

D3.4

Report on Plasma Treatment of Flax and Hemp Fibres for Unsaturated Polyester Matrices



UltraFibre



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1. Introduction

Fibre reinforced polymers find wide commercial application in the aerospace, leisure, automotive, construction and sporting industries. In recent years there has been much interest in developing natural fibre reinforced polymers for sustainable substitution of synthetic materials. However, natural fibres do not automatically have good interaction with polymers, which is required for optimal material performance. The UltraFibre project aims to apply plasma treatment processing for surface modification of flax and hemp fibres in order to obtain improved compatibility and adhesion to polymer matrices conferring a 25% increase in mechanical properties compared with the untreated fibre.

This Deliverable 3.4, reports on the plasma treatment of flax and hemp fibres for unsaturated polyester matrix polymers. This report is an additional report to the 3 reports originally planned for WP3 to cover work on plasma treatment for SMC composites. Results on PP and PLA based extrusion compounds have been addressed in Deliverable 3.3.

Activities on surface treatment development are addressed in WP3 of the UltraFibre project. The **objectives** for WP3 as stated in the technical annex 1 are as follows:

- To produce a sustainable fibre treatment method based on AcXys Technology's atmospheric soft plasma process
- To prove the efficacy of the SoftPlasma process for natural fibre modification
- To benchmark against alternative fibre modification processes
- To modify the fibre-handling machine configuration to allow surface treatment of fibres using plasma treatment and suitable polymers and its integration into the UltraFibre process

The **goal** of the development of an atmospheric plasma unit is to obtain improved compatibility and adhesion to polymer matrices conferring a **25% increase in mechanical properties** compared with the untreated fibre **at competitive price**.

Activities in WP3 run from Months 1 – 30. The **work-plan** for WP3 as stated in the Technical Annex 1 is presented below.

Task 3.1: Fibre modification survey

Natural fibres must be treated to improve the adhesion between the fibre and the plastic matrix and the fibre dispersion during compounding. To avoid repetition of previously carried out experimental studies, an update to the available literature survey of techniques reported for natural fibre coupling,



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especially data reported for flax and hemp composites, will be carried out at the start of the UltraFibre project. Candidate strategies for coupling will be short-listed based upon the data generated in WP1. These data will serve as benchmarks for the SoftPlasma process developed in this project in light of the surface morphology and chemical characterisation data generated in WP5. Chemical, physical, and plasma treatments will be considered. The emphasis will be upon the modification process that can be most efficiently integrated into the UltraFibre process system.

Results on Fibre modification survey were extensively **addressed in** Appendix A of **Deliverable 3.1** (submitted in Month 11).

Task 3.2: Soft plasma pilot plant development

AcXys, in cooperation with DLO-FBR, will investigate modifications needed to adapt the existing equipment to make use of the SoftPlasma technique for fibre treatment. This will allow the fibres to be pre-treated to allow for their use in a wide variety of possible applications. A design of experiments will screen variables such as:

- Exposure time
- Feed gas composition
- Interaction between hydro-acoustic decortication variables and SoftPlasma conditions
- Stability of modification after processing
- Effect of secondary operations

Initial trials will be carried out with fibres produced by conventional mechanical processing and retting methods. In parallel, preparatory work will be performed on the small-scale decorticated fibres produced in work package 2. Through interaction with work package 5, characterization, the effects of the SoftPlasma and its interaction with the hydro-acoustic process will be understood.

The **development, design and performance of the atmospheric plasma unit** for treatment of natural fibres, was **reported in Deliverable 3.2** (submitted in Month 20).

Task 3.3: Surface treatment of natural fibres

Once the equipment has been modified, a variety of natural fibres will be surface treated to determine how well the soft plasma process performs with these fibres. Modifications to the equipment/processing conditions will be made, if necessary, through a series of iterative steps.

Task 3.4: Compatibilisation for different polymers

A series of experiments will be run to determine the operating conditions required for a surface treatment that would allow natural fibres to be incorporated into a series of polymers which are currently reinforced with carbon, aramid or glass fibres, specifically polyester and trans furan



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thermosetting resin, and polypropylene and poly(lactic acid) thermoplastic matrices, with polyester and polypropylene representing petrochemical resins and trans furan and poly(lactic acid) as crop-derived resins.

Task 3.5: Process experimentation / optimisation

Conditions for surface treatment will be optimized. A report on the best practice identified will be prepared. Particular attention will be paid to monitoring the environmental aspects of the process such as emissions and energy consumption. These data will be generated and supplied to the LCA, technical, economic, and environmental analyses in WP9.

The atmospheric plasma technology is a very clean technology and no waste water is produced. Background information to the atmospheric plasma technology is presented in D3.2.

Results on surface treatment of hemp and flax fibres for improved adhesion to PP and PLA matrices in extrusion compounds have been addressed in Deliverable 3.3 (submitted in Month 27). This Deliverable 3.4 report presents the work performed on plasma treatment of flax and hemp fibres for unsaturated polyester (UP) matrix polymers:

- Surface treatment of flax and hemp fibres (Task 3.3, Sections 2.1).
- Adhesion of treated fibres to UP polymer (Tasks 3.4, Section 2.2).
- Optimisation and life cycle analysis data collection of plasma treatment for UP matrix (Task 3.5, Section 2.3).
- Pilot scale trials on plasma treatment and UP based SMC production and moulding (WP6, Section 2.4)
- Techno-economic evaluation (Task 3.5, Section 2.5)
- Issues and solutions (Section 2.6).

Conclusions are presented in Chapter 3.

Annex 1 provides the mould design for making SMC composites prepared in joint consultation with Movevirgo and DLO-FBR. The mould was actually made by Movevirgo with help of RAPRA.

The procedure followed to establish the best method to evaluate plasma treatment for making natural fibre reinforced SMC composite test plaques at lab scale is presented in Annex 2.



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2. Results

Background information to the atmospheric plasma technology is presented in D3.2 (section 1.1).

The procedure for making natural fibre reinforced SMC composite test plaques at lab scale is presented in Annex 2.

Test methods for analysis of materials have been described in Deliverables 5.2 and 5.3.

2.1 Task 3.3 Plasma surface treatment of flax and hemp fibres

The lab scale plasma unit built by AcXys, which is extensively described in D3.2, has been used for all further trials addressed in sections 2.1–2.3. The experimental procedure of pilot scale plasma trials is described in D6.1 and a summary is presented in section 2.4 of this report.

The atmospheric plasma treatment of hemp and flax fibre surfaces was as described in D3.3, sections 2.2. Fibres samples include:

1. steam exploded flax air laid non-woven originating from Reutlingen Research Institute (Germany)
2. hemp needle punched non-woven originating from Hemp Technology (UK) and supplied by Movevirgo
3. PLA thermobonded hemp non-woven originating from Advance Nonwoven (Danmark) and supplied by Movevirgo (Figure 1).

Non-woven samples were cut to 21.7 x 5.9 cm in order to fit in the 6 cm wide tunnel around the belt in the plasma unit (ref. D3.3, section 2.2) and in the 21.9 cm long SMC mould (Annex 1).



Figure 1: Non-woven fibre samples used for plasma trials: Steam exploded flax (left), needle punched hemp (middle), PLA thermobonded hemp (right).



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Prior to plasma treatment, fibre samples were dried overnight in an oven at 105 °C (Figure 2) and cooled in a desiccator for 1 hour (Figure 3). In order to keep fibres dry as much as possible, they were transported to and from the plasma unit in a closed plastic bucket containing pre-dried silica gel (Figure 4).



Figure 2: Oven to dry fibre non-woven samples prior to SMC production.



Figure 3: Desiccator to cool pre-dried fibre samples.





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Figure 4: Bucket containing pre-dried silica gel for transportation of natural fibre mats to and from plasma unit.

Feed gas compositions for the plasma trials were based on AcXys' experience: N_2 , $N_2 + 0.1\% O_2$, $N_2 + 0.5\% CO_2$, $N_2 + 0.5\% N_2O$, $N_2 + 1\% H_2$. Actually, AcXys suggests to apply 0.05% of O_2 , however it appeared that the O_2 gas flow of the lab scale plasma unit could not be set accurately at a flow below 0.06 L/min.

In order to apply thorough plasma treatment conditions to evaluate the effect of feed gas composition, samples were treated at 2 sides, passing 6 times under the plasma flame at lowest speed possible (2.9 m/min, effective speed 0.48 m/min), and at maximum nitrogen flow (60 L/min).

Plasma treated fibre samples were impregnated with SMC resin paste within 30 minutes (Annex 2), and kept in a closed plastic bucket containing pre-dried silica gel until impregnation.

The effect of these plasma treatments on fibre surface modification and fibre strength was addressed in D3.3, section 2.2, already. Therefore, no specific analysis was performed on the treated fibre for SMC composites.

2.2 Task 3.4 Compatibilisation to unsaturated polyester (UP) polymers

Flax and hemp fibre samples were prepared and plasma treated as described in section 2.1. Plasma treated fibre samples were kept in a closed plastic bucket containing pre-dried silica gel until impregnation with SMC. Impregnation was performed within 30 minutes after plasma treatment. Unless stated otherwise, 3 layers of impregnated fibre were stacked to mould into 1 composite test plaque. Further details of the moulding procedure have been described in Appendix 2. The test plaques were cut into test specimens of 80 x 10 mm.

As flexural strength gives a good indication of fibre-matrix adhesion, while showing the composite mechanical performance at the same time, this method was selected to analyse fibre-polymer compatibilisation (D5.2, section 2.1.1).

2.2.1 Hemp-UP

As a result of plasma treatment of hemp fibres, hemp-UP composite flexural strength increases by 20% and 15% for $N_2 + CO_2$ (SMC-22) and $N_2 + N_2O$ (SMC-23) plasma, respectively (Table 1). Also improved strain at maximum stress of 26% confirms improved fibre-matrix adhesion. Flexural modulus, however, hardly increases, as may be expected for long fibre composites.



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N₂ (SMC-20) and N₂ + O₂ (SMC-21) feed gasses seem not to have a positive effect on composite flexural strength. N₂ + H₂ was evaluated in a separate series, but also did not show a positive effect on composite flexural strength (Table 6, SMC-41).

It should be noted that the flexural strength performance of the untreated fibre-UP composite (SMC-27) is lower than during the trials performed to establish optimized SMC composition and moulding conditions (Annex 2). This may be due to reduced resin paste flow as a result of ageing of the resin paste: The age of the resin paste during SMC preparation and moulding was about 2 and 9 weeks, respectively.

Scanning electron microscopy (SEM) has been applied in order to better understand the results collected so far. SEM images of fracture surfaces of untreated and plasma treated hemp-UP composites have been presented in Figure 5. Fibre pull out length seems to be shorter for the for N₂ + CO₂ plasma treated hemp fibre composite (SMC-22) than for the untreated fibre composite (SMC-27), suggesting better fibre-matrix adhesion after N₂ + CO₂ 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 5). However, poor bonding predominates in the untreated hemp fibre SMC, and good bonding predominates in the N₂ + CO₂ plasma treated hemp fibre composite.

SEM images also show some voids. It is not clear whether these arise from residual water in the fibres or incomplete impregnation of the fibres after SMC sheet preparation.

Table 1: Properties of hemp fibre SMC composites: Effect of plasma.

Code	Plasma	Fibre Content	Density	Flexural strength		Flexural modulus		Strain at max Stress	
		(wt%)	(g/cm ³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-27	-	23.6%	1.56	64.3	3.9	7.65	0.41	1.38	0.18
SMC-20	N ₂	23.8%	1.47	64.3	3.9	7.54	0.35	1.57	0.18
SMC-21	N ₂ + 0.1% O ₂	24.5%	1.49	67.2	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 ₂ O	26.4%	1.44	74.1	3.6	7.91	0.45	1.76	0.15

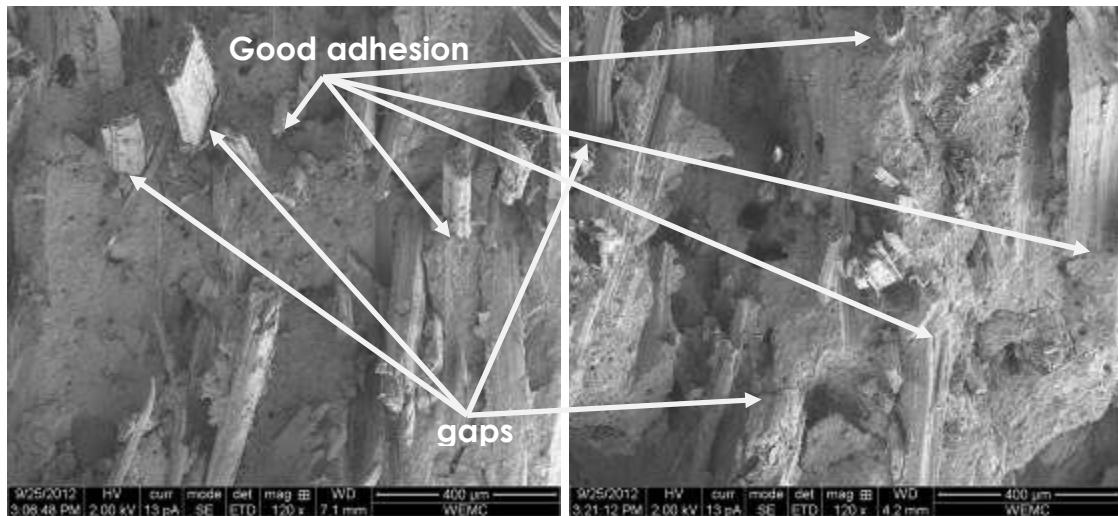


Figure 5: SEM pictures of fracture surfaces of UP composites based on untreated (left) and N₂ + CO₂ plasma treated (right) hemp fibres.

2.2.2 Hemp (PLA bonded)-UP

As it was expected that PLA thermobonded hemp non-wovens might exhibit better 'fibre flow' during SMC moulding, UP composites based on this material were evaluated. Mechanical properties (SMC-25 & 26, Table 2) appear much lower than for needle punched (100%) hemp non-woven based UP composites (SMC-27). The lower performance is likely not caused by fibre content as this is in the range evaluated for needle punched non-wovens (30-31% vs. 24-35%). Further, the density of the PLA thermobonded hemp based composites (1.40-1.42 g/cm³) is similar to the lower range of densities found for needle punched hemp non-wovens (1.44-1.61 g/cm³) and steam exploded flax non-wovens (1.40-1.59 g/cm³). However, the latter two fibre grades exhibit much better composite flexural strength performance. Also, no explanation for the poor composite flexural strength performance can be derived from SEM images (Figure 6).

Further, N₂ plasma treatment has no significant effect on flexural strength, like for the needle punched hemp fibre mat based UP composites.

Table 2: Properties of thermobonded hemp fibre SMC composites: Effect of plasma.

Code	Plasma	Fibre	Density	Flexural		Flexural		Strain at max	
		Conten		Strength	Modulus	Stress			
		(wt%)	(g/cm ³)	(MPa)	Stdev	(GPa)	stdev	(%)	stdev
SMC-26	-	30.1%	1.42	44.6	2.0	7.09	0.52	0.76	0.08
SMC-25	N ₂	31.3%	1.40	46.4	4.0	7.17	0.25	0.81	0.11



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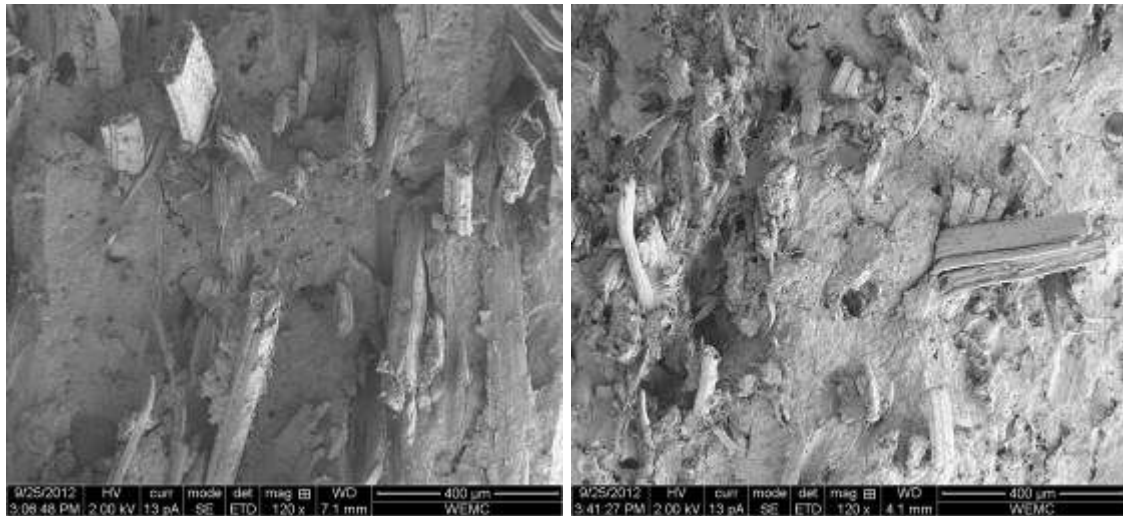


Figure 6: SEM pictures of fracture surfaces of UP composites based on untreated needle punched hemp (left) and N₂ plasma treated PLA thermobonded hemp fibres (right).

2.2.3 Flax-UP

In order to get an impression of fibre impregnation and composite performance for very fine fibres, steam exploded flax 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 untreated and ultrasonically treated hemp fibres have a diameter in the range of 40-150 micron (also see Figures 6, 8 and 10).

It should be noted that the m²-weight of the steam exploded flax was about 3 times lower than for the needle punched hemp non-wovens. In order to obtain a similar composite thickness and fibre content (Table 3), 9 or 10 layers of steam exploded flax were used to make an SMC composite.

SMC composite based on steam exploded flax appears to be (somewhat) stronger than hemp based composites (Table 3). Results for N₂ plasma treated flax fibres (SMC-24) are shadowed by poor impregnation of the central part (30 – 50%) of the composite (Figure 7). Poor impregnation is likely caused by the reduced resin paste flow as a result of ageing as explained at the hemp composites discussion. Also, the steam exploded flax fibres are much finer than the hemp fibres (Figure 8), which may hamper resin flow. Still, the best 2 specimens show a strength improvement of 12% up to 101 MPa relative to the original composite (SMC-7) where a better flow was obtained, considering the impregnation in the central part of the composite (Figure 7). It may be concluded that good fibre impregnation requires better resin paste flow for fine steam exploded flax fibres than for coarse unrefined hemp fibres.

Table 3: Properties of (steam exploded) flax fibre SMC composites: Effect of plasma.



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Code	Plasma	Fibre content (wt%)	Density (g/cm ³)	Flexural strength		Flexural modulus		Strain at max Stress	
				(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 7: SMC specimens based on (steam exploded) flax fibre, the central section of the composite showing incomplete fibre impregnation. SMC-7 (left), SMC-24 (right).

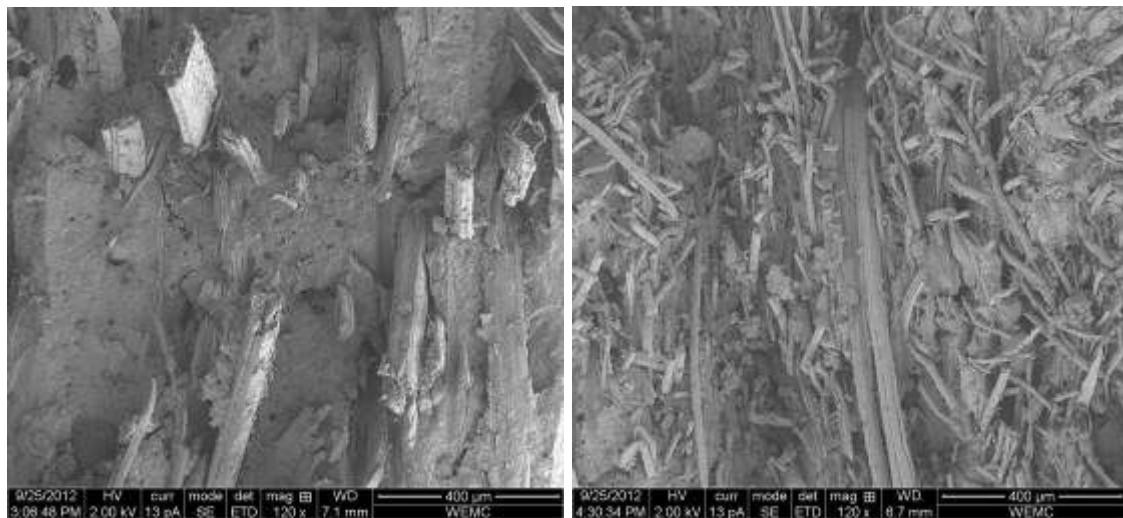


Figure 8: SEM pictures of fracture surfaces of UP composites based on untreated hemp (left) and steam exploded flax fibres (right).

2.2.4 Conclusions on compatibilisation to UP matrix

Plasma treatment of hemp fibre using N₂ + CO₂ feed gas, exhibits an improvement of SMC composite flexural strength by up to 20%. 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.



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2.3 Task 3.5 Process experimentation / optimisation for UP polymers

2.3.1 Optimisation of plasma processing

In order to study the effect of processing rate on efficiency of the plasma treatment, hemp samples were plasma treated at higher speeds: 1.45 and 2.9 m/min versus 0.48 m/min for trials described in section 2.2 (corresponding to 2 and 1 versus 6 passages through the plasma flame at the minimum belt speed of 2.9 m/min, and coded 2/2, 1/2 and 6/2, respectively).

For making the SMC materials, a second batch of fresh resin paste was used. This results in a flexural strength performance for the untreated hemp reference SMC (Table 4, SMC-31) which is intermediate between that of the series to establish optimized SMC composition and moulding conditions (Annex 2, Table 14, SMC-5) and the series on the effect of plasma on hemp-UP composite performance (Table 1, SMC-27). In this series, only a 5% improvement of flexural strength is obtained for CO₂ dopant gas (SMC-32). At increased plasma treatment speed, no strength improvement is observed anymore (SMC-33,34). For N₂O dopant gas even a reduction in strength is observed (SMC-35).

Table 4: Properties of hemp fibre SMC composites: Optimisation of plasma.

Code	Plasma	Fibre content	Density	Flexural strength		Flexural modulus		Strain at max Stress	
		(wt%)	(g/cm ³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-31	-	25.8%	1.56	77.8	3.5	7.79	0.32	1.91	0.15
SMC-32	N ₂ + 0.5% CO ₂ (6/2)	25.7%	1.64	81.9	6.1	8.49	0.59	1.81	0.18
SMC-33	N ₂ + 0.5% CO ₂ (2/2)	25.1%	1.61	77.1	1	7.95	0.23	1.94	0.05
SMC-34	N ₂ + 0.5% CO ₂ (1/2)	24.9%	1.61	78.1	4.3	8.37	0.47	1.84	0.27
SMC-35	N ₂ +0.5% N ₂ O (2/2)	25.0%	1.57	73.0	2.7	8.12	0.17	1.76	0.09

2.3.2 Cleaning of fibre (Ultrasonically treated hemp)

The effectiveness of the plasma treatment on fibre-matrix adhesion may be limited if the fibre surface contains contaminants which are not firmly bonded to the fibre. Ultrasonic (US) treatment is supposed to clean fibre surfaces, and as a consequence improved fibre-matrix interaction may be expected. Ultrasonically 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, except that 4 instead of 3 layers of fibres needed to be used in order to achieve a fibre content of about 25 wt.%. Table 5 shows the US treated hemp-UP composite performance relative to the untreated hemp-UP composite. It appears that just US treatment results in a 14% higher composite flexural strength. From SEM images, both from the pure fibres (Figure 9) as well as composite fracture surfaces (Figure 10), no explanation can be derived.



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Ultrasonically treated and untreated fibres appear to exhibit similar fibre diameter range, surface morphology (cleanness) and fibre pull out length.

Table 5: 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/cm ³)	(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

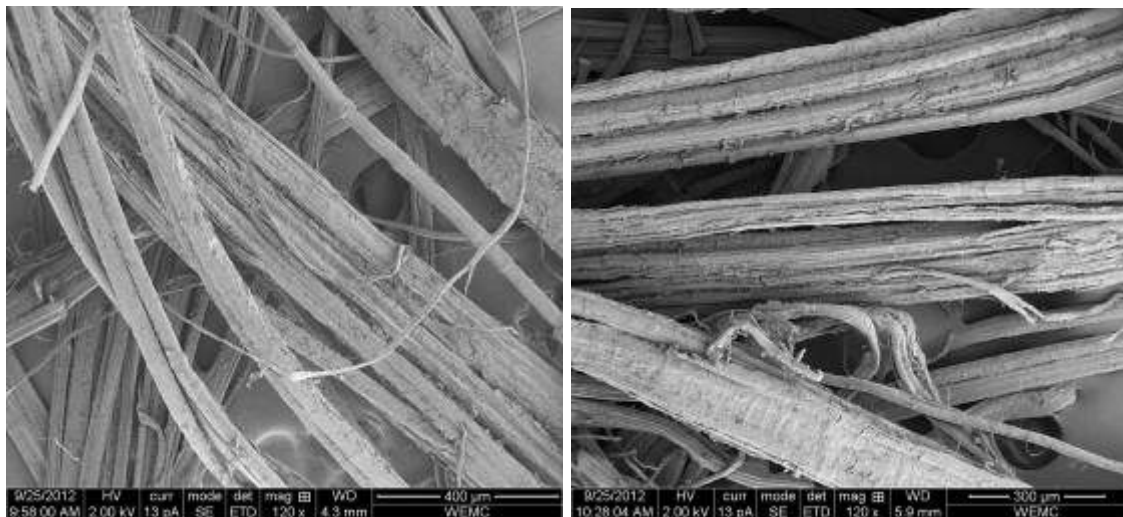


Figure 9: SEM pictures of untreated (left) and ultrasonically treated hemp (right).

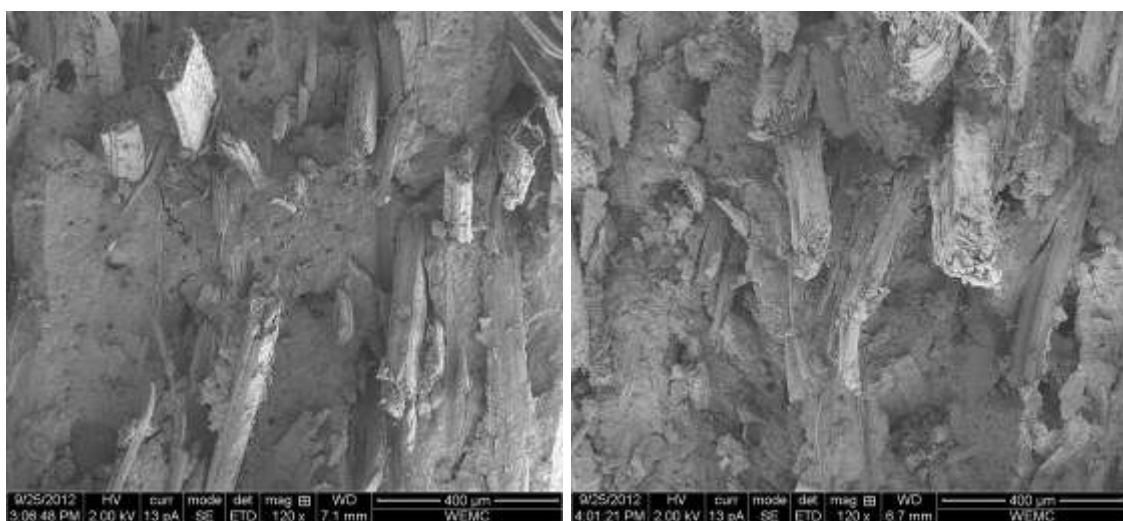


Figure 10: SEM pictures of fracture surfaces of UP composites based on untreated hemp (left) and ultrasonically (and N₂ plasma) treated hemp fibres (right).



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2.3.3 Application of chemical 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 has 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 polymerize 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.

Negative aspect 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, for instance (γ -methacryloxypropyl-trimethoxysilane). The silane moiety easily reacts with glass fibre. For condensation onto natural fibres, reaction temperature should be above 90°C (Belgacem, 2008¹). 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 (f.i. 2,3-epoxypropyl-methacrylate) contains 2 functional groups: an epoxy and a vinyl functionality. The epoxy moiety easily reacts with amine groups (NH₂), 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.

¹ Belgacem and Gandini, 2008. Surface modification of cellulose fibres, Chapter 18 in 'Monomers, Polymers and Composites from Renewable Resources', Eds. Belgacem and Gandini, Elsevier, Amsterdam.



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Papers on coupling of GMA to carrier materials are based on different processing techniques: solution methods, melt processing, low pressure plasma (for details see below). 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 (83-85°C; for more details, see below). 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 (Zou, 2000 ²).
- Si(100) wafers using low pressure plasma for improved adhesion to PI: method, potential reaction schemes and kinetics (Zou et al., 2001 ³).
- 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 (Pracella, 2010 ⁴).
- PTFE sheets using GA 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 (Tanfani, 1990 ⁵).

The majority of the papers focusses 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

² Zou, Kang, Neoh, Cui and Lim, 2000. Surface modification of poly(tetrafluoroethylene) films by plasma pre-activation and plasma polymerisation of glycidyl methacrylate, *Plasmas and Polymers* 5 (3/4), 219-234.

³ Zou, Kang, Neoh, Zhang, Tan, Cui and Lim, 2001. Plasma polymerization and deposition of glycidyl methacrylate on Si(100) surface for adhesion improvement with polyimide, *Polymers for Advanced Technologies* 12, 582-595.

⁴ Pracella M, Minhaz-UI Haque Md and Alvarez V, 2010. Functionalization, compatibilization and properties of polyolefin composites with natural fibres, *Polymers* 2, 554-574.

⁵ Tanfani F, Durrani AA, Kojima M and Chapman D, 1990. Glycidyl acrylate plasma glow discharged polymers, *Biomaterials* 11, 585-589.



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natural fibres are mainly based on solution methods (f.i. Sreekala et al., 2000 ⁶; Kalia et al., 2009 ⁷; but certainly also Bledzki et al, etc.).

Experimental trials using combined plasma treatment and GMA

This project focusses on atmospheric plasma and we will try 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 cm² containing GMA (Figure 11). 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 6), however, it appears that this improvement is independent of plasma treatment or not. From SEM images (Figure 12), no explanation can be derived.



Figure 11: Set-up for applying GMA onto plasma treated hemp non-woven.

Table 6: Properties of hemp fibre SMC composites: Effect of Coupling agent.

⁶ Sreekala, MS, Kumaran MG, Joseph S, Jacob M, Thomas S, 2000. Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modification on the mechanical performance, *Applied Composite Materials* 7, 295-329.

⁷ Kalia S, Kaith BS and Kaur I, 2009. Pretreatments of natural fibres and their application as reinforcing material in polymer composites – A Review, *Polymer Engineering and Science* , 1253-1272.



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Code	Plasma + GMA time	Fibre content	Density	Flexural strength		Flexural modulus		Strain at max Stress	
		(wt%)	(g/cm ³)	(MPa)	stdev	(GPa)	stdev	(%)	stdev
SMC-40	-	26.3%	1.66	80.0	4.8	8.71	0.19	1.68	0.16
SMC-41	N ₂ + 1% H ₂ (6/2)	27.0%	1.61	79.0	6.1	8.66	0.39	1.67	0.17
SMC-42	N ₂ +1%H ₂ (1/2) + 60 min GMA	27.4%	1.64	86.3	4.3	9.1	0.33	1.7	0.06
SMC-43	N ₂ +1%H ₂ (1/2) + 10 min GMA	26.4%	1.67	80.0	5.3	8.83	0.18	1.65	0.2
SMC-44	N ₂ (1/2) + 60 min GMA	26.4%	1.69	85.0	3.9	9.51	0.23	1.66	0.14
SMC-45	85 min GMA	28.1%	1.65	85.4	6.7	9.21	0.12	1.72	0.24

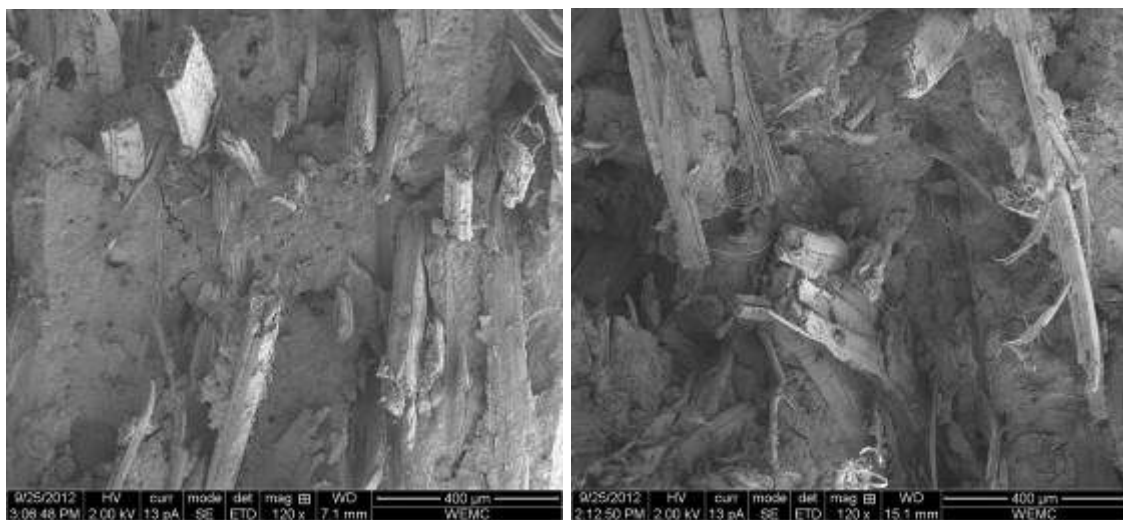


Figure 12: SEM pictures of fracture surfaces of UP composites based on untreated hemp (left) and ultrasonically (and N₂ plasma) treated hemp fibres (right).

2.3.4 Comparison to glass fibre based SMC

Glass fibre based SMC (commercial grade) was provided by Movevirgo, moulded by DLO-FBR at 140°C for 3 minutes, 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:

- For hemp, ultrasonic treatment followed by N₂ + CO₂ 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.
- N₂ 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.
- After composite fracture, the glass fibre surfaces are basically as clean as the hemp and flax fibres (no resin adhering to surface), although no gaps between glass fibres and UP matrix are observed, which would



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indicate an overall better bonding between the glass fibre and the UP resin than achieved for the natural fibres (Figure 13). Glass fibre pull out lengths are very long compared to flax and in particular the hemp fibres (Figure 14), which suggests that the strength of the natural fibres is low.

Table 7: 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/cm ³)	(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

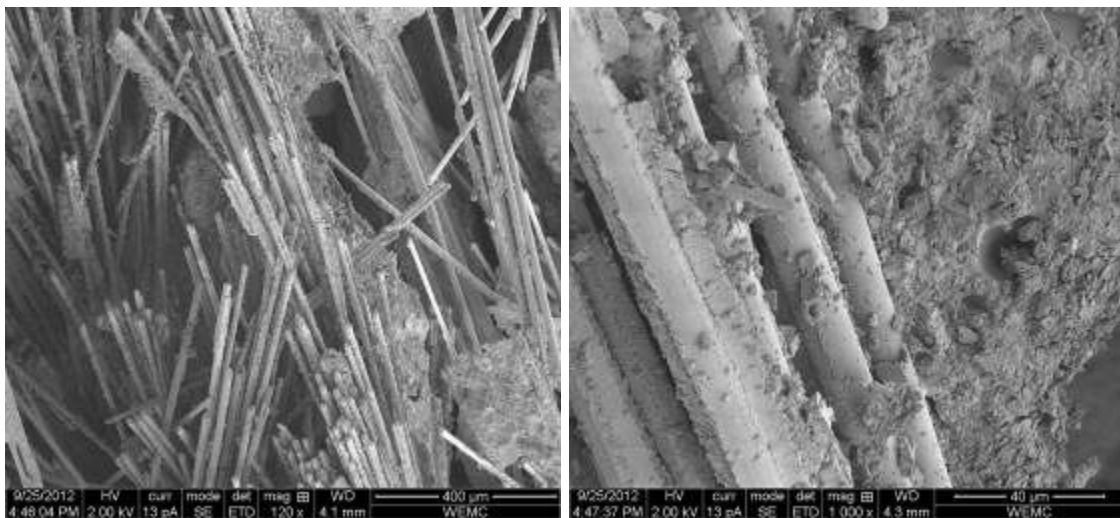


Figure 13: SEM pictures of fracture surfaces of glass fibre based UP composites.





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Figure 14: Fibre pull out of impacted glass (left) and hemp (right) fibre based UP composites.

2.3.5 Energy consumption and emissions

Energy consumption and emissions depend on feed gas composition and processing speeds. Plasma processing parameters were in the same range for UP based composites as for previously evaluated PP and PLA based composites (D3.3). Therefore, energy consumption and emission data for UP composites may be considered as presented in D3.3, section 2.4.

2.3.6 Conclusions on process optimization

Whereas composite flexural strength appears to increase by up to 20% for thorough plasma treatment using N₂ + CO₂ feed gas, no strength improvement is observed anymore at increased treatment speed. Ultrasonic treatment shows a 14% increase in composite flexural strength. This improvement, however, appears not due to fibre refining or surface cleaning. The use of an additional bi-functional coupling agent, glycidyl methacrylate, which is expected to exhibit chemical interaction with both plasma induced NH₂ sites on the fibre surface and with unsaturated polyester formulations, only shows a flexural strength increase of 6–8 %, independent of applying plasma treatment or not. Comparing to commercial glass fibre based SMC, N₂ 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.

2.4 WP6 Pilot scale trials

Pilot trials on plasma treatment and SMC manufacturing will be extensively addressed in D6.1 In this D3.4 report, a summary of the pilot trial results will be discussed in order to allow direct correlation to the lab scale trial results presented in sections 2.1 – 2.3.

2.4.1 Fibre non-woven preparation

It is expected that PLA thermobonded hemp non-wovens might exhibit better 'fibre flow' during SMC moulding than needle punched non-wovens. Therefore, a PLA thermobonded hemp fibre non-woven of 25 cm wide and 30 m long was sourced from Advance Non-Woven (Denmark) and provided by Movevirgo.

Production of thermobonded non-wovens based on fibres from the UltraFibre project appeared to consume disproportionately amount of resources. Therefore, unbonded and needle punched mats were prepared at Leeds University - Nonwovens Innovation & Research Institute (NIRI) (organized by InControl and RAPRA).



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Needle punching comprised 75 punches/cm² (pscm) and was 6 and 9 mm deep. Non-wovens were prepared based on untreated hemp tow and ultrasonically treated hemp tow. In order to achieve sufficient mat handling properties, 15% Tencel fibre (1.7 dtex, 38 mm) was applied as carrier fibre (Figure 15). 4 'Mats' of Tencel and hemp fibre were stacked, carded and needle punched into non-wovens of about 70 * 70 cm².

The needle punched mats were cut at CTP to a width of 25 cm in order to fit in the pilot scale plasma unit. Non-woven density data and codes are presented in Table 8.



Figure 15: Hemp fibre non-woven produced at Leeds University with (white) Tencel as carrier fibre.

Table 8: Density data and codes of non-wovens subjected to pilot scale plasma treatment at CTP.



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	Code	Weight	Length	Density
		250 mm sheets		
		(g)	(cm)	(g/m ²)
Untreated				
Not Bonded	U1	58	64.5	360
	U2	56.9	64	356
6 mm, 75 pscm	U3	55.8	69	323
	U4	53.9	69.5	310
	U5	51.4	69	298
	U6	48.6	68.5	284
9 mm, 75 pscm	U7	49.4	69	286
	U8	47.3	68	278
	U9	58.7	71	331
	U10	52.9	70.5	300
Ultrasonically treated				
Not Bonded	T1	52.3	59	355
	T2	50.8	58	350
6 mm, 75 pscm	T3	59.1	69.5	340
	T4	58.4	69	339
	T5	53.5	68.5	312
	T6	53.9	69	312
9 mm, 75 pscm	T7	52.8	69	306
	T8	51.5	69	299
	T9	51.1	72	284
	T10	51.5	70.5	292

2.4.2 Pilot scale plasma treatment

Pilot scale plasma treatments were performed at CTP (Grenoble, France) and organized by AcXys, DLO-FBR, Movevirgo, InControl and RAPRA. The plasma unit at CTP has been produced by AcXys.

Hemp fibre mats were placed on a paper belt without fixation (Figure 16) and plasma treated at 2 sides. The PLA thermobonded hemp fibre non-woven was plasma treated the same way. Video recordings are available.



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Figure 16: Plasma unit of 25 cm wide used for pilot scale trials.

Feed gas composition for these plasma trials was $N_2 + 0.5\% CO_2$, based on lab scale trials performed at DLO-FBR (see section 2.2). 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 (may be selected from 2000-3000 W) = 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 (Figure 17).
- Gloves were used to handle the fibre material.



Figure 17: Plasma treatment of natural fibre non-woven.



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Plasma treated fibre samples were wrapped in subsequently aluminium foil and a PE bag and sent to Gloucester Composites (UK) for SMC production 4 days later. Based on AcXys' experience, surface modification is best retained when the treated material is packed in aluminium foil. Best way to store plasma treated samples would be in vacuum, however, this would destroy the non-woven structure to such extent that successful further processing into SMCs will not be possible anymore.

2.4.3 Pilot scale SMC sheet production

Pilot scale SMC sheet production was performed at Gloucester Composites and organized by Movevirgo, RAPRA and DLO-FBR.

3 Runs were performed:

- 1) Run 1
 - a. Untreated PLA thermobonded hemp mat
 - b. Blade set at 1.35 mm resulting in resin:fibre ratio of about 6:1
- 2) Run 2 and 3
 - a. Blade set at 0.9 mm, as close to resin:fibre = 3:1 as possible.
 - b. Materials treated:
 - i. Ultrasonically and Plasma treated non-wovens T1-T10
 - ii. Plasma treated non-wovens U1-U10
 - iii. Ultrasonically treated non-bonded, 6 mm and 9 mm punched non-wovens
 - iv. Untreated non-bonded, 6 mm and 9 mm punched non-wovens
 - v. Plasma treated PLA thermobonded hemp non-woven
 - vi. Untreated PLA thermobonded hemp non-woven

The SMC sheets were shipped to DLO-FBR and reached the institute 5 days later. The SMC sheets were stored at 4°C until moulding.

The amount of resin paste on the hemp fibre mats seemed very low (Figure 18). Nevertheless, the ratio of resin:hemp was about 3:1 for the 500 g/m² PLA thermobonded hemp mats, and about 5:1 for the 300 g/m² needle punched hemp mats. The blade gap of 0.9 mm was the absolute minimum for the SMC production equipment.



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Figure 18: Protecting film released from SMC sheet, showing distribution of resin paste on hemp mat.

2.4.4 Moulding of pilot scale produced SMC sheets to test plaques

SMC sheets were moulded to test plaques using the mould presented in Figure 43 (Appendix 2). Moulding was performed 1, 13 and 14 days after arrival of the SMC material. SMC sheets were cut to pieces with sizes tuned to obtain good filling of the mould (Figure 19). Sizes cut were in the range 7.2 * 18 cm² to 9.5 * 21.5 cm², and 3–3.5 SMC sheets were stacked to obtain good filling of the mould. SMC sheets were moulded for 3 minutes at 140°C (mould surface temperature was checked and was in the range 140–143°C). 7 Plaques per SMC composition were moulded (Figure 20). Coding was as follows:

- First letter refers to fibre: H = hemp G = glass
- Second character: P = PLA bonded, U = non-bonded (= no needle punching), 9 = 9 mm punching. In the Glass-SMC, 2 refers to 2nd series.
- Third character: U = no Ultrasonics, T = Ultrasonic treatment
- Fourth character: U = no Plasma, T = Plasma treatment
- Last number is sample number within the series.

It appeared that the glass fibre based SMC composites were difficult to remove from the Teflon coated mould and that the glass fibre accelerates the Teflon deterioration due to flow of the glass fibres during moulding.

As mentioned in section 2.2.2, needle punched hemp mats show poor flow performance in a 3D mould. 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. Therefore, it is important that the fibres flow with the resin during moulding (also see section 2.4.6, below Table 12).

Fibre content in final test plaques was determined by taking into account the fibre non-woven m²-weight, number of SMC sheet layers in the SMC composite, the total weight of SMC composite released from the mould. This calculation is based on the observation that no hemp fibre has flown out of the mould during moulding. Fibre content values are presented in Table 9 and Table 10.



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Figure 19: Required SMC sheet dimensions were determined at cut.

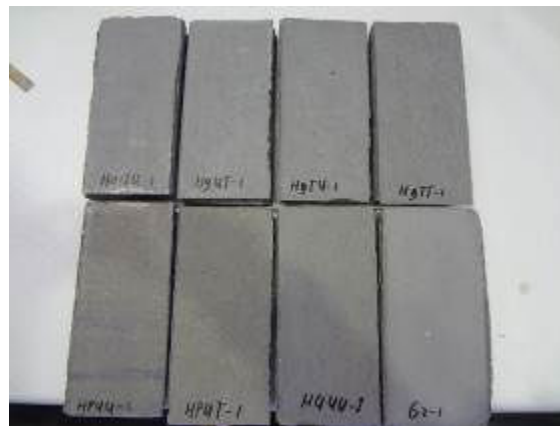


Figure 20: SMC composite test plaques.

Table 9: Fibre content in SMC composite test plaques.



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Non-woven		Composite		Non-woven		Composite	
Density (g/m ²)	Number Layers	Code	Fibre content (wt.%)	Density (g/m ²)	Number Layers	Code	Fibre content (wt.%)
500	3	HPUU-1	27.6%	295	3	H9TU-1	17.4%
500	3	HPUU-2	26.8%	295	3	H9TU-2	16.0%
500	3	HPUU-3	28.3%	295	3	H9TU-3	15.1%
500	3	HPUU-4	26.8%	295	3	H9TU-4	16.1%
500	3	HPUU-5	27.2%	295	3	H9TU-5	15.7%
500	3	HPUU-6	27.8%	295	3	H9TU-6	16.3%
500	3	HPUU-7	27.3%	295	3	H9TU-7	15.6%
500	3	HPUT-1	27.0%	300	3	H9UT-1	15.3%
500	3	HPUT-2	29.0%	300	3	H9UT-2	16.9%
500	3	HPUT-3	28.9%	331	3	H9UT-3	19.1%
500	3	HPUT-4	28.7%	331	3	H9UT-4	17.7%
500	3	HPUT-5	28.3%	278	3	H9UT-5	15.3%
500	3	HPUT-6	28.6%	278	3	H9UT-6	14.4%
500	3	HPUT-7	28.9%	286	3	H9UT-7	14.8%
360	3.5	HUUU-1	23.4%	292	3	H9TT-1	16.6%
360	3.5	HUUU-2	23.0%	292	3	H9TT-2	15.2%
350	3	HUTU-1	18.8%	284	3	H9TT-3	16.3%
350	3.5	HUTU-2	22.2%	284	3	H9TT-4	16.0%
350	3	HUTT-1	19.2%	299	3	H9TT-5	15.6%
350	3	HUTT-2	18.3%	299	3	H9TT-6	16.7%
				306	3	H9TT-7	15.9%
300	3	H9UU-1	17.3%	1297	2	G2-1	25.6%
300	3	H9UU-2	16.1%	1297	2	G2-2	24.8%
300	3	H9UU-3	16.5%	1297	2	G2-3	25.2%
300	3	H9UU-4	17.1%	1297	2	G2-4	25.4%
300	3	H9UU-5	15.9%	1297	2	G2-5	25.3%
300	3	H9UU-6	16.7%	1297	2	G2-6	25.4%
300	3	H9UU-7	16.7%	1297	2	G2-7	25.6%

The ratio of SMC sheet material going in the mould and SMC composite coming out of the mould varies a lot. This ratio is about 90–92% for the PLA thermobonded hemp SMCs, 94% for the unbounded hemp SMCs, 96–98% for the 9 mm needle punched hemp SMCs and 99% for the glass fibre based SMCs. As hemp fibres may contain about 10% moisture at equilibrium conditions, the 25 wt.% hemp based SMC sheets may be considered to contain about 2.5% moisture. Moreover, the SMCs are kept dry in a closed bucket containing pre-dried silica gel until moulding. Transfer from the bucket to closure of the mould takes about 1 minute. So it is impossible that the weight loss is only due to evaporation of water.



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A further observation is that the hemp based SMC sheets are much more lofty than the glass SMCs. Actually, the trend found for material loss roughly corresponds to the trend for airiness (not quantified) of the hemp SMC sheets. As styrene is the most volatile component in the SMC sheet by far, the majority of material loss in the hemp based SMCs is probably due to evaporation of styrene.

A cross check during moulding trials at Movevirgo show similar values for standard glass SMC: a weight reduction of 1.75 % for the compact SMC sheet is very likely to be fully attributed to evaporation of styrene.

Several plaques started showed bending a bit directly after moulding. Therefore, warping was determined as defined in D5.3. Warping of 3 test plaques per series was determined: numbers 1,2 and 7:

- 'Hollow' side of the test plaque is top side in all cases.
- Variation in warping is very high, and it is not clear what exactly causes warping of the SMC composite. At least no correlation with poor fibre impregnation at the edges is found.
- Figure 21 suggests that warping correlates with fibre content: warping decreases with increasing fibre content.

Table 10: Fibre content, density and warping of SMC composite test plaques.

	Fibre content	Density		Warping	
	(wt%)	(g/cm ³)	StDev	(mm/mm)	Variation
HPUU	27.2%	1.42	0.017	0.013	97%
HPUT	28.0%	1.44	0.017	0.019	21%
HUUU	23.2%	1.42	0.035	0.016	62%
HUTU	20.5%	1.46	0.007	0.017	103%
HUTT	18.7%	1.49	0.009	0.023	36%
H9UU	16.7%	1.43	0.014	0.042	59%
H9TU	16.7%	1.44	0.035	0.030	108%
H9UT	16.1%	1.57	0.106	0.033	64%
H9TT	15.9%	1.41	0.079	0.045	93%
G2	25.2%	1.64	0.077	0.002	87%



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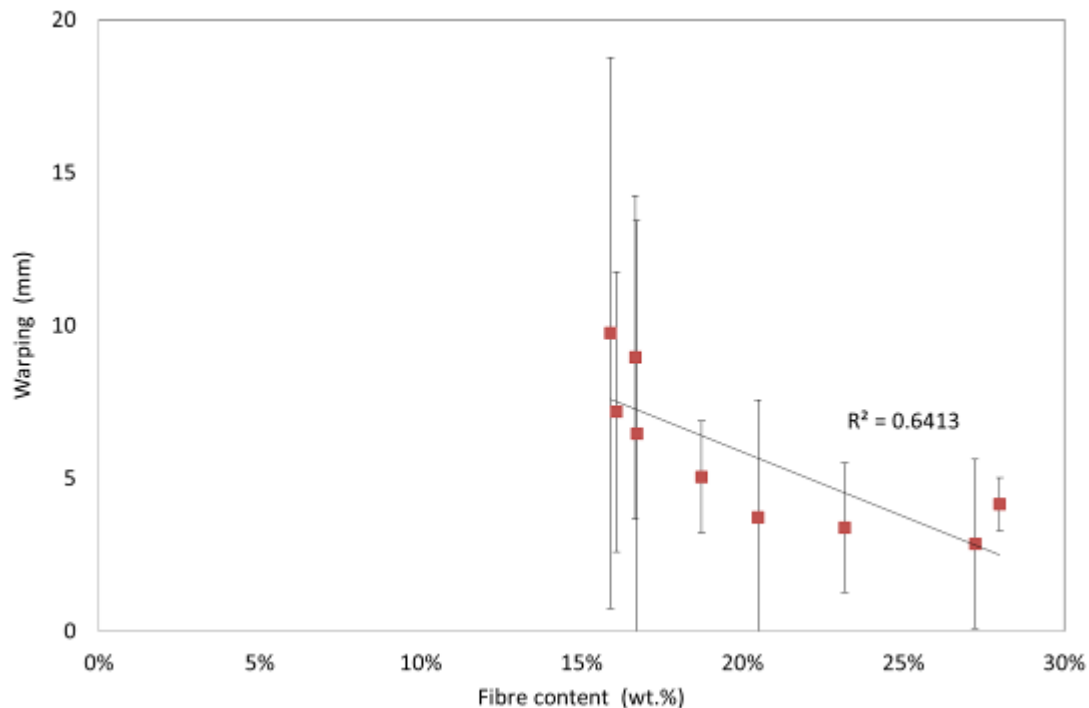


Figure 21: Warping of SMC composite plaques versus fibre content.

Part of the SMC composite plaques (numbers 1 & 2) were conditioned for 1 week and cut to test specimens for further analysis: flexural properties, Charpy impact, HDT.

Part of the SMC composite plaques (numbers 3–7) were sent to RAPRA for further analysis: tensile properties, water absorption, flexural properties before and after water absorption.

2.4.5 SMC composite performance of pilot scale produced material

SMC composite plaques were evaluated for a range of properties, which are presented and discussed in this section.

Results are presented in Table 11, Figure 23 and Figure 24 following may be concluded:

- Flexural strength increases by 13% after plasma treatment of 9 mm needle punched hemp (H9UT vs. H9UU). Strength of hemp based SMC composites is 33–47% of glass based SMC only, although variation for glass performance is 23%. However, strength is also lower than for the lab trials, f.i. comparing the best performances 70 MPa for HUTU vs. 89 MPa for SMC-36.
- Ultrasonics gives a 10% increase in flexural strength (HUTU s. HUUU).
- The effect of plasma on flexural modulus is ambivalent: 13% positive for H9UT vs. H9UU, 5% negative for H9TT vs. H9TU. Flexural modulus of hemp based SMC composites is 74–89% of glass based SMC. This is significantly lower than observed for lab scale trials where modulus of hemp SMC



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was up to 100% of glass SMC (while modulus of flax SMC was even 15% higher than for glass SMC).

- Ultrasonics gives a 10% increase in flexural modulus (HUTU s. HUUU).
- The effect of plasma on HDT is ambivalent: 41% positive for H9UT vs. H9UU, 5-15% negative for other SMC composites. Although variation in HDT values is very large, as large as 80°C for H9TU, individual HDT values approach HDT of glass SMC, which is > 200°C. The large variation was suggested to be due to incomplete curing of the UP resin for particular SMC composite materials. However, both HUUU-2 (HDT = 105°C) and HUTU-2 (HDT = 201°C) composites showed a small and similar size exothermic peak around 180°C only (Figure 22). The small exothermic peak suggests that the resin has not cured for 100% after the 140°C moulding cycle, and that mechanical properties may benefit from a post curing step.
- Ultrasonics gives a 17-35% increase in HDT (H9TU vs. H9UU and HUTU vs. HUUU).
- Natural fibres are known for poor impact performance. For the present hemp fibre SMC composites, Charpy impact strength is 7–16 % of glass SMC only. Charpy impact appears to be slightly negatively affected by both ultrasonics and plasma treatment. Hemp SMC can only be used in applications which are not critical for impact performance.
- Water absorption was determined at RAPRA (D6.1) and is highest for the PLA thermobonded hemp SMCs, about 11% after 8 weeks soaking in demi water. Water absorption is lowest for ultrasonically and plasma treated needle punched hemp SMC, about 8-8.5% for H9TU, H9UT and H9TT. Untreated needle punched hemp SMC shows water absorption value of 10.5% after 8 weeks. The glass SMC only absorbs about 2-2.5% after 8 weeks. None of the composites seems to have reached equilibrium water absorption after 8 weeks.
- The water was visibly clear after the 8 weeks absorption test, indicating that no significant amount of material is leaching from the composites.
- Flexural strength of SMC composites after water absorption (Figure 23) was determined at RAPRA and decreases with increasing water absorption time, in particular during the first 2 weeks. Plasma treatment of the hemp fibres seems to have a slightly positive effect on strength conservation for needle punched hemp SMCs, effect for PLA thermobonded hemp SMCs is negative, however.
- Flexural modulus of SMC composites after water absorption (Figure 24) was determined at RAPRA and decreases with increasing water absorption time, in particular during the first 2 weeks. No clear effect of plasma treatment of the hemp fibres on composite modulus can be observed.



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- The hemp fibre based SMC test plaques seem to have a high void content (Figure 25). The presented image is representative for all hemp fibre based SMC composite test plaques. Even the glass based SMCs contain a few voids. It may be concluded that the compression forces were not sufficient to obtain a fully condensed material. The large void content certainly negatively affects the composite mechanical and physical properties, and properties presented in Table 11, Figure 23 and Figure 24 will underestimate the full potential of natural fibre SMC composite performance.

Table 11: Flexural, Charpy impact and HDT properties of SMC composite test plaques.

	Flexural strength		Flexural modulus		Strain at max Strength		HDT-1.8 MPa 0.1% strain		Charpy impact 1fU	
	(MPa)	StDev	(GPa)	StDev	(%)	StDev	(°C)	StDev	(kJ/m ²)	StDev
HPUU	55.8	2.4	6.8	0.3	1.03	0.07	135.7	35.3	3.5	0.4
HPUT	53.5	2.7	6.82	0.33	0.94	0.06	129.3	3.5	3.3	0.5
HUUU	63.1	4.1	6.85	0.46	1.66	0.33	119.4	20.1	7.2	0.7
HUTU	69.5	3.9	7.55	0.19	1.58	0.11	160.6	56.6	6.8	1.2
HUTT	68.1	3.5	7.65	0.44	1.42	0.16	137.4	5.0	5.4	0.7
H9UU	52.2	4.5	6.4	0.28	1.28	0.3	135.2	15.1	5.1	0.4
H9TU	52.6	5.4	6.53	0.49	1.19	0.11	158.1	59.3	4.6	0.9
H9UT	59.0	7.0	7.21	0.3	1.26	0.3	190.3	0.6	4.4	0.5
H9TT	49.3	3.9	6.19	0.23	1.19	0.14	142.2	23.6	3.8	0.4
G2	149.2	35.0	8.61	0.852	2.84	0.4	>200		46.1	9.6



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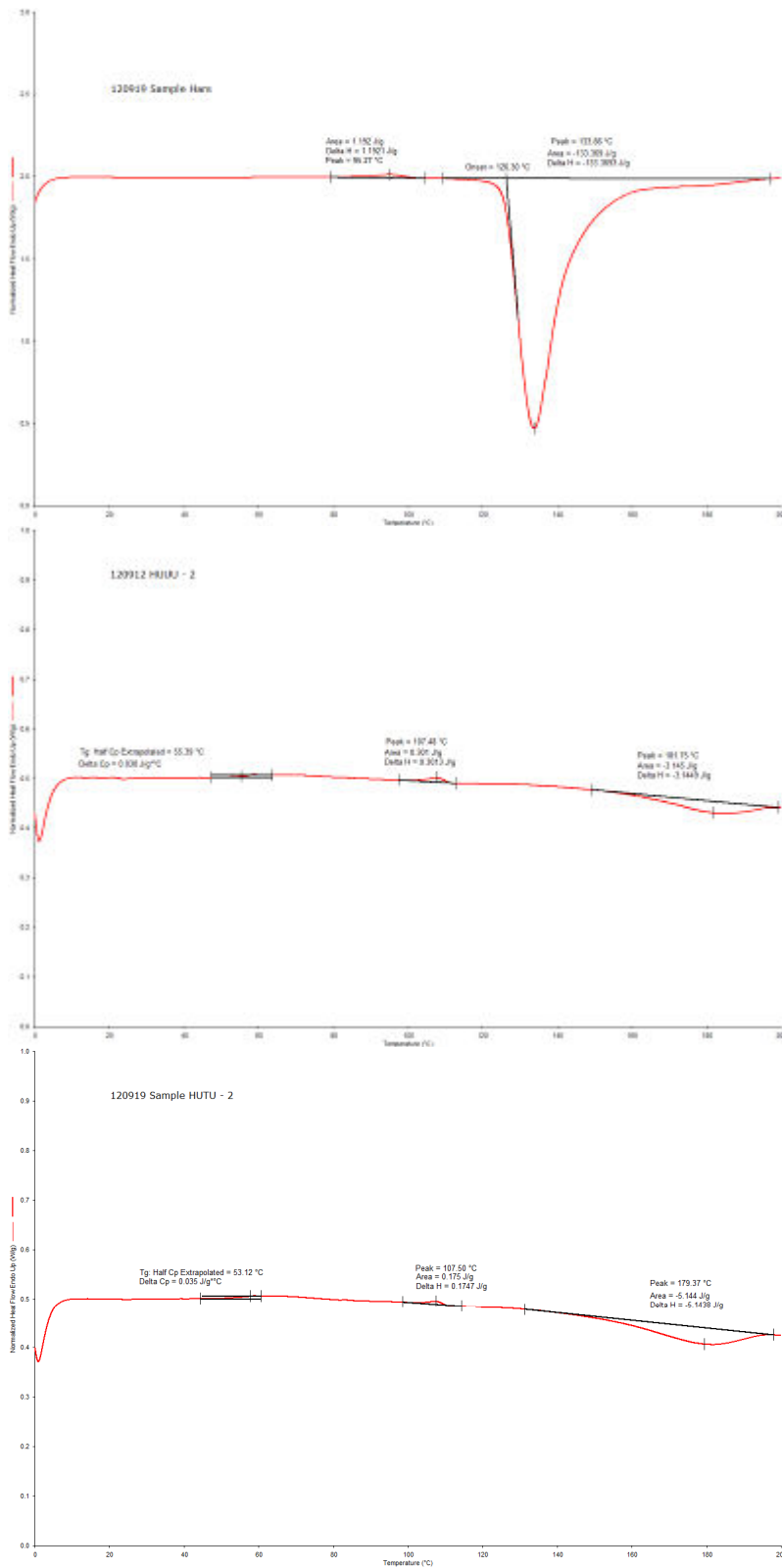


Figure 22: DSC curves for uncured resin paste (upper scan) and SMC composites (middle and lower scan).



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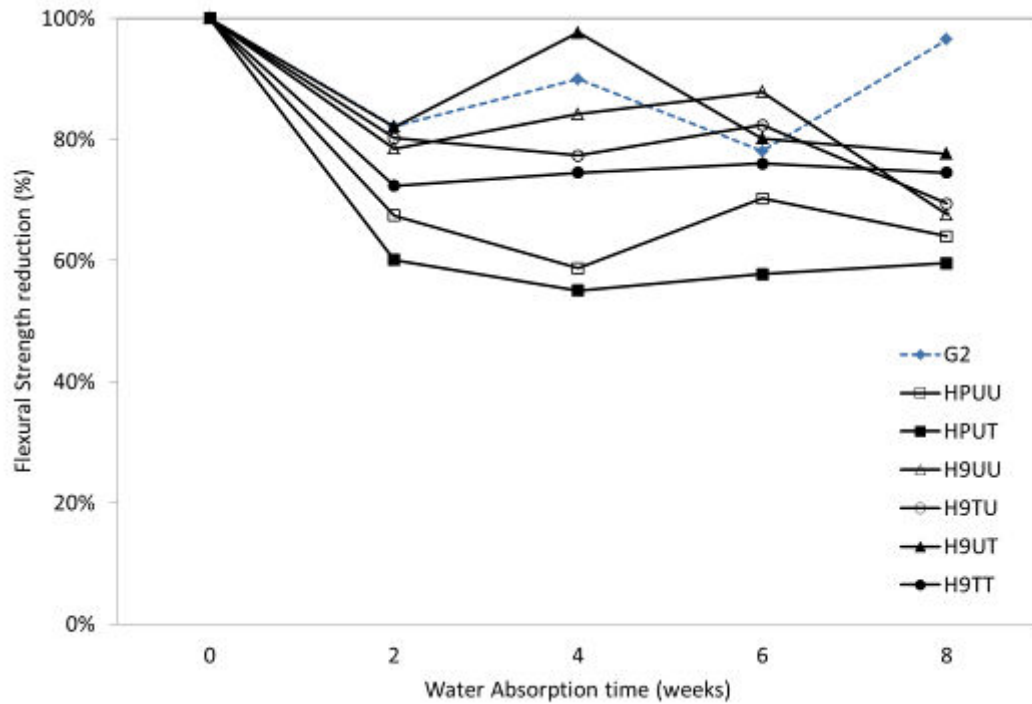


Figure 23: Flexural strength of SMC composites versus water absorption time.

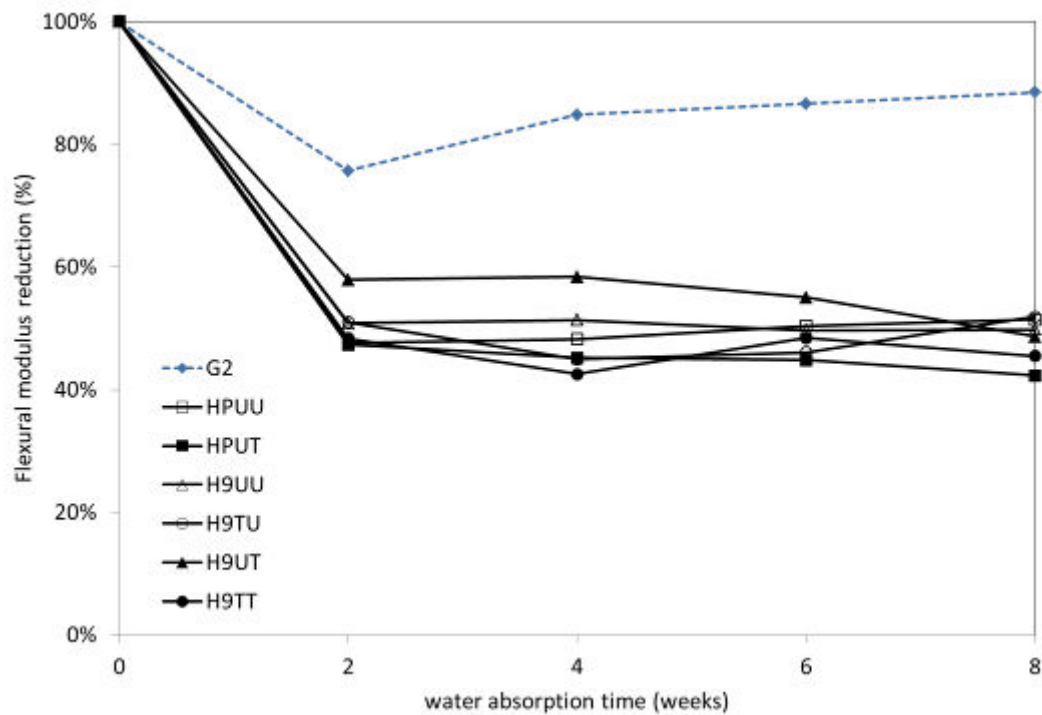


Figure 24: Flexural modulus of SMC composites versus water absorption time.



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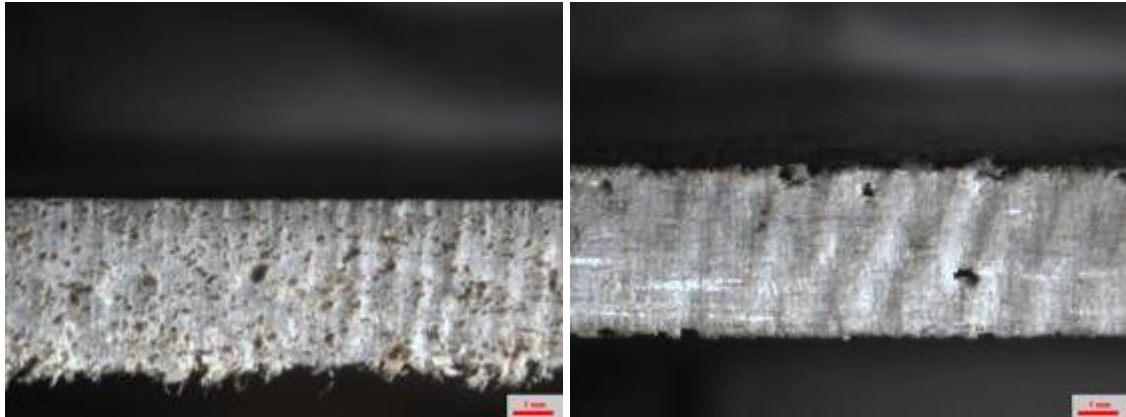


Figure 25: Cross section of SMC composite test plaques (hemp based, HPUT, left and glass fibre based, G2, right).

2.4.6 Industrial moulding of pilot scale produced SMC sheets

Movevirgo has produced several series of electrical joint connectors (EJC, Figure 26) based on flax and hemp fibre based SMC sheets.

Preliminary moulding trials based on steam exploded flax and impregnated in house with UP resin paste by Movevirgo (D6.1, section 2.2), resulted in poor mechanical performance due to the presence of voids, which were suggested to be caused by using small SMC sheets, too small to fill the entire mould cavity.



Figure 26: Electrical joint connector, moulded by Movevirgo.

Follow up moulding trials included the evaluation of mould filling degree (Test 4, D6.1, section 2.5). 2 needle punched hemp based SMC sheets were impregnated with UP resin paste by Movevirgo and placed overlapping in the middle section of the mould, 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 layers is the fibre content. Test specimens were cut from the flat areas of the EJC and evaluated for flexural



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performance (Table 12). Lab scale trials are confirmed (Table 14): Composite performance increases with fibre content.

Table 12: Flexural properties of test specimens cut from industrially moulded SMC composite product (moulded 13 & 14 April 2012).

Code	Movevirgo code	Flexural strength		Flexural modulus		Strain at max Strength	
		(MPa)	StDev	(GPa)	StDev	(%)	StDev
MV-2	Test 4, 1 layer of hemp SMC	49.5	11.7	5.72	0.08	1.68	0.58
MV-3	Test 4, 2 layers of hemp SMC	112.8	12.1	5.43	0.91	3.39	0.09

As needle punched mats (above mentioned follow up trials) show a low level of stretching during 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. With the PLA thermobonded mat, SMC cutting and placing is 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.

As needle punching restricts stretching of a fibre web too much, it was decided to also evaluate a just air laid fibre web without needle punching. This material has been referred to as 'non-bonded' and samples were coded HUUU, HUTU and HUTT, respectively, depending on ultrasonic and plasma treatments applied. 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. The only 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.

The thermobonded hemp mat exhibited rather uneven fibre distribution, which could 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 13). The effect of plasma may be overshadowed by the negative effect of inhomogeneous fibre mats. Also, these composites contain voids (Figure 27), though less than the lab scale composites (Figure 25).



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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. Again, it is confirmed that SMC composite mechanical performance increases with fibre content.

It may be concluded that for optimal natural fibre based SMC composites should: 1) contain high enough fibre content, 2) show sufficient fibre stretch/flow, 3) the negative parameter in the PLA thermobonded hemp non-woven should be identified (parameters may be inhomogeneous fibre distribution causing fibre poor/resin rich areas or the PLA itself).

Table 13: Flexural properties of test specimens cut from industrially moulded SMC composite product (moulded 17 July 2012).

Code	Corresponding to SMC sheet codes	Flexural strength		Flexural modulus		Strain at max Strength	
		(MPa)	StDev	(GPa)	StDev	(%)	StDev
MV-4	HPUU (Run 1, 6:1 resin ratio)	54.7	9.7	6.96	0.66	0.91	0.24
MV-5	HPUU (Run 2, 3:1 resin ratio)	75.3	9.3	7.52	0.43	1.53	0.31
MV-6	HPUT (Run 3, 3:1 resin ratio)	73.7	5.7	7.27	0.12	1.44	0.19
MV-7	G-2(commercial glass fibre SMC)	116.3	71	9.5	2.18	1.97	0.98

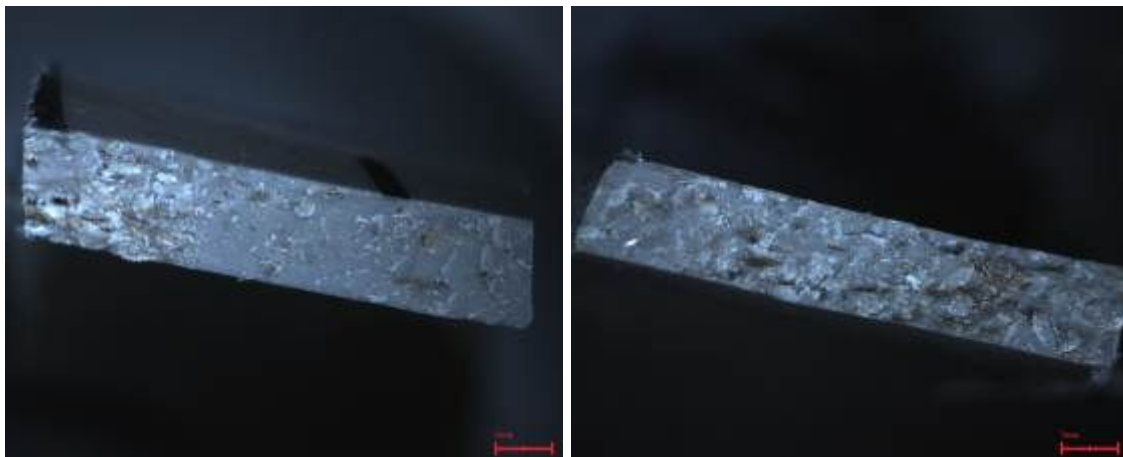


Figure 27: Cross section of moulded electrical joint connector (EJC). MV-5 (left) and MV-6 (right).

2.4.7 Conclusions on pilot scale trials

Fibre non-wovens can be very well plasma treated at large scale. Due to the lofty character of natural fibre mats, even distribution of SMC resin paste and styrene evaporation may be an issue. Thermobonded natural fibre based SMCs show enough stretch to be industrially moulded. The performance of the lab scale moulded test plaques base on pilot scale produces SMC sheets did not equal the fully lab scale SMCs, which is considered due to insufficient moulding and resulting high void content. The performance of the industrially moulded



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EJC exceeds the fully lab scale SMCs, which is due to better moulding and resulting low void content.

2.5 Techno-economic evaluation for UP composites

After completion of a full optimization cycle of plasma treatment of flax and hemp for UP based SMC composites, a techno-economic evaluation was performed. The set-up for the techno-economic evaluation of natural fibre-UP based SMC composites is equal to that presented for PP and PLA based extrusion compounds in D3.3, section 2.5. Cost aspects of plasma treatment were quantified as follows:

- 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 DLO-FBR for liquid N₂ in tank and dopant gasses in bottles:
 - N₂: 10 L_{gas}/min.cm at 646 L_{gas}/L_{liquid} at 0.156 €/L_{liquid}
 - O₂: 0.05 L_{gas}/min.cm at 798 L_{gas}/L_{liquid} at 1.95 €/L_{liquid}
 - CO₂: 0.05 L_{gas}/min.cm at 513 L_{gas}/L_{liquid} at 1.18 €/L_{liquid}
 - N₂O: 0.05 L_{gas}/min.cm at 664 L_{gas}/L_{liquid} at 2.68 €/L_{liquid}
 - H₂: 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/m² for flax and hemp as for current lab and pilot scale trials, or 1000 g/m² as estimated upper limits. Hemp m²-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 = 178 W/cm ULD at 0.22 €/kWh.

From the assumptions indicated above, plasma treatment costs can be calculated as presented in Figure 28 – Figure 30 below. Conclusions are:

- 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



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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 (E-mail Movevirgo 20 November 2012), 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 28, Figure 29).

- Optimisation of processing in terms of production hours/day (8 → 16 h) and gas consumption (at the November 2011 meeting, AcXys has suggested that as a result of gas 'recycling technology, effective gas flow consumption may be reduced from 60 → 15 L/min) shows that the plasma process can only be economically feasible for fibre mats of higher mat m² weight or at higher processing speed (Figure 30). At 500 g/m² hemp fibre mats, breakeven will be achieved at about 2.3 m/min, similar to the value for PLA compounds, however, much lower than about 4.5 m/min for PP compounds (D3.3).
- 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 4-10 compared to rates applied in this study, while providing the same adhesion and strength improvement.
- The estimated cost of 3 €/kg for natural fibre based SMC is significantly larger than about 1.8 €/kg for commercial glass fibre based SMC sheet. The way to decrease natural fibre SMC cost is by higher production volumes and ideally the ability to generate short natural fibres rather than having to use the a form of mat. The 10% lower density of hemp based SMC compared to glass SMC, 1.5 vs. 1.67 g/cm³ (Tables 7 and 10), respectively, does not compensate for the present cost difference.



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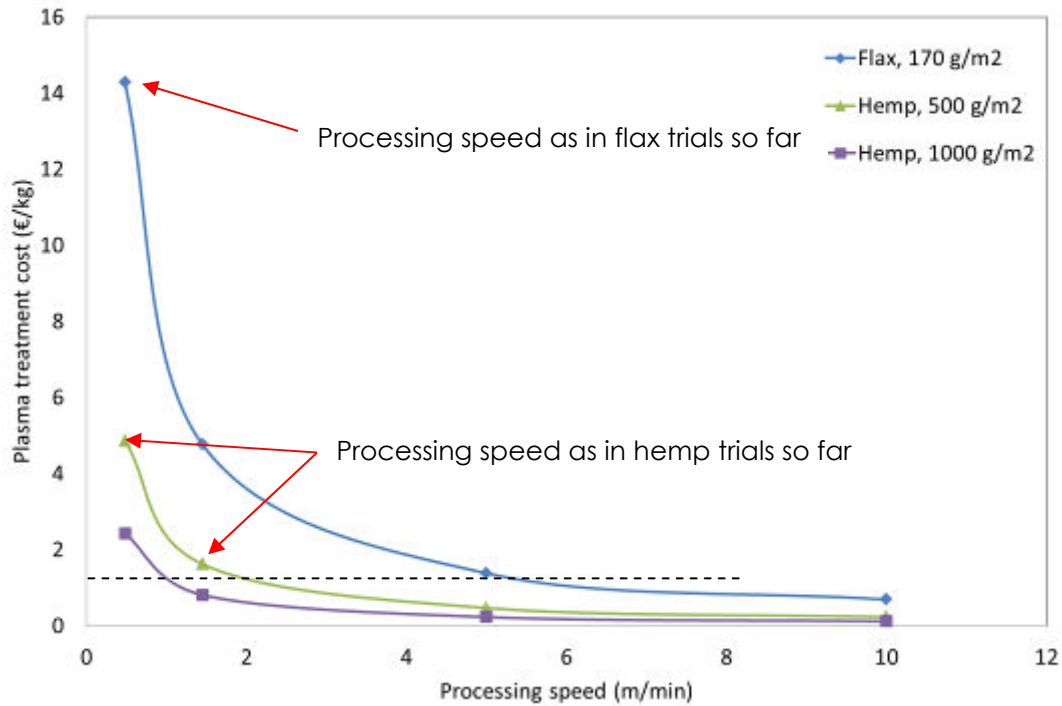


Figure 28: Plasma treatment cost per kg of fibre based on assumptions summarized above.

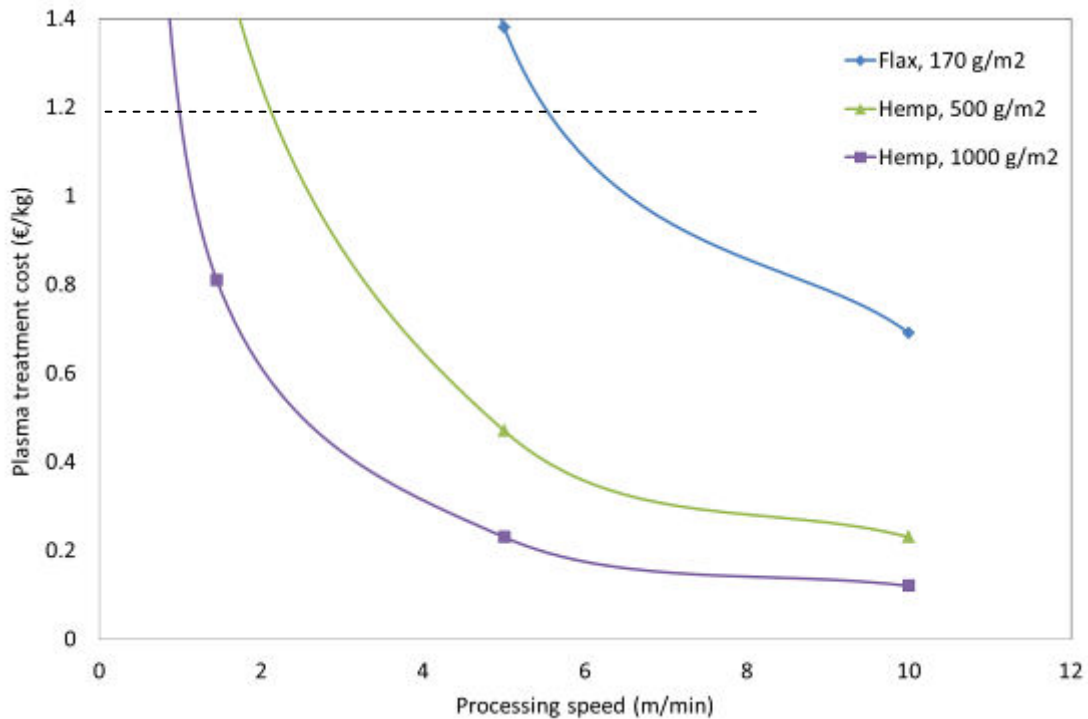


Figure 29: Plasma treatment cost per kg of fibre based on assumptions summarized above (Zoom of Figure 28). Dashed line represents cost savings level for hemp-UP SMC with 20% improvement of strength.



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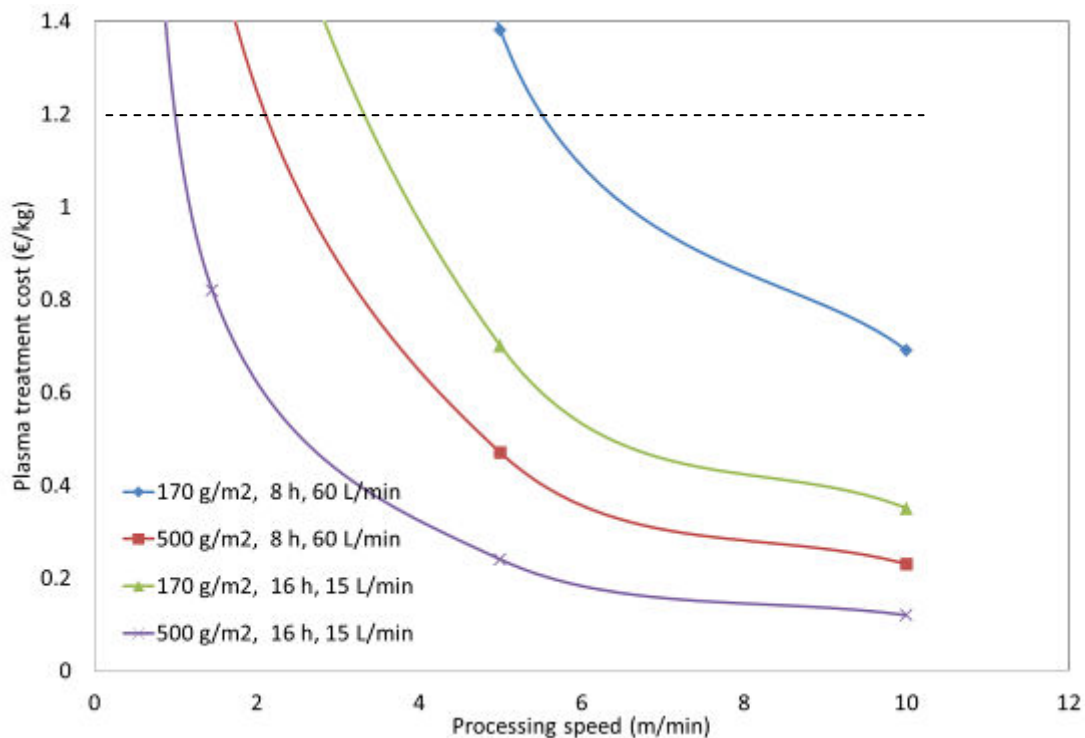


Figure 30: Plasma treatment cost based on assumptions summarized above, except for operating 16 h/day instead of 8 h, and having a gas flow of 15 L/min instead of 60 L/min. Dashed line represents material cost savings level for hemp-UP SMC with 20% improvement of flexural strength.

2.5.1 Conclusions on techno-economic analysis

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 4-10 compared to rates applied in this study, while providing the same adhesion and strength improvement. 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.

2.6 Issues and solutions

SMC composites are based on a formulation containing UP resin, low shrink additives, CaCO₃ 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



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about 2 month 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.

Due to a delay in resin paste supply, optimized plasma treatment parameters for SMC applications could not be fully determined before the pilot scale plasma trials had to be performed. Parameters for scale up trials at CTP (plasma treatment) and Gloucester Composites (SMC sheet production) have been based on results collected till that moment and determined in joint consultation with partners involved: Movevirgo, DLO-FBR, AcXys, InControl and RAPRA. The results are still very useful for further industrial implementation.



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3. Summary of results and Conclusions

The results on the effect of atmospheric plasma treatment on natural fibre based PP and PLA composite characteristics was addressed in D3.3 report and may be summarized as follows:

- Different levels of fibre surface modification can be achieved for flax and hemp using a range of feed gas compositions, while retaining fibre strength.
- 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 treatment of refined flax fibres results in a 23% increase of Flax-PP composite flexural strength. This is close to the performance of commercially applied MAPP and similar to low vacuum plasma treatment. Low vacuum plasma treatment, however, cannot be scaled up to high volume processing as will be required for mass production composite applications.
- Hemp-PLA composite flexural strength increases by 20-24%. This would allow a 10% thinner product having the same performance under loading.
- Surface modification resulting from plasma treatment is quite durable, however, under evaluated conditions, plasma treatment needs to be thorough in order to obtain significantly improved adhesion for PP composites.
- Regarding the most critical (harmful) emissions, ozone and NO_x may need to be extracted to protect operators, depending on concentration of O₂ dopant to the feed gas. Once in air, ozone quickly decomposes and there are no legal regulations. Annual NO_x emissions of an industrial scale plasma unit are calculated to be in the range of a car traveling 160 – 1200 km. Plasma emission data of most critical components, ozone and NO_x, were collected for LCA purposes, which results will be presented in D9.2.
- A techno-economic evaluation of plasma treatment indicates that processing costs of effective plasma treatment of refined fibres for PP and PLA based injection moulding compounds are higher than costs for using commercial MAPP coupling agent. Higher plasma treatment rates, and consequently lower costs, seem possible for composites based on coarser fibres such as SMCs and NMTs.
- From the literature search results (D3.1) it was concluded that natural fibres exhibit good bonding to furan resin already.



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From research on the effect of natural fibre plasma treatment on PP and PLA composite performance (D3.3), it was concluded that plasma treatment may be more profitable for composites based on coarse fibres. The results from the work on atmospheric plasma treatment of coarser natural fibres and its effect on unsaturated polyester (UP) based SMC composites may be summarized as follows:

- Hemp tow fibre comprises a diameter in the range of a few hundred micron typically and is a good example of a coarse fibre grade. In order to evaluate the effect of fibre fineness on UP resin impregnation and SMC mechanical performance, steam exploded flax with a diameter in the range of 10-30 micron was included in the evaluation as well.
- Lab scale SMC composite manufacturing was optimized prior to develop plasma treatment of natural fibres for SMC composites. Parameters included fibre content, flow and wetting agents, and moulding temperature.
- Plasma treatment of hemp fibres results in a 20% improvement of SMC composite flexural strength when using N₂ + CO₂ feed gas. Hemp SMC composite performance reaches 73% of glass based SMC flexural strength and 100% of its flexural modulus.
- Flax SMC composite performance reaches 82% of glass based SMC flexural strength and 115% of its flexural modulus.
- The effect of plasma treatment is lost when increasing treatment rate from 0.5 to 2.9 m/min. Applying the bi-functional coupling agent glycidyl methacrylate, which is expected to exhibit chemical interaction with both plasma induced NH₂ sites on the fibre surface and with unsaturated polyester formulations, following the 2.9 m/min plasma treatment, a flexural strength increase of 6–8 % has been determined.
- Plasma processing parameters were in the same range for UP based composites as for previously evaluated PP and PLA based composites (D3.3). Therefore, energy consumption and emission data for UP composites are considered as presented in D3.3, section 2.4.
- Plasma treated natural fibres may retain their surface modification best when wrapped in aluminium foil and a PE bag. Best way to store plasma treated samples would be in vacuum, however, this would destroy the non-woven structure to such extent that successful further processing into SMCs would not be possible anymore.
- Ultrasonic treatment of hemp fibres results in a 14% higher SMC composite flexural strength.
- The resin paste thickens over time and limits fibre impregnation. For the present trials, this issue has been overcome by including a standard hemp based SMC composite in all series.
- Pilot scale trials based on thermobonded hemp mats, including industrial non-woven production, plasma treatment, SMC sheet manufacturing and



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industrial moulding, were performed. The composite products show about 65% of glass fibre SMC flexural strength and about 80% of glass fibre SMC modulus, which 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 (MV-3) is similar to that of the commercial glass fibre based SMC (MV-7).

- 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 mats are easier to stretch in the mould and SMC cutting and placing is more forgiving. The thermobonded mats used in the present study, however, exhibited rather uneven fibre distribution, which results in inhomogeneous composites as well, showing relatively poor performance.
- Natural fibres contain typically about 10% of moisture at regular environmental conditions. 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.

Overall conclusions relative to the WP3 objectives:

- An atmospheric SoftPlasma process has been developed which allows industrial scale plasma treatment of natural fibres, both non-woven mats, sliver and short fibres with length above 5 mm. The most critical emissions, being ozone and NO_x, may need to be extracted to protect operators, depending on feed gas composition. Ozone quickly decomposes once in air and no legal regulations apply. The annual NO_x emissions of an industrial scale plasma unit are calculated to be in the range of a car traveling 160 – 1200 km (D3.3). This is considered a small emission for the production of 250 tonnes of treated fibre at economic breakeven point for UP and PLA composites as calculated in section 2.5 (500 g/m² mats treated at 2.3 m/min).
- Hemp and flax fibre surface composition can be modified considerably by applying the SoftPlasma process, without losing fibre strength.
- Flexural strength performance could be increased by 23% for PP composites, 24% for PLA composites and by 20% for UP composites. Herewith, the goal of a 25% increase in mechanical properties is nearly achieved.



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- The improvement for PP composites is similar to that of using commercial grade MAPP as a coupling agent, however commercial feasibility still needs to be improved (D3.1, Appendix A & D3.3).
- The improvement for PLA composites is similar to the best alternative methods found in literature (D3.1 & D3.3). No commercial method to improve natural fibre-PLA adhesion is available so far, and also commercial feasibility of plasma treatment needs to be improved (D3.3).
- The improvement for UP composites seems lower than that of best alternative methods found in literature, although comparison is difficult as different types of composites were evaluated (D3.1 & D3.4). The improvement of 20% is also less than the theoretically predicted 60% which could be potentially achieved (D3.1, section B4.3).
- From literature it was concluded that natural fibres exhibit good bonding to furan resin already (D3.1). Therefore, it was decided to focus plasma treatment on improved adhesion to the other target polymers PP, PLA and UP.
- Plasma treatment is a dry process and the ultrasonic treatment has to be applied under wet conditions. Therefore, ultrasonic and plasma treatment processes cannot be fully integrated, however, processing in series is the logical way for implementation.

Conclusions and recommendations for industrial implementation of plasma treatment for SMC composite manufacturing:

- Plasma treatment (using evaluated feed gas systems) needs to be thoroughly in order to achieve significant improvement of fibre-matrix adhesion.
- Industrial SMC moulding will benefit from a minimum level of fibre stretch/flow during moulding. Needle punched mats show insufficient stretch in complex 3D moulds. For thermobonded mat, SMC cutting and placing is more forgiving: due to its almost elastic property the mat can move inside the mould cavity.
- SMC composite mechanical properties will benefit from:
 - Homogeneous distribution of fibres in the SMC
 - Fibre content higher than 20%
 - Drying the fibres prior to moulding in order to minimise void content
- Resin viscosity needs to allow good impregnation of the fibres in order to achieve effective reinforcement.
- Results on plasma treatment of natural fibres for improved adhesion in polymer matrix composites appear not interestingly enough to apply for a patent. Improved results, both technically and economically, may be found in the direction of combining optimised combination of plasma



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treatment (feed gas composition) and applying reactive coupling agents in order to achieve improved treatment rate, durability of the modification, and effectiveness of the modified fibre-polymer matrix adhesion. Initial suggestions to proceed on this route are presented in section 2.3.3 of this report.



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Annex 1 Mould design for making lab scale SMC test samples

A mould design for making lab scale SMC composite samples was prepared in joint consultation with Movevirgo and DLO-FBR in order to efficiently evaluate the effect of plasma treatments on natural fibre reinforced SMC composite properties. The mould was actually manufactured by Movevirgo with help of RAPRA. The mould was covered with PTFE sheets to allow proper release of the SMC composite after moulding.

Side view of mould

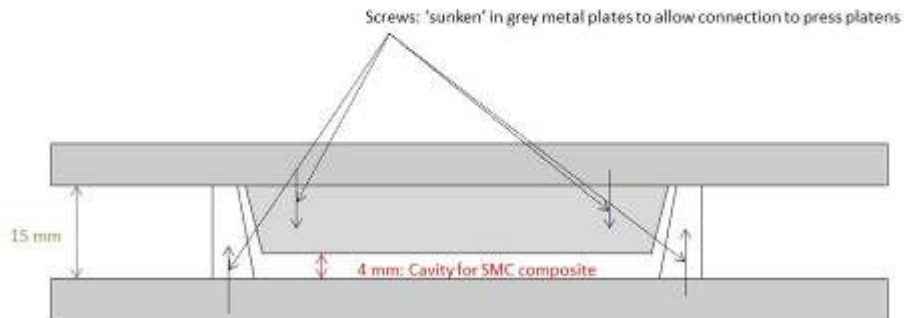


Figure 31: Mould desing, side view.

Side view of mould

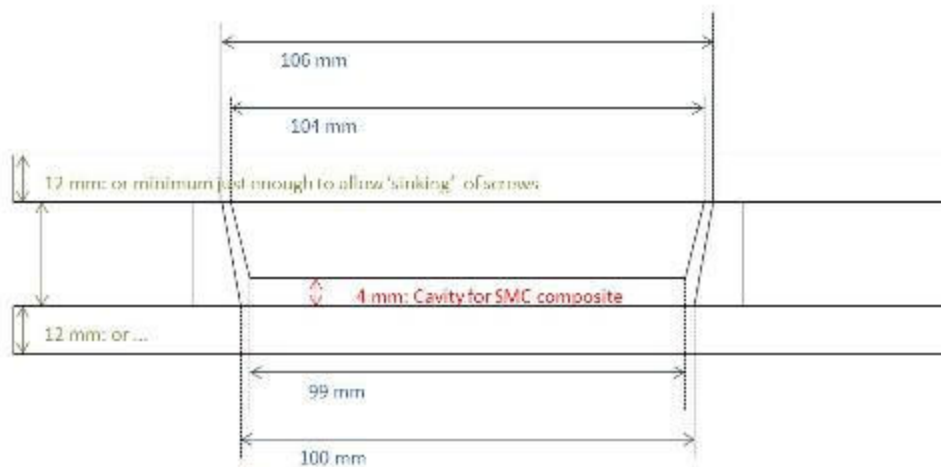
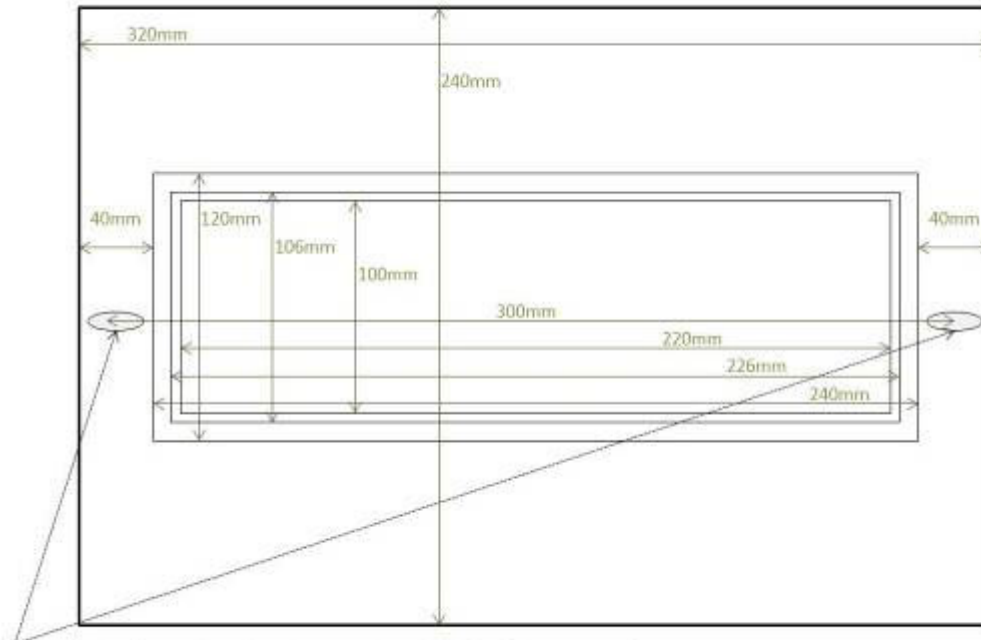


Figure 32: Mould design, side view.

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Top view of female mould half, to be connected to bottom press platen



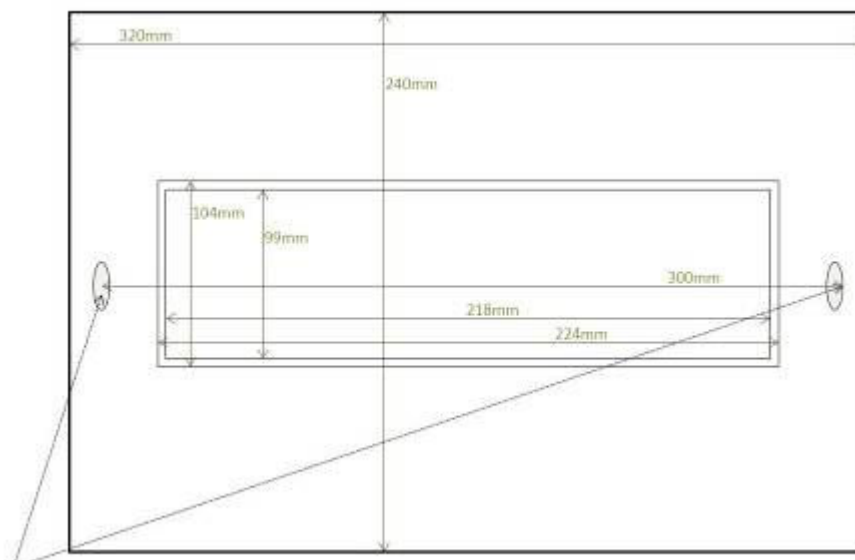
Slits to allow M8 hexagon head screw to connect mould half to bottom press platen.

Slit of 'few mm length' to allow positioning of the mould halves.

Note: outer length dimensions to be adjusted if 40 mm space would not be enough to release M8 screws.

Figure 33: Mould design, top view of lower half.

Top view of male mould half, to be connected to upper press platen



Slits to allow M8 hexagon head screw to connect mould half to upper press platen.

Slit of 'few mm length' to allow positioning of the mould halves.

Figure 34: Mould design, top view of upper half.



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Figure 35: Mould covered with PTFE (Teflon ®) sheets.



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Annex 2 Procedure for making lab scale SMC test samples

A series of SMC trials was performed to find (more or less) optimised moulding conditions for natural fibre SMC composites. This is required for adequate evaluation of the effect of plasma on SMC composite performance.

Considerations related to the optimisation:

- In Deliverable 3.3 it was concluded that coarse natural fibres may be very suitable for application in plasma treated fibre reinforced composites. Hemp tow fibre comprises a diameter in the range of a few hundred micron typically and is a good example of such coarse fibres. In order to evaluate the effect of fibre fineness on SMC preparation (fibre impregnation) and SMC mechanical performance, steam exploded flax was included in the series as well. Steam exploded flax basically consists of elementary plant cell fibres with diameters typically in the range of 10-30 micron.
- 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. Therefore, fibres were dried and stored at dry conditions as much as possible until final SMC moulding.
- Additives were used in order to obtain improved resin flow and fibre wetting, aiming at improved composite performance. Additives used include BYK-W 996 and BYK-P 9065. BYK-W 996 is a conventional additive used to reduce the viscosity of UP resin for SMC applications. BYK-P 9065 is an additive used to improve mould release and surface appearance, but it should also improve natural fibre-matrix wetting/adhesion.
- Consolidation temperature to be set at about 140 °C (temperature measured on mould wall), similar to the temperature applied by Movevirgo for this type of resin. In order to study the effect of mould temperature on resin flow and consequently fibre wetting and composite performance, 2 reference SMCs were consolidated at 160 °C.

Starting materials include:

- Hemp non-woven, supplied by Hemp Technology and made available through Movevirgo.
- Steam exploded flax, provided by DLO.
- Unsaturated polyester (UP) resin paste, supplied by Gloucester Composites and made available through Movevirgo.
- BYK-W 996 and BYK-P 9065 additives, provided by Movevirgo and BYK, respectively.



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The procedure for making SMC samples was as follows:

- Overnight drying of fibre samples in an oven at 105 °C (Figure 36).
- Cooling the fibre samples in a desiccator for 1 h (Figure 37).
- Manually mixing resin paste and MgO (Figure 38). In case of using additives, these were mixed with the resin paste prior to mixing with MgO.
- Preparing a layer of resin paste onto a release film (baking paper) (Figure 39).
- Impregnating fibre non-woven with resin paste using fluted rollers (Figure 40).
- Maturing the resin paste in the SMC samples under a 10 kg weight, in a closed bucket containing pre-dried silica gel (Figure 41) for 1 or 2 nights. The resin appeared to release from the baking paper better after 2 nights instead of 1 night of maturing (Figure 42).
- Pressing the SMC sample in a PHI hot press at 140-160 °C for 3 minutes in the specially designed and produced mould (see Q9 report) (Figure 43). Unless stated otherwise, 3 layers of impregnated fibre were stacked for making 1 composite plaque.



Figure 36: Oven to dry fibre non-woven samples prior to SMC production.

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Figure 37: Desiccator to cool pre-dried fibre samples.



Figure 38: Mixing of resin paste and MgO.

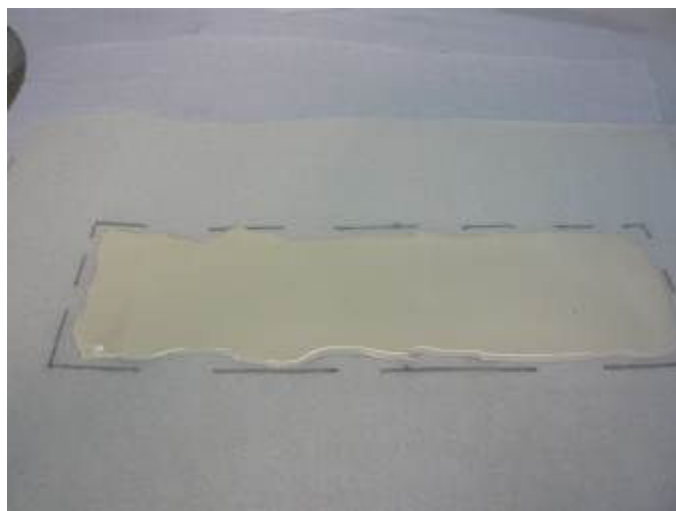


Figure 39: Layer of resin paste on a release film.

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Figure 40: Impregnating fibre non-woven with resin.



Figure 41: Impregnated fibre samples are matured under 10 kg weight in a closed bucket containing silica gel.



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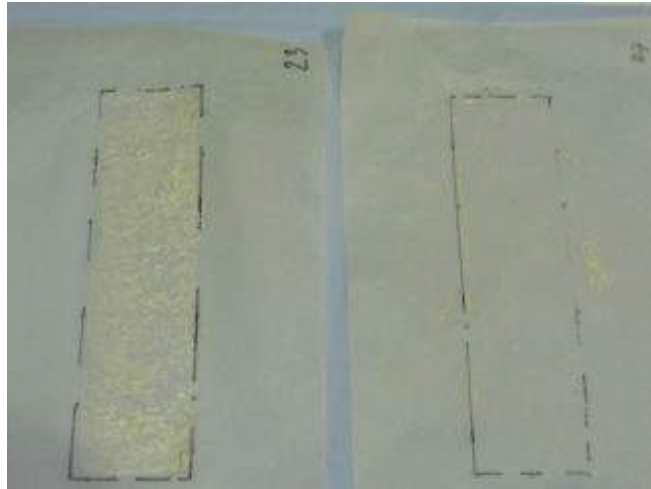


Figure 42: Resin remaining on the baking paper after maturing for 1 night (left) and 2 nights (right).



Figure 43: Specially designed mould for lab scale SMC production, fixed in hot press.

Fibre weight content in the composite (wt.%) was estimated by dividing fibre mat weight by the sum of fibre mat weight and amount of resin. Fibre volume content (vol.%) was determined assuming a fibre density of 1.4 g/cm^3 , and a resin density of 1.5 g/cm^3 .

Edges of the consolidated SMC composites were cut off and composite density was determined by dividing its weight by its length and width and by an average of 5 thickness values. Next, the SMC composites were cut to $80 \times 10 \text{ mm}$ specimens and evaluated for flexural properties. Specimens were conditions at 20°C and $50\% \text{ RH}$ for about 1 week or more prior to further analysis.



D3.4 – Report on Plasma Treatment of Flax and Hemp Fibres for Unsaturated Polyester Matrices

Fibre content, composite density, flexural strength and modulus data are presented in Table 14. Following may be concluded regarding SMC composition and moulding conditions:

- Flexural Strength increases with increasing fibre content. Density decreases with increasing fibre content.
- Flax performs better than Hemp, both in Strength and in Modulus.
- No significant effect of increased moulding temperature has been observed.
- Additives, as used, do not have positive effect on composite mechanical performance. BYK brochures suggest that the additives have to be mixed with the resin prior to mixing with the CaCO₃ filler for effect. Unfortunately, no SMC nor additive manufacturer to properly address this topic is included in this project.

Table 14: Properties of SMC composites; SMC composition and moulding optimisation.

Code	Fibre grade	Nr of Mats	Fibre content (wt%)	Density (g/cm ³)	Flexural strength (MPa)	Flexural modulus (Gpa)	Strain at max Stress (%)
SMC-4	Hemp	2	17.5%	1.66	62.5	7.63	1.56
SMC-5	Hemp	3	26.1%	1.61	83.1	7.74	1.99
SMC-6	Hemp	4	34.7%	1.58	87.7	7.43	2.02
SMC-7	Flax	10	28.2%	1.59	89.8	9.12	1.88
SMC-8 (158°C)	Hemp	3	26.3%	1.60	74.8	7.08	1.91
SMC-9 (156°C)	Hemp	4	35.3%	1.58	85.7	7.46	1.97
SMC-10 (W996)	Hemp	3	26.3%	1.63	70.2	6.63	1.86
SMC-11 (W996+P9065)	Hemp	3	26.0%	1.63	76.1	6.70	2.12
SMC-12 (P9065)	Hemp	3	26.3%	1.56	74.5	6.83	2.01

Based on the results from Table 14, it was decided that the effect of plasma treatment for SMC applications will be evaluated on composites based on about 25 wt.% (3 layers of hemp non-woven) which will be moulded at 140 °C for 3 minutes.