with the adapted RAINS 10 model, describing the fate and deposition of acidifying substances. AP is expressed as kg SO_2 equivalents/kg emission. The time span is eternity and the geographical scale varies between local scale and continental scale. Characterisation factors including fate were used when available. When not available, the factors excluding fate were used (In the CML baseline version only factors including fate were used). The method was extended for nitric acid, soil, water and air; sulphuric acid, water; sulphur trioxide, air; hydrogen chloride, water, soil; hydrogen fluoride, water, soil; phosphoric acid, water, soil; hydrogen sulphide, soil, all not including fate. Nitric oxide, air (is nitrogen monoxide) was added including fate.

- Eutrophication

Eutrophication (also known as nutrification) includes all impacts due to excessive levels of macronutrients in the environment caused by emissions of nutrients to air, water and soil. Nutrification potential (NP) is based on the stoichiometric procedure of Heijungs (1992), and expressed as kg PO_4 equivalents/kg emission. Fate and exposure is not included, time span is eternity, and the geographical scale varies between local and continental scale.

5.2.2 The damage-oriented methods (end points)

The damage-oriented methods also start by classifying a system's flows in to various environmental themes, but model each environmental theme's damage to human health, ecosystem health and damage to resources [1].

- **Human Health:** Effect of environmental changes to humans measured in "Disability Adjusted Life Years" (DALYs) taking into account the effects of climate change, ozone layer depletion, carcinogenic and respiratory effects and radiation

- **Ecosystem Quality:** Effect of eco-toxicity, acidification, eutrophication and land use on species diversity. This is measured as "Potentially Disappeared of Affected Fraction" (PDF of PAF.m^2.year)

- **Resources:** The surplus energy needed in the future to extract lower quality mineral and fossil resources. The depletion of bulk resources is considered under land use

For example, acidification – often related to acid rain – may cause damage to ecosystems (e.g. in the Black Forest in Germany), but also to buildings or monuments. In essence, this method aims to answer the question, "Why should we worry about climate change or ozone depletion?" Eco-Indicator 99 is an example of a damage-oriented method. Endpoint results have a higher level of uncertainty compared to midpoint results but are easier to understand by decision makers.

For this report, both mid-point and end-point assessments will be conducted using the CML 2 baseline 2000 v2.05 and The Eco-indicator 99 (H/A) v2.07 methods, recently updated to v2.09. The H/A denotes the "Hierarchest perspective" and "Average" methodology.

These methods aim at simplifying the complexity of hundreds of flows into a few environmental areas of interest.

5.3 Case Studies

5.3.1 Surf-board skeg

Table 5.1 shows a comparison of mechanical test data between the Nylon-6,6 and the UltraFibre skeg.

Table 5.1: Comparison of mechanical properties of the nylon and UltraFibre skeg

Mechanical Property	Nylon (PA-6,6) reference Skeg	Sonicated Hemp/PP Skeg	UltraFibre Property improvement/%
Flexural strength /MPa	33.0	67.7	101
Flexural modulus /GPa	0.88	3.46	293
Strain at break /%	Greater than test parameter	3.78	Reduced
Charpy impact (notched)/kJ/m^2	Not broken	18.0	Reduction in impact strength

The hemp/PP moulded skeg has much higher flexural properties than the commercial nylon skeg. However, the impact strength of the nylon skeg is much higher. Field trials at Movevirgo are on-going at the time of writing this report to ascertain as to whether the hemp/PP has sufficient impact strength for use as a replacement material for the skeg. Please see project website (www.ultrafibre.org) for an up to date assessment.

Note that the data for Nylon-6,6 refer to dry as moulded (DAM) specimens, whereas the tested sample was moulded after moisture absorption.

Moisture absorption causes a decrease in modulus and strength and an increase in impact performance.

5.3.1.1 LCA results

Figure 5.5 shows the CML baseline plot comparing the UltraFibre hemp (30%)/PP with the commercial Nylon-6,6 materials. The comparison is for 1 kg of each material.

Figure 5.6 shows the eco indicator 99 plot analysis comparing 1 kg of the UltraFibre hemp/PP with the commercial Nylon-6,6. Eco indicator 99 is an indicator for impact on human health per capita in Europe.

Figure 5.7 shows an accumulated single score plot from the eco indicator 99. This is a different graphical representation of the eco indicator 99 which shows a single chart for ease of comparison of the total environmental impact for the compared processes.

5.3.1.2 LCA analysis

As described in the introduction, the data in the inventory is aggregated according to relative contributions made to the surveyable environmental concerns, as shown in the chart (x-axis inputs).

The comparison is for 1 kg of each material, however the hemp/PP skeg weighs 132 g and the nylon skeg weighs 141 g. Therefore the environmental impact of the actual hemp/PP part is less than is shown in **Figure 5.5, Figure 5.6** and **Figure 5.7.**

- **Abiotic Depletion** is related to the extraction of minerals and fossil fuels due to inputs in the system. The Abiotic Depletion Factor (ADF) is determined for each extraction of minerals and fossil fuels (kg antimony equivalents/kg extraction) based on concentration reserves and rate of de-accumulation. The output from the UltraFibre hemp/PP skeg shows an almost three fold decrease over the commercial nylon skeg. This is mainly due to the polypropylene in the composite which reduces the fossil fuel based component, which is high for nylon manufacture due to the starting materials used. See **Figure 5.8**
- **Acidification** or Acidifying substances cause a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials (buildings). Acidification Potentials (AP) for emissions to air is calculated with the adapted "RAINS 10" model, describing the fate and deposition of acidifying substances. AP is

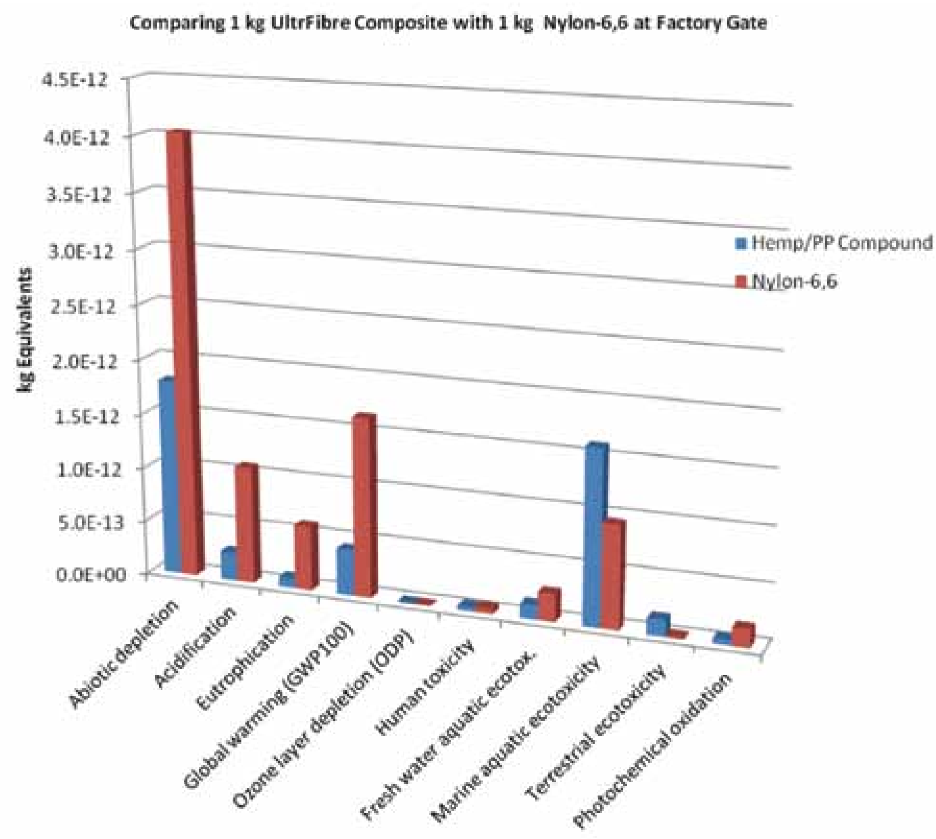

Figure 5.5*: Showing the CML baseline plot comparing the UltraFibre hemp (30%)/PP with the commercial Nylon-6,6 materials [2]*

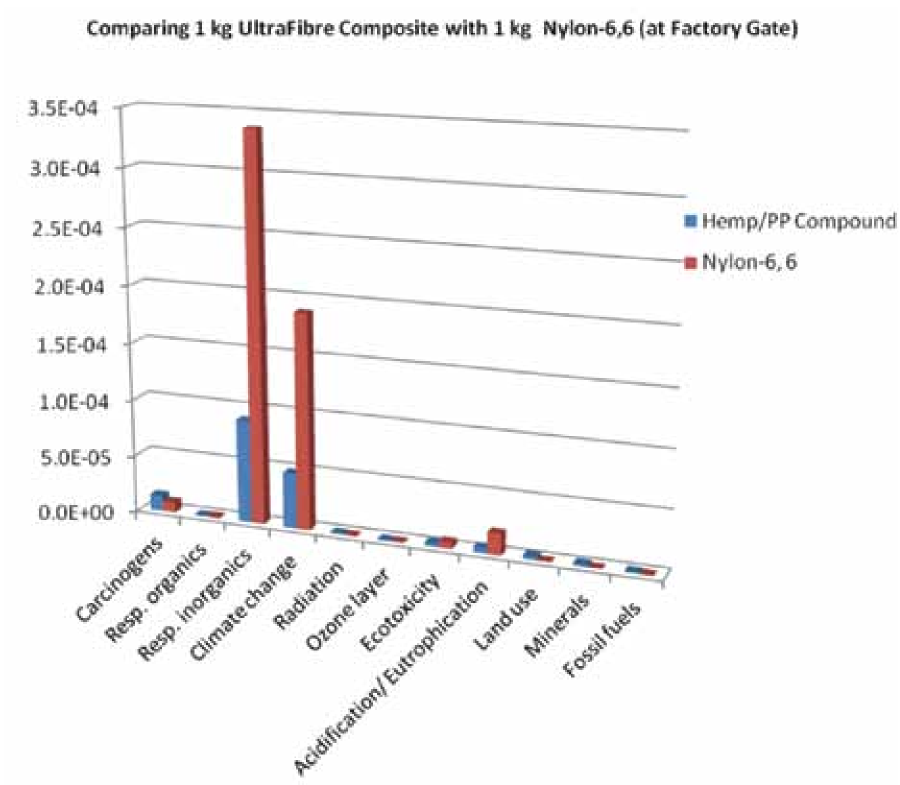

Figure 5.6: Showing the eco indicator 99 chart comparing the UltraFibre hemp (30%)/PP with the commercial Nylon-6,6 [3]

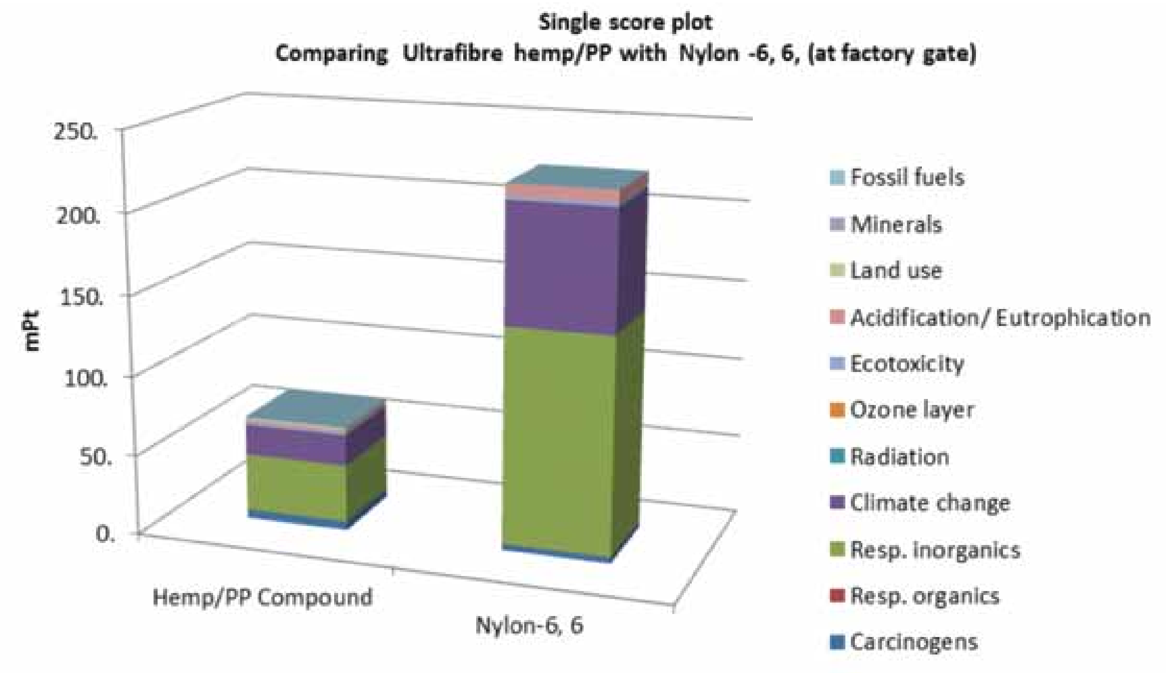

***Figure 5.7**: Single score plot, showing total loading for each material [4]*

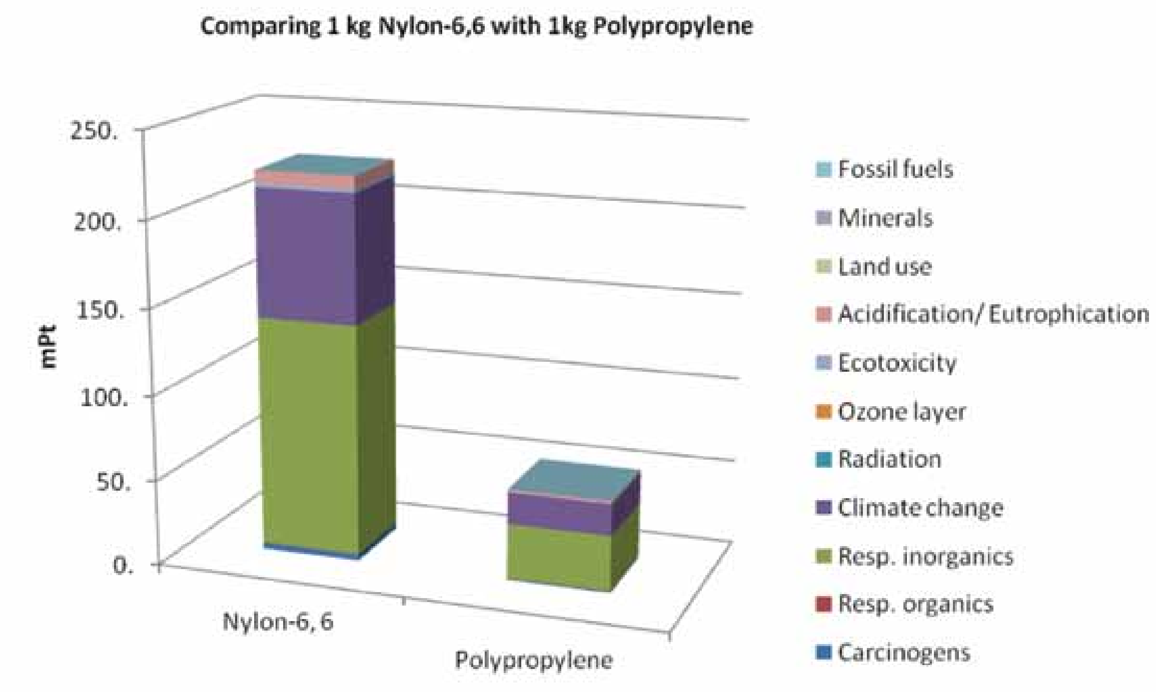

***Figure 5.8**: Single point score chart of PP versus Nylon-6,6*

expressed as kg SO_2 equivalents/kg emission. A fivefold reduction in acidification is seen for the hemp/PP skeg over the nylon skeg; due to less petrochemical use/refinement, which has a knock on effect for energy consumption and therefore emissions to air etc...

- **Eutrophication** (also known as nutrification) includes all impacts due to excessive levels of macronutrients in the environment caused by emissions of nutrients to air, water and soil. Nutrification potential (NP) is based on the stoichiometric procedure of Heijungs (1992), and expressed as kg PO_4 equivalents/kg emission. Again a fivefold reduction in eutrophication is observed when substituting the nylon skeg with hemp/PP

- **Global warming potential or climate change** Factors are expressed as Global Warming Potential for time horizon 100 years (GWP100), in kg carbon dioxide/kg emission. A fourfold decrease in GWP when replacing nylon with hemp/PP
- **Marine eco-toxicity** refers to the impact on marine water ecosystems, as a result of emissions of toxic substances to air, water and soil. Eco-toxicity Potential (FAETP) is calculated with USES-LCA, describing fate, exposure and effects of toxic substances. Characterisation factors are expressed as 1,4-dichlorobenzene equivalents/kg emission. This category shows a 30% increased output for the hemp/PP material over the nylon
- **Stratospheric Ozone depletion, Terrestrial eco-toxicity, Fresh-water aquatic eco-toxicity and Photo-oxidant formation** show very little comparative impacts for either material
- **Respiratory inorganics and Climate change factors** are comparatively high with a marked reduction for hemp/PP over the Nylon-6,6

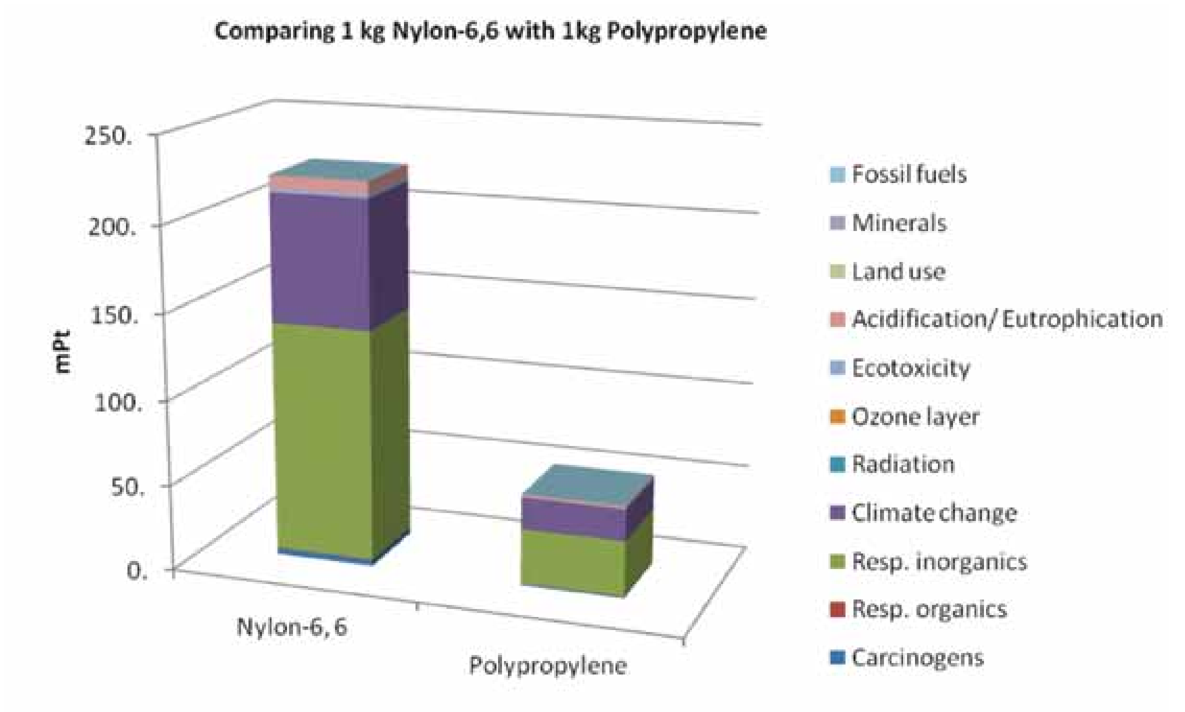

***Figure 5.8**: Single point score chart of PP versus Nylon-6,6*

5.3.1.3 Cost analysis

The cost of the UltraFibre skeg was calculated to be ≤ 50% of the cost of the Nylon-6,6 skeg. The calculations were based on all the stages for the skeg manufacture being processed at the same location and in one company. This means that no transportation costs were used and that there was no commercial mark-up for each processing stage.

5.3.2 Electrical joint connector

A detailed account of the methodology and test results is described in **chapter 3**.

Flax SMC composite performance reaches 82% of glass based SMC flexural strength and 115% of its flexural modulus.

Pilot scale trials based on thermobonded hemp mats, including industrial non-woven production, plasma treatment, SMC sheet manufacturing and industrial moulding, were performed. The composite products show about 65% of glass fibre SMC flexural strength and about 80% of glass fibre SMC modulus. Relatively low performance is considered due to areas with low fibre content. Although variation of glass fibre SMC flexural strength is very high, the average strength of a lab scale produced SMC with high hemp fibre content is similar to that of the commercial glass fibre based SMC.

Insufficient drying on the pilot scaled trial also caused poorer mechanical properties than expected.

5.3.2.1 LCA RESULTS

Figure 5.9, **Figure 5.10, Figure 5.11** and **Figure 5.12** show the CML base-line, eco-99 and single point eco-99 charts.

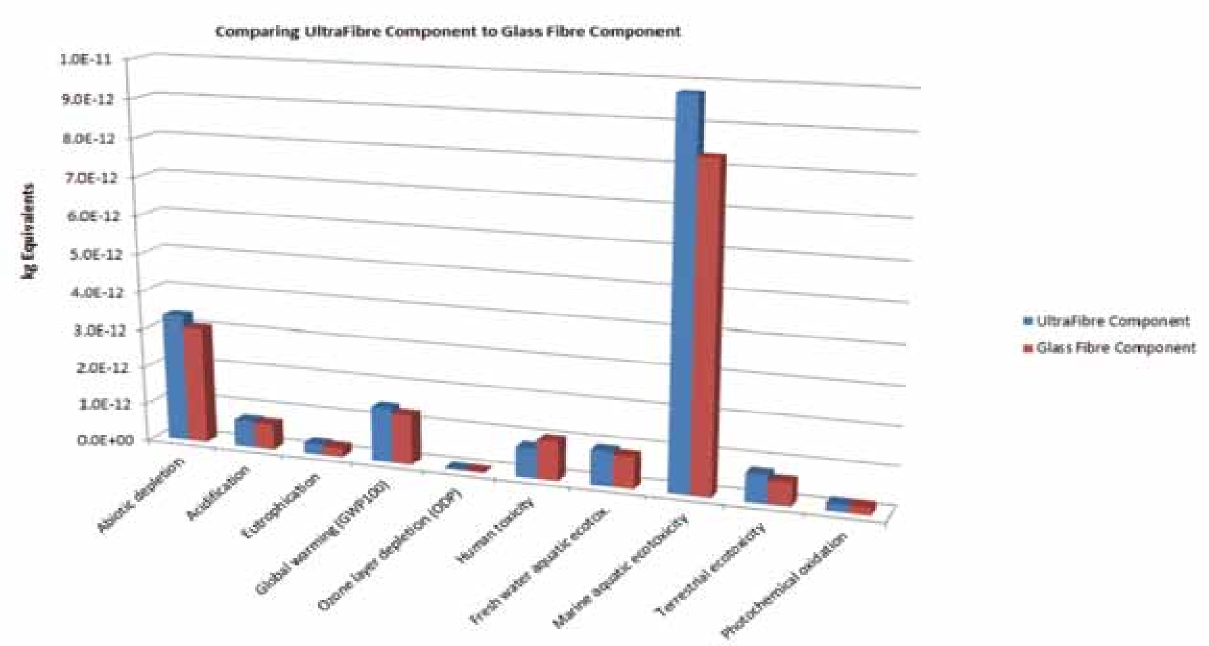

***Figure 5.9**: CML chart for the comparison of the hemp fibre reinforced UP composite with the glass fibre reinforced composite*

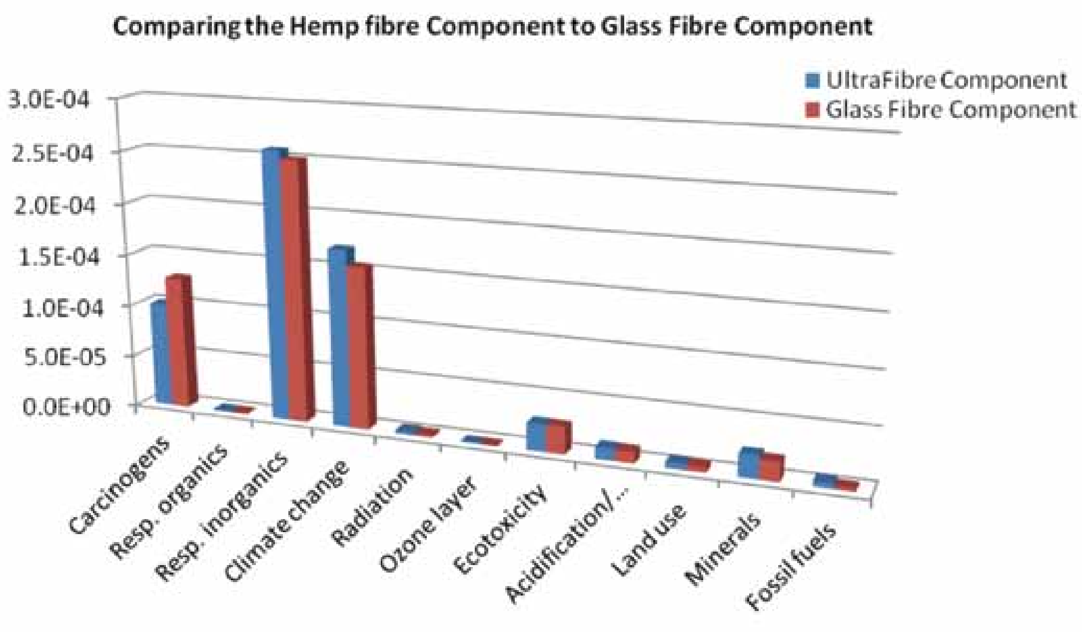

***Figure 5.10**: Eco indicator 99 comparing hemp and glass reinforced UP resin*

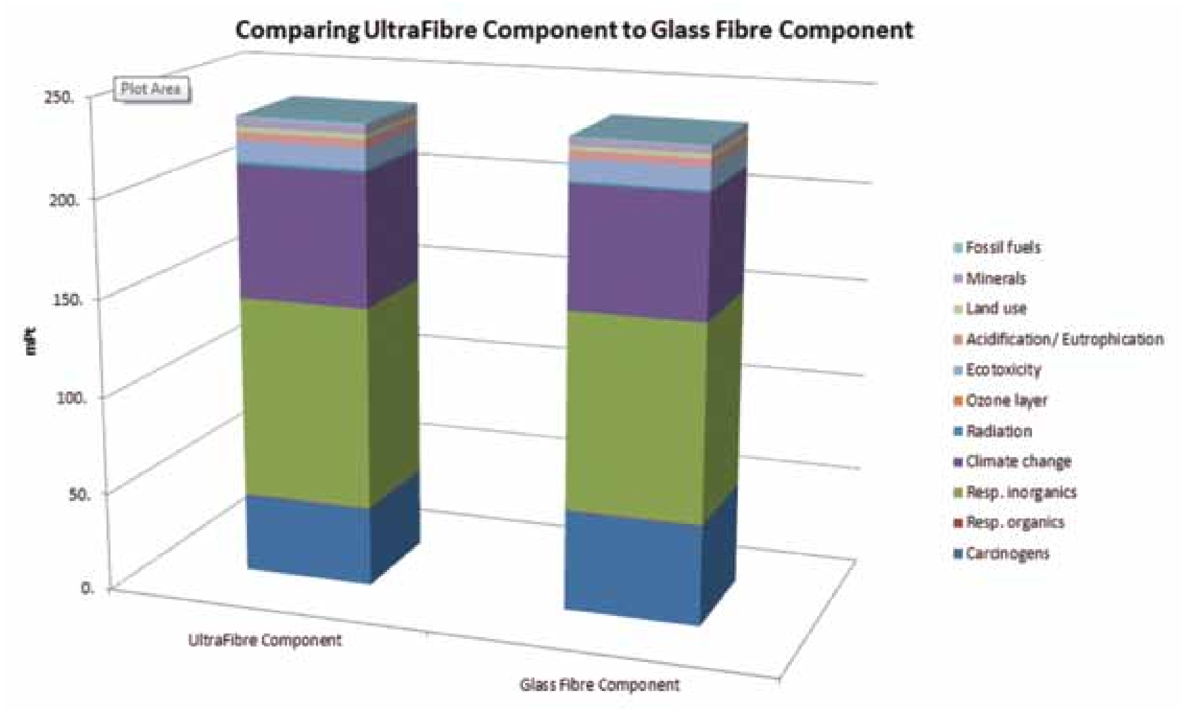

***Figure 5.11**: Single point score of the glass reinforced and hemp (UltraFibre) reinforced UP composite*

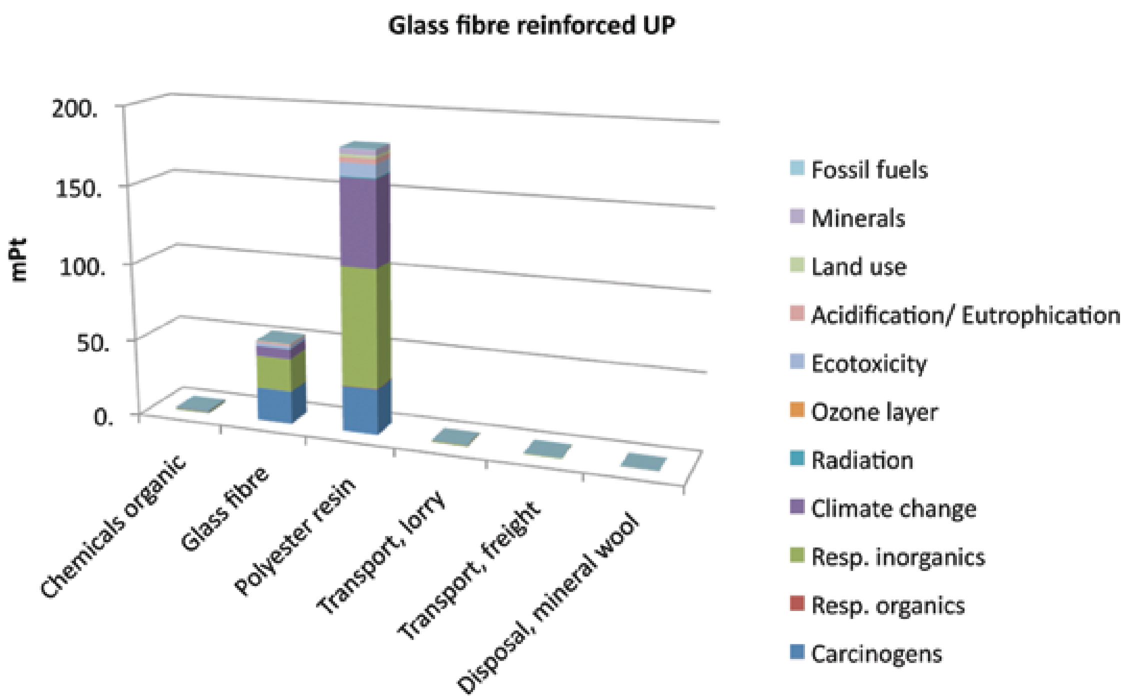

***Figure 5.12**: Chart showing the UP component in the composite [4]*

5.3.2.2 LCA analysis

There are very little environmental impact differences between glass and hemp reinforced UP resin composites. The main loadings come from the UP resin itself as shown in **Figure 5.12**.

No cost data is available, please contact Movevirgo for details.

5.4 Conclusions

5.4.1 Skeg

Mechanical test data shows an increase in flexural strength and modulus with a reduction in impact strength. Hemp/PP skeg field trials are underway at beneficiary Movevirgo. See www.ultrafibre.org for up to date details.

The environmental loading of the UltraFibre hemp/PP composite skeg is markedly reduced compared with the Nylon-6,6 skeg; this will enable beneficiary Movevirgo a strongly marketable product from an environmental and economic point of view; the hemp/PP skeg was produced at a reduced cost.

Both of these factors offer a considerable commercial benefit in replacing the nylon with the UltraFibre hemp/PP.

5.4.2 EJC

The Hemp reinforced unsaturated polyester composite products show about 65% of glass fibre SMC flexural strength and about 80% of glass fibre SMC modulus. Relatively low performance is considered due to areas with low fibre content and poor drying procedures at the pilot scale.

The environmental impact of the Electrical joint connector is dominated by the unsaturated polyester resin component for both fibre reinforcing types. Very little environmental impact differences between glass and hemp fibre composites were found.

It is postulated that end of life disposal and or recycling would be favourable for the hemp reinforced composite, but a cradle to grave LCA was out of the scope of this study.

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4. Method: Eco-indicator 99 (H) V2.09/Europe EI 99 H/A/Single score.

6

Contact Details and Useful References

6.1 Acknowledgements

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6.2 Contact details for the consortium partners

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Founded in 1960, ASSOCOMAPLAST, a non-profit Association, now represents 162 companies, Italian plastics and rubber machinery, ancillary equipment and moulds manufacturers.

Website: www.assocomaplast.org

EUROPEAN INDUSTRIAL HEMP ASSOCIATION (address: Chemiepark Knapsack Industriestrasse, Huerth, 50354, Germany)

The “European Industrial Hemp Association (EIHA)” officially founded on 23 November 2005 has formed itself as an association of Hemp primary processing companies within the EU (regular members). Associate members are associations, national organisations, companies and individuals working in the field of Hemp or other natural fibres.

Website: www.eiha.org

BRITISH PLASTICS FEDERATION (address: Bath Place, 6 Rivington Street, London, EC2A 3JE UK)

The British Plastics Federation (BPF) is the leading trade association for the UK Plastics Industry, with over 400 members and 1200 affiliated members.

Website: www.bpf.co.uk

ACXYS TECHNOLOGIES (address: 148 Rue des vingt toises, SAINT MARTIN LE VINOUX, 38950, France)

AcXys Technologies is a private French corporation created in 2000 by Dr. Thierry Sindzingre. Its core of competencies is based on a unique and patented atmospheric plasma technology, developed by Air-Liquide Company.

Website: www.acxys.com

MOVEVIRGO LIMITED (address: New Portreath Road, Redruth, Cornwall, TR16 4OL, UK)

Movevirgo Limited were established in 1982, and specialise in Moulding of silicone based products, Compression moulding (300 and 400 tonne machines), Cold press moulding, Vacuum moulding (in polyester and phenolic resins), Polyurethane foam moulding, Resin casting, Injection moulding, Moulding of phenolic syntactic foam components, Hand lay-up laminating.

Website: www.movevirgo.co.uk

CENTRO EUROPEO SVILUPPO APPLICAZIONI PLASTICHE (address: Via Vienna, 56, 24040, Verdellino/ Zingonia BG, Italy)

CESAP (European Centre for Development Applications Plastics) Ltd. consortium - Zingonia, via Vienna 56 - was established in June 1983 by a group of entrepreneurs working in the field of plastics and from the Industrial Union of Bergamo, to offer technical services to industrial processors.

Website: www.cesap.com

SMITHERS RAPRA AND SMITHERS PIRA LTD. (address: Shrewsbury Road, Shawbury, Shropshire, SY4 4NR, UK)

Smithers Rapra provides services for the polymer industry and industries using plastics and rubber in any component, product or production process.

Website: www.rapra.net

GREENGRAN BV (address: 1, Galvanistraat, Ede, 6716 AG, Netherlands)

GreenGran produces thermoplastic granules reinforced with natural fibres that are six times stiffer and 2.5 times stronger than virgin PP. The compounding process can be carried out on standard extrusion equipment with commonly used screw elements. Moreover, the granules can be injection moulded into both thin and thick wall applications under standard conditions.

Website: www.greengran.com

INCONTROL ULTRASONICS LTD (address: 8a Swan Street, Sileby, LE12 7NW, UK)

InControl Ultrasonics specialises in application technology of high power ultrasonic energy. The company has a broad base of customers spread right across British industry, including many household multi-national names such as GEC, ICI, Unilever, Nestles (Rowntree Mackintosh), Tioxide, Pilkingtons, Smith and Nephew, W S Atkins, Purac and Anglia Water plc, plus various smaller firms of about 200 in total.

Website: www.ffr-ultrasonics.co.uk

STICHTING DIENST LANDBOUWKUNDIG ONDERZOEK, INSTITUTE FOOD AND BIOBASED RESEARCH (address: Bornse Weilanden 9, 6708 WG, WAGENINGEN, Netherlands ("the Cobeneficiary")

Wageningen UR - Food & Biobased Research is the R&D organisation for sustainable innovation in the areas of healthy food, sustainable fresh food chains and biobased products. National and international contracting authorities choose Food & Biobased Research because it is professional, provides innovative market-oriented solutions and has a high scientific standing.

Website: www.fbr.wur.nl

ICMA San Giorgio

(address: Via Madonnina 75 – 20010 San Giorgio su Legnano MILANO, Italy)

ICMA San Giorgio manufactures state-of-the-art corotating extruders and complete extrusion systems for the production of a wide range of compound & masterbatch, special sheets and WPC profiles.

Website: www.icmasg.it

Abbreviations and Acronyms

3D	Three dimensional
ADF	Abiotic depletion factor
AP	Acidification potentials
APP	Atmospheric pressure plasma
BPF	British Plastics Federation
$CaCO_3$	Calcium carbonate
CESAP	Centro Europeo Sviluppo Applicazioni Plastiche
CFC-11	Trichlorofluoromethane
CO_2	Carbon dioxide
CSIRO	Commonwealth Scientific and Industrial Research
DALY	Disability Adjusted Life Years
EC	European Community
EIHA	European Industrial Hemp Association
EJC	Electrical joint connector(s)
EO	Ethylene oxide
EU	European Union
FAETP	Freshwater eco-toxicity potential
FBR	Food & Biobased Research
FFR	Previous name for InControl Ultrasonics
FT-IR	Fourier-transform infrared
GMA	Glycidyl methacrylate
GPC	Gel permeation chromatography
GWP	Global warming potential
H/A	Hierarchical perspective and average methodology
H_2	Hydrogen
HCFC	Hydrochlorfluorocarbon
HCFC-21	Dichlorofluoromethane
HDT	Heat deflection temperature

HTP	Human toxicity potential(s)
IPCC	Intergovernmental Panel on Climate Change
ISO	The International Organization for Standardisation
LCA	Life Cycle Analysis
MAPP	Maleic anhydride-grafted-polypropylene
MDI	Methylene diphenyl di-isocyanate
MEKP	Methyl ethyl ketone peroxide
MgO	Magnesium oxide
N_2	Nitrogen
N_2O	Nitrogen dioxide
NH_2	Amine groups
NMT	Natural fibre mat thermoplastic
NO_x	Nitrogen oxides
NP	Nutrification potential
O_2	Oxygen
PA-6,6	Polyamide-6,6
PDF of PAF	Potentially disappeared of affected fraction
PHA	Polyhydroxy alkanoate(s)
PI	Polyimide
PLA	Polylactic acid
PO	Propylene oxide
PP	Polypropylene
ppm	Parts per million
PTFE	Polytetrafluoroethylene
R&D	Research and Development
RAINS 10	Regional Air Pollution Information and Simulation model
REA	Research Executive Agency
RTD	Research and Technology Developers
SD	Standard deviation
SEM	Scanning electron microscopy
SMC	Sheet moulding compound(s)
SME	Small/medium size enterprise(s)
SR	Smithers Rapra
TiO_2	Titanium dioxide
UD	Uni-directional
UNECE	United Nations Economic Commission for Europe
UP	Unsaturated polyester

USES-LCA	Uniform System for the Evaluation of Substances – adapted for LCA purposes
USF	Ultrasound fibre treatment
UV-B	Ultraviolet light with a wavelength range of 315-280 nm
VA-RTM	Vacuum assisted resin transfer moulding
WHO	World Health Organization
WMO	World Meteorological Organisation
WPC	Wood plastic composite
XPS	X-ray photoelectron spectroscopy

UltraFibre

Trade Associations

www.assocomaplast.org

www.eiha.org

www.bpf.co.uk

Other Partners

www.rapra.net

www.ffr-ultrasonics.co.uk

www.fbr.wur.nl

www.greengran.com

www.ekotex.com.pl

www.movevirgo.co.uk

www.kenaf-fiber.com

www.icmasangiorgio.it

www.acxys.com

www.cesap.com

www.ultrafibre.org