# D3.3

## *Report on Plasma Treatment of Flax and Hemp Fibres for PP and PLA Matrices*



UltraFibre

**D3.3 – Report on Plasma Treatment
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# Contents

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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 3.3, reports on the plasma treatment of flax and hemp fibres for target matrix polymers.

According to the Annex 1 the due date of this report was originally planned for Month 22, linked to the completion of Task 3.4. However, WP3 runs until Month 30, and in order to draw on the relevant conclusions of the full potential of the plasma treatment for improved fibre-matrix adhesion, results on plasma process experimentation and optimization (Task 3.5) need to be included. Therefore, this report now includes additional information, not planned in the original report.

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**.

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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 experimental studies, an update to the available literature survey of techniques reported for natural fibre coupling, especially data reported for flax and hemp composites, was carried out at the start of the UltraFibre project. Candidate strategies for coupling were short-listed based upon the data generated in WP1. These data served 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 were considered. The emphasis is on 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, have investigated modifications needed to adapt the existing equipment to make use of the SoftPlasma technique for fibre treatment. This has allowed the fibres to be pre-treated to allow for their use in a wide variety of possible applications. A design of experiments has screened 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 were carried out with fibres produced by conventional mechanical processing and retting methods. In parallel, preparatory work has been 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 are being addressed.
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).

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*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 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.

This deliverable report presents the work performed on:
- Surface treatment of flax and hemp fibres (Task 3.3, Sections 2.1 and 2.2).
- Adhesion of treated fibres to PP and PLA polymers (Tasks 3.4 and 3.5, Section 2.3).
- Optimisation and economic evaluation of plasma treatment for PP and PLA matrix extrusion compounds (Task 3.5, Sections 2.4 and 2.5).
- Environmental aspects (Task 2.5, Section 2.4).

From the results on PP and PLA based extrusion compounds obtained so far, it was concluded that plasma treatment of natural fibres has the best techno-economic potential for composites based on relatively coarse fibres like for instance SMC and NMT composites. Therefore, at the partner meeting in November 2011 it was decided to focus further plasma work on SMC composites. This work follows the experimental approach as in Tasks 3.4 and 3.5 and is planned to be completed in Month 32. Herewith, this **Deliverable 3.3 is an interim report, covering all the work on the plasma treatment of flax and hemp fibres as well as work on adhesion to PP and PLA matrices**. Work on plasma

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treatment for unsaturated polyester (SMC) composites will be addressed in the chapter on future work (chapter 4). An addendum to this D3.3 report will cover the work and results on SMC composites, and is suggested to be numbered **Deliverable 3.4**, and to be **due in Month 32**.

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# 2. Results

Background information to the atmospheric plasma technology is presented in D3.2 (section 1.1).
Analysis test methods have been described in Deliverable 5.2 report.

## 2.1  Task 3.3 Surface treatment of flax fibres (Initial trials)

In order to get an indication of the modification potential of atmospheric plasma, as received flax sliver (Ekotex) was treated using standard plasma treatment equipment at AcXys' facilities (Figure 1). An indication of the required level of treatment conditions for $N_2$ gas was obtained by performing water droplet absorption test (Figure 2). After about 20s treatment time, fibres appeared to exhibit higher water absorption compared to untreated fibres.
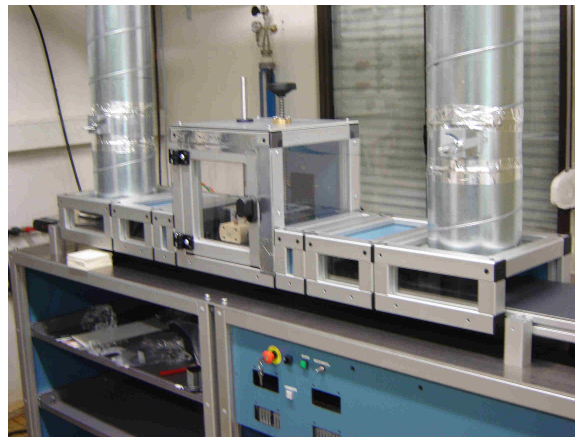


**Figure 1: Standard plasma treatment unit at AcXys' facilities.**



**Figure 2: Water droplet absorption. Left fibre sample on each picture is the untreated reference, right fibre sample is the plasma treated fibre. Left picture does not show change of water absorption, the right picture does.**

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Flax fibre samples were 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% $N_2O$. As AcXys has the experience that aluminium protects the surface modification achieved with plasma treatment, treated flax fibres were wrapped in aluminium foil before putting in a plastic bag. Part of pure $N_2$ treated fibres was stored in a plastic bag only until further analysis in order to study the effect of storage conditions.

Plasma treated flax fibres and an untreated reference sample were dried overnight at 50°C under vacuum and analysed with XPS 2.5 weeks after plasma treatment. XPS analyses the elemental composition of the very few nm top layer of a material surface (details on the XPS analysis method have been presented in D5.2, section 2.1.5). Part of the $N_2$ + $CO_2$ treated sample was dried at 105°C to study the effect of drying temperature.

A summary of the XPS results is presented in Table 1. The table shows a few data from D5.2, but the full overview is presented here in order to make this report a *stand alone* report as much as possible. More details to the results have been presented in D5.2, Figure 31. Conclusions that can be drawn from these data:

- 2.5 weeks after plasma treatment, a large change in Carbon, Oxygen and Nitrogen element composition at the fibre surface can be observed.
- Results from storing treated fibres without wrapping in aluminium foil are ambiguous: change of Nitrogen content is less, but change of Oxygen content is larger compared to the sample wrapped in aluminium. Overall this suggests a slight protective effect by the aluminium wrap.
- At high (drying) temperature, part of the surface modification is lost.

**Table 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 |

The fibre tensile strength is retained after plasma treatment (see Figure 3).

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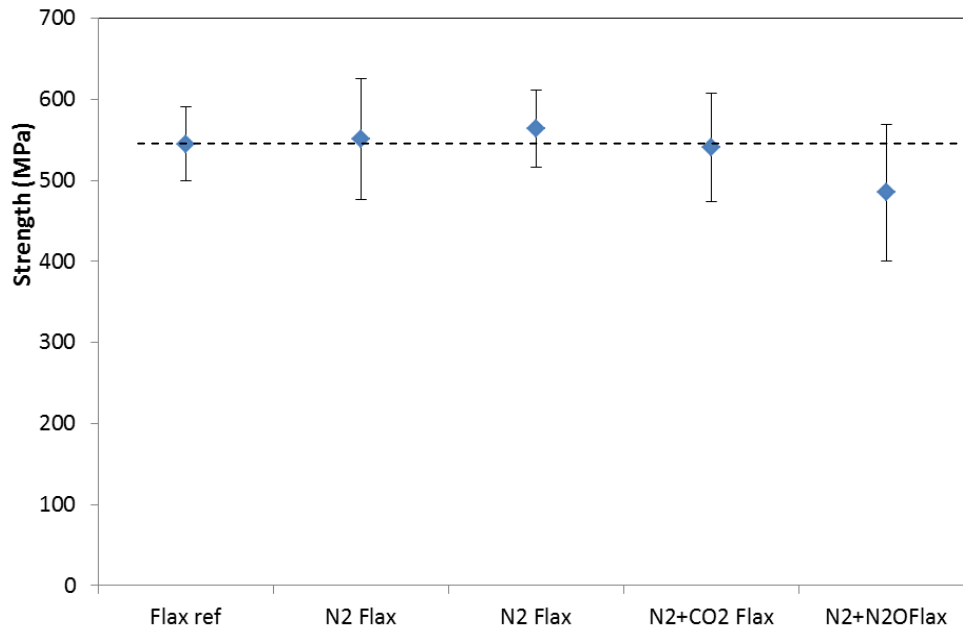of Flax and Hemp Fibres
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**Figure 3: Collective fibre tensile strength of untreated and (AcXys) plasma treated flax fibres. Dashed line representing level of untreated fibres.**

Conclusion on initial surface treatment trials
It was concluded that atmospheric plasma can be used to modify natural fibre surface significantly.

## 2.2  Task 3.3 Surface treatment of flax and hemp fibres

Based on the results addressed in section 2.1, and in joint consultation with DLO-FBR, Movevirgo and RAPRA, AcXys has designed and built a lab scale plasma unit, which is extensively described in D3.2. This plasma unit has been used for all further trials, except for 1 case, which will be clearly noted in the text below.

Fibres should not refine after plasma treatment, as fresh untreated surface will be created (explained in detail in D3.1, section A2.1). In order to avoid fibre refining, for instance during extrusion compounds, fibres were refined prior to plasma treatment using a Shirley trash separator (described in detail in D5.2, section 2.1.2). Fibres samples include flax sliver from Ekotex and hemp tow originating from Hemp Technology and supplied by RAPRA. Refined flax fibres were manually made into mats having a width of about 6 cm (width of tunnel around the belt, see Figure 4) and a length of about 25 cm (dimension suitable for manual handling to feed to the plasma unit). Hemp mat length could be optimized to 35 cm, while still having good handling properties, thus allowing higher production rate on lab scale.

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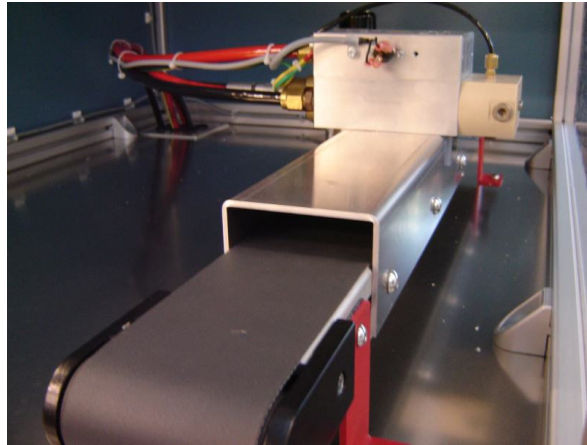for PP and PLA Matrices**



**Figure 4: Belt system of plasma unit.**

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% $N_2O$. 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). In order to study the effect of processing rate, a flax sample was treated at 3 times higher speed as well (2 passages only). Treated fibres were wrapped in aluminium foil and stored in a plastic container until further analysis. This method of storing is based on AcXys' experience that surface modification is better retained when the treated material is packed in aluminium foil. Best way to store plasma treated samples would be in vacuum. Plasma treated fibres were analysed for surface characteristics (XPS and SEM) and collective strength.

Plasma treated fibres and untreated reference samples were dried at 50°C under vacuum for about 3 hours and analysed with XPS 4 days after plasma treatment. In order to study the durability of surface modification, one flax sample was treated with pure $N_2$ plasma 52 days prior to XPS analysis.

A summary of the XPS results is presented in Table 2. Conclusions that can be drawn from these data are 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.
- Increasing production rate by a factor of 3 (= 1/3rd of residence time in the plasma conditions) reduces the relative surface modification by a factor of 3.

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- Durability of plasma treatment is not infinite (as expected). 52 Days after plasma treatment, fibre surface modification is about 1/3rd compared to after 4 days.

**Table 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      |

The fibre tensile strength is retained after plasma treatment (see Figure 5), and as a consequence the reinforcing potential of the fibres.
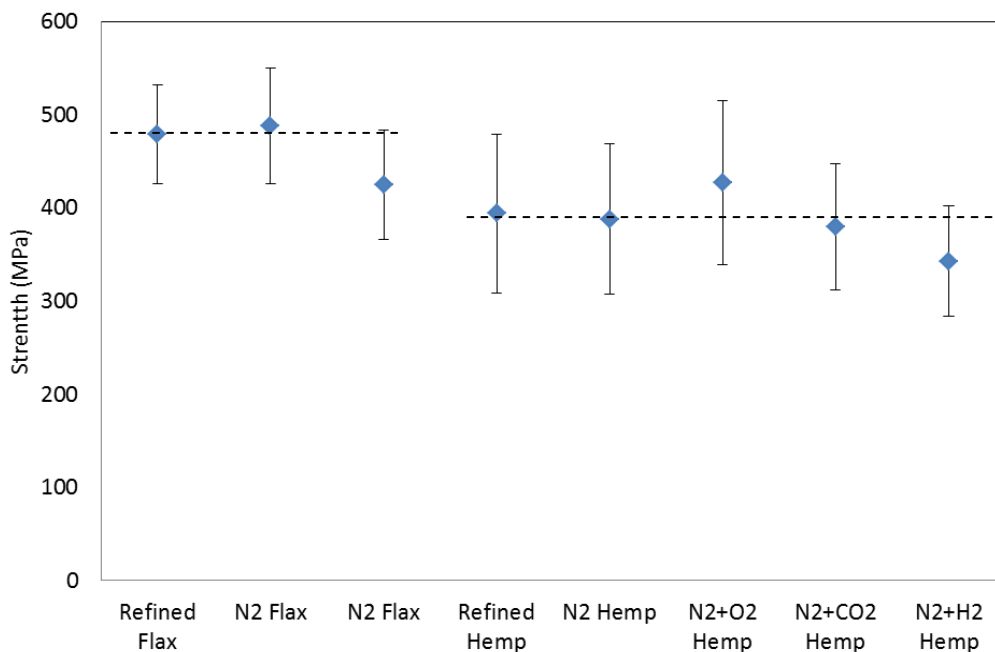


**Figure 5: Collective fibre tensile strength of Shirley refined and (DLO-FBR) plasma treated and untreated flax and hemp fibres. Dashed lines representing level of untreated fibres.**

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Scanning electron microscopy (SEM) analysis does not show any effect of plasma treatments on fibre surface morphology (Figures 6 and 7), so no advantage or disadvantage related to mechanical interaction with polymers is to be expected.
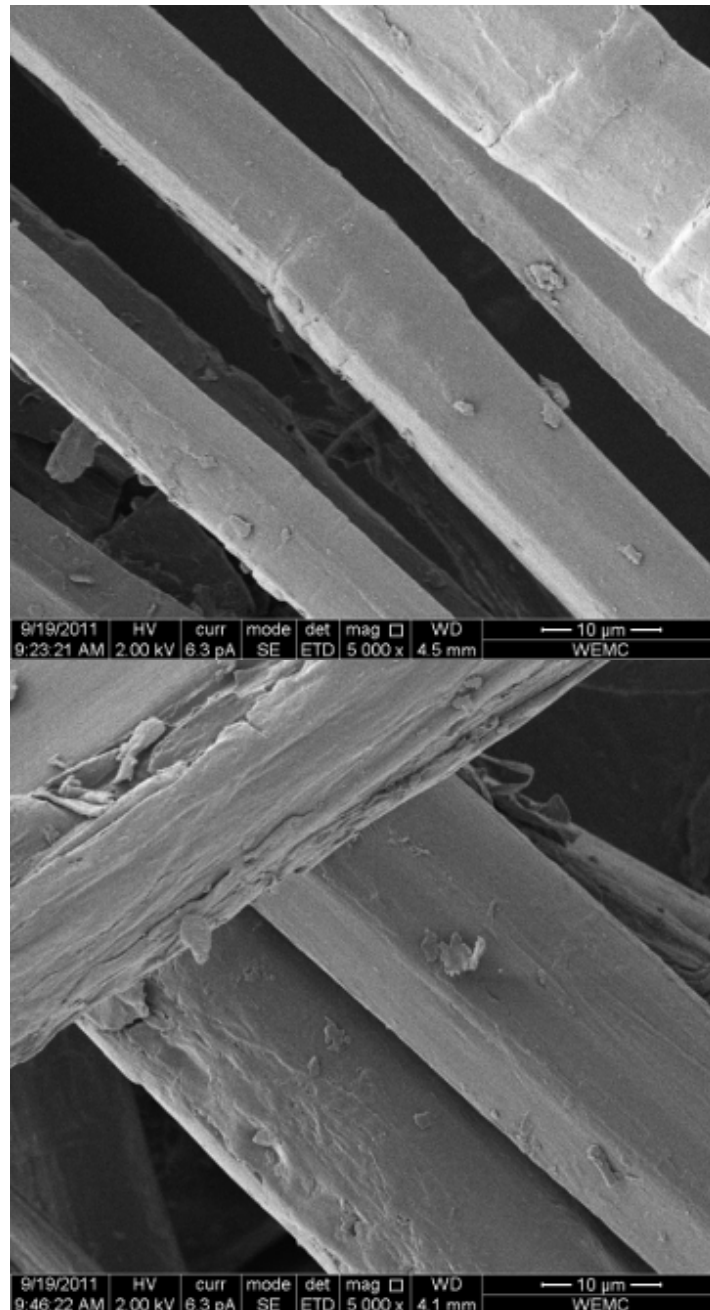


**Figure 6: SEM pictures of untreated (upper) and N$_2$ plasma treated flax fibres (lower picture).**

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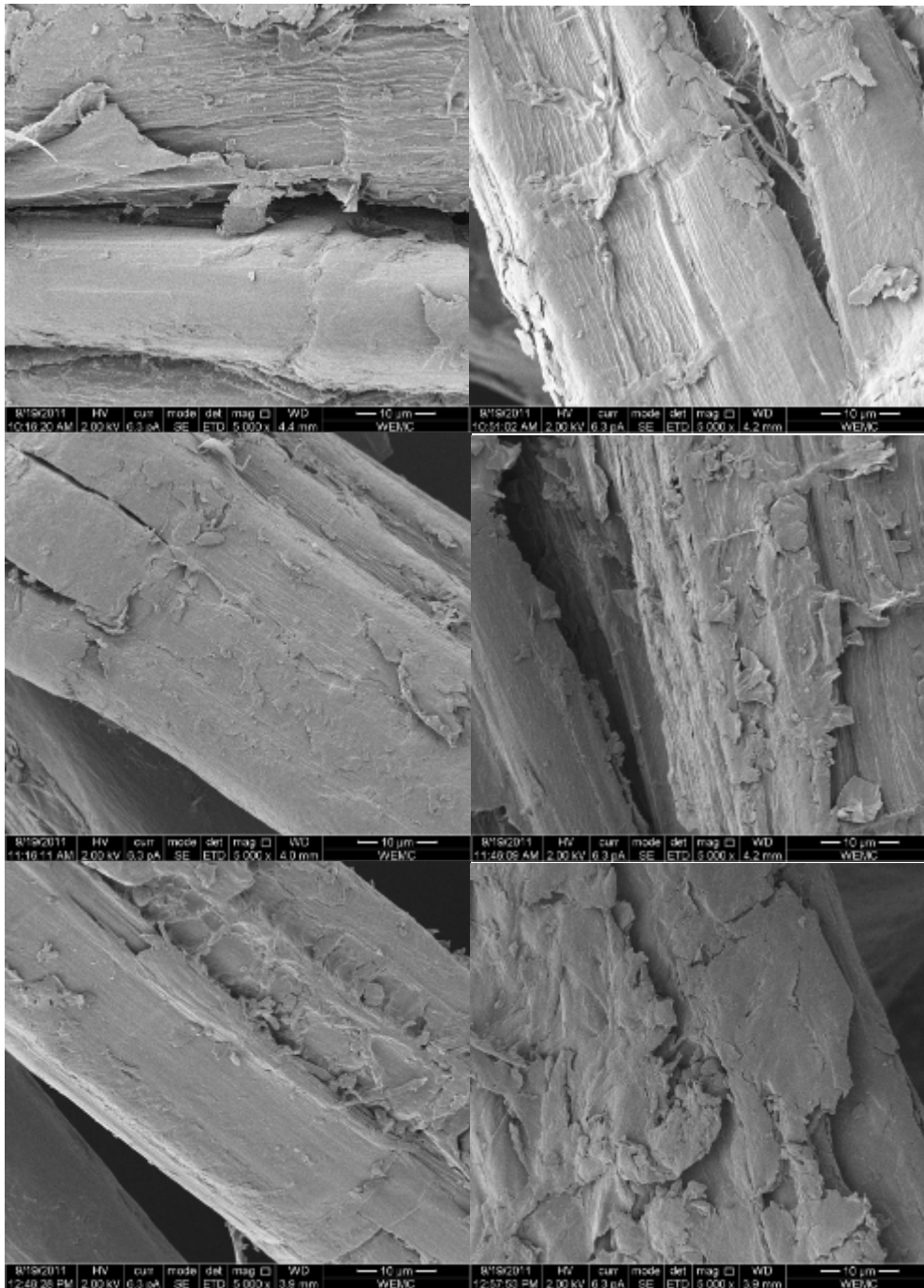of Flax and Hemp Fibres
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**Figure 7: SEM pictures of untreated and N₂, N₂ + O₂, N₂ + CO₂, N₂ + H₂, N₂ + N₂O plasma treated hemp fibres (going from upper left corner to lower right corner).**

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Conclusion on surface treatment of flax and hemp
Different levels of fibre surface modification have been achieved for flax and hemp using a range of feed gas compositions, while retaining fibre strength. The actual value of the surface modification can only be derived from the fibre reinforcing performance in polymer composites, which will be addressed in the next section.

## 2.3  Task 3.4 Compatibilisation to PP and PLA polymers
In Annex 1, the single fibre fragmentation test (SFFT) was proposed to analyse fibre-matrix adhesion. This method was evaluated and appeared to work well for PP matrix system, however not for PLA matrix (see D5.2, section 2.4). As the 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.

Flax and hemp fibres were prepared and plasma treated as described in section 2.2. These fibres were compounded in PP and PLA matrices and injection moulded into test specimens according to the procedure described in Appendix 1 of D5.2. 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. Scanning electron microscopy (SEM) was applied in order to better understand the results collected so far. Composite mechanical properties are described in detail in D5.2, sections 2.5.1 and 2.5.2. The key mechanical properties are summarized and discussed below.

Flax-PP
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 8). $N_2$ treated flax-1% MAPP performs similar to untreated flax-3% MAPP.

The effect of plasma treatment is confirmed by SEM of flax-PP composites, showing that the level of fibre-matrix adhesion (which may be considered proportional to fibre pull out length) after plasma treatment is in between untreated fibre-PP and untreated fibre-MAPP (Figure 9).

The increase in PP composite performance due to atmospheric plasma treatment is close to improvements found for composites based on MAPP and similar to low vacuum plasma treated fibres, which data were collected in the literature survey previously presented in D3.1, sections A2.2 and A3.4. Contrary to atmospheric plasma, however, the low vacuum plasma technique can not be scaled up for high volume processing as will be required for mass production composite applications.

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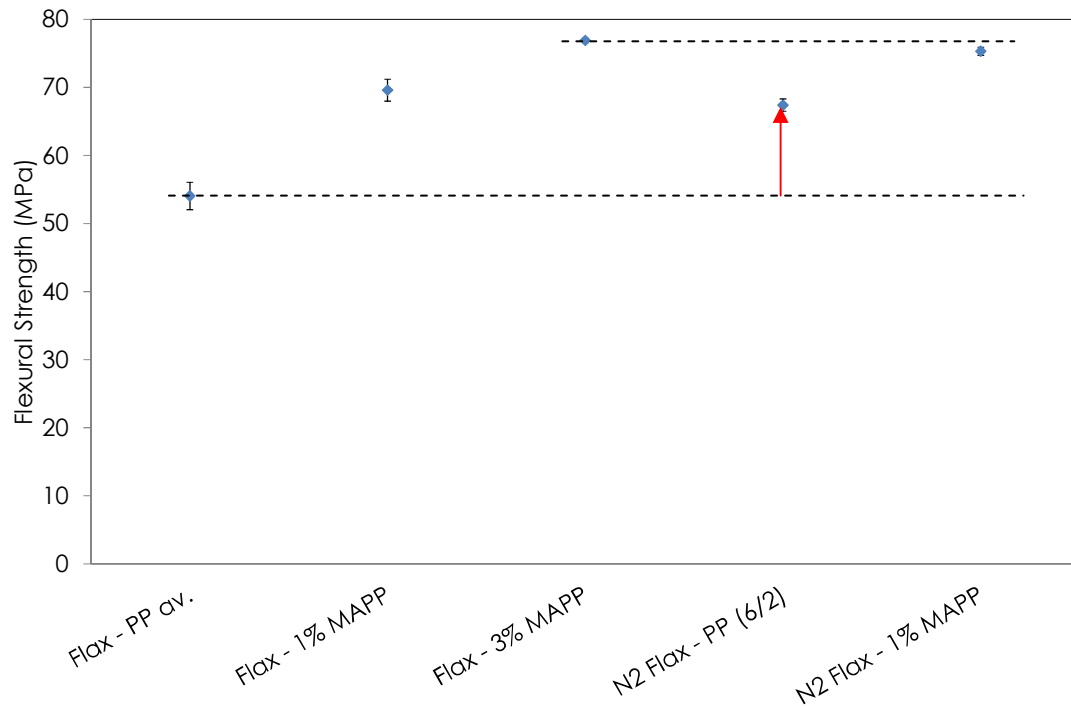of Flax and Hemp Fibres
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**Figure 8: Flexural strength of PP composites based on (refined) $N_2$ plasma treated flax fibres and untreated references. Dashed lines represent level of untreated fibres in PP and untreated fibres in PP/3% MAPP.**

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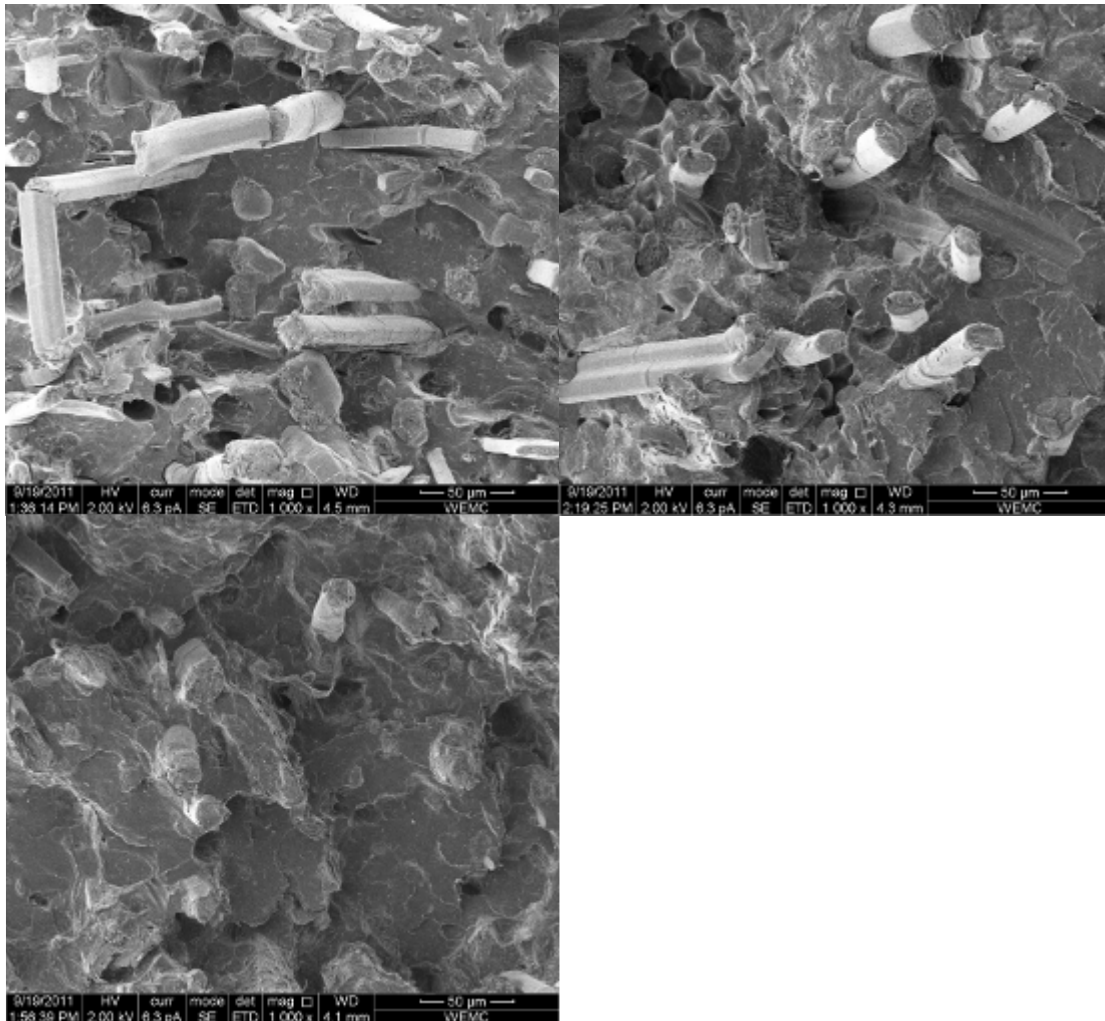of Flax and Hemp Fibres
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**Figure 9: SEM pictures of fracture surfaces of untreated flax-PP (top left), plasma treated flax-PP (top right) and untreated flax-MAPP (bottom) composites.**

Hemp-PP

For hemp-PP composites, no improved strength performance was observed for a range of plasma feed gas compositions (D5.2, Figure 41). Hemp fibres appear to refine during compounding, thus creating fresh untreated fibre surface, whereas flax fibres do not refine (Figure 10). 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 7), which hinders potential 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

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fibre surface, thus allowing better adhesion between the fibre and the matrix. However, no such effect was found (Figure 11).

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 13). 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.
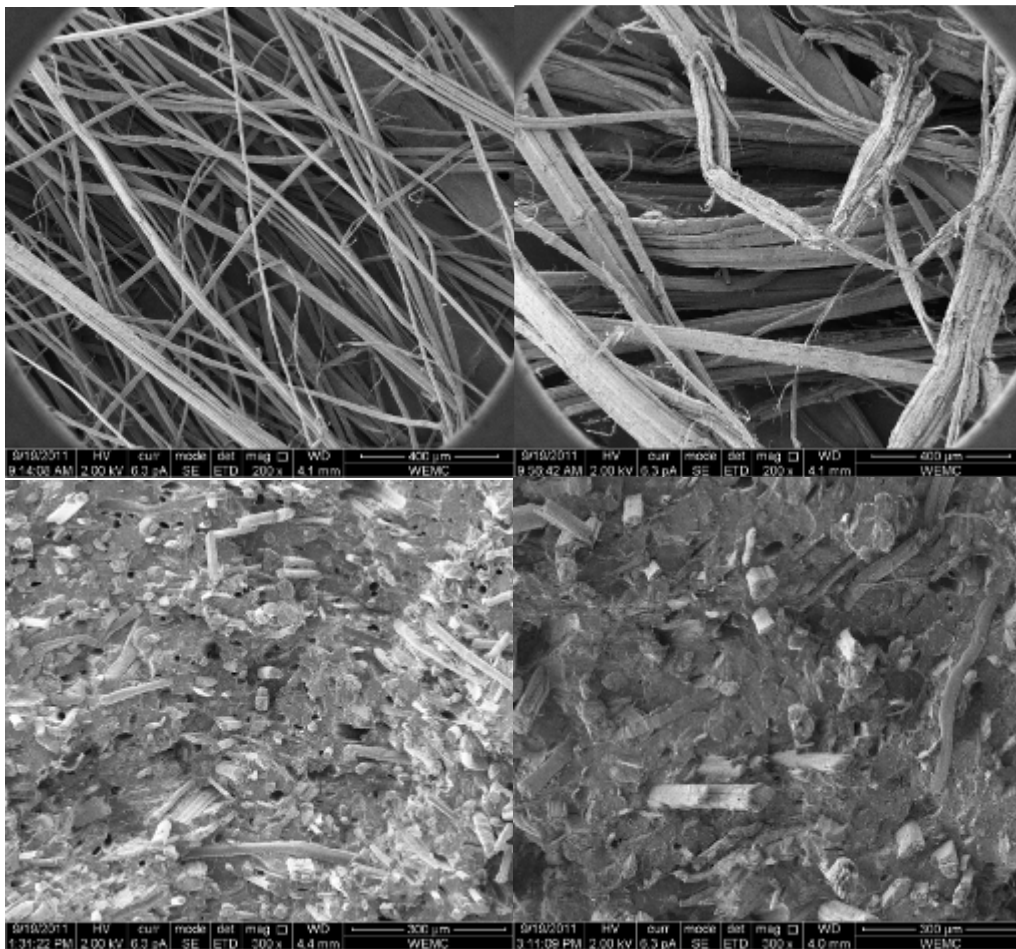


**Figure 10: SEM pictures of Shirley refined flax (left) and hemp (right) fibres (top) and fracture surfaces of their composites (bottom).**

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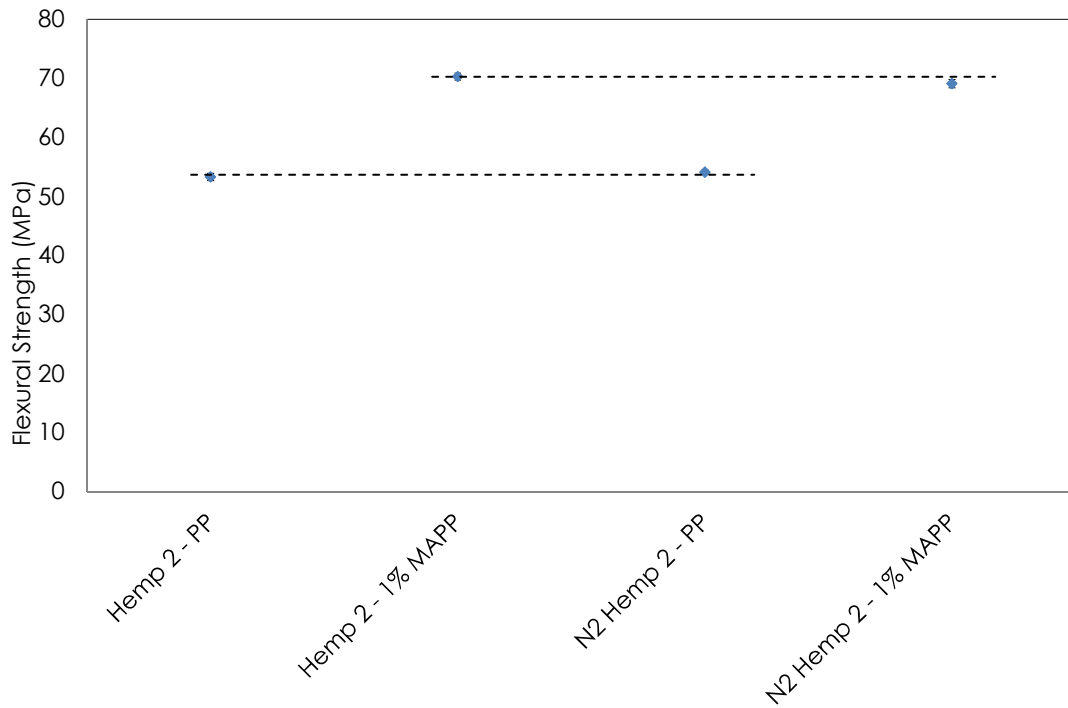of Flax and Hemp Fibres
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**Figure 11: Flexural strength of PP composites based on (refined) plasma treated fibres
and an untreated reference.**

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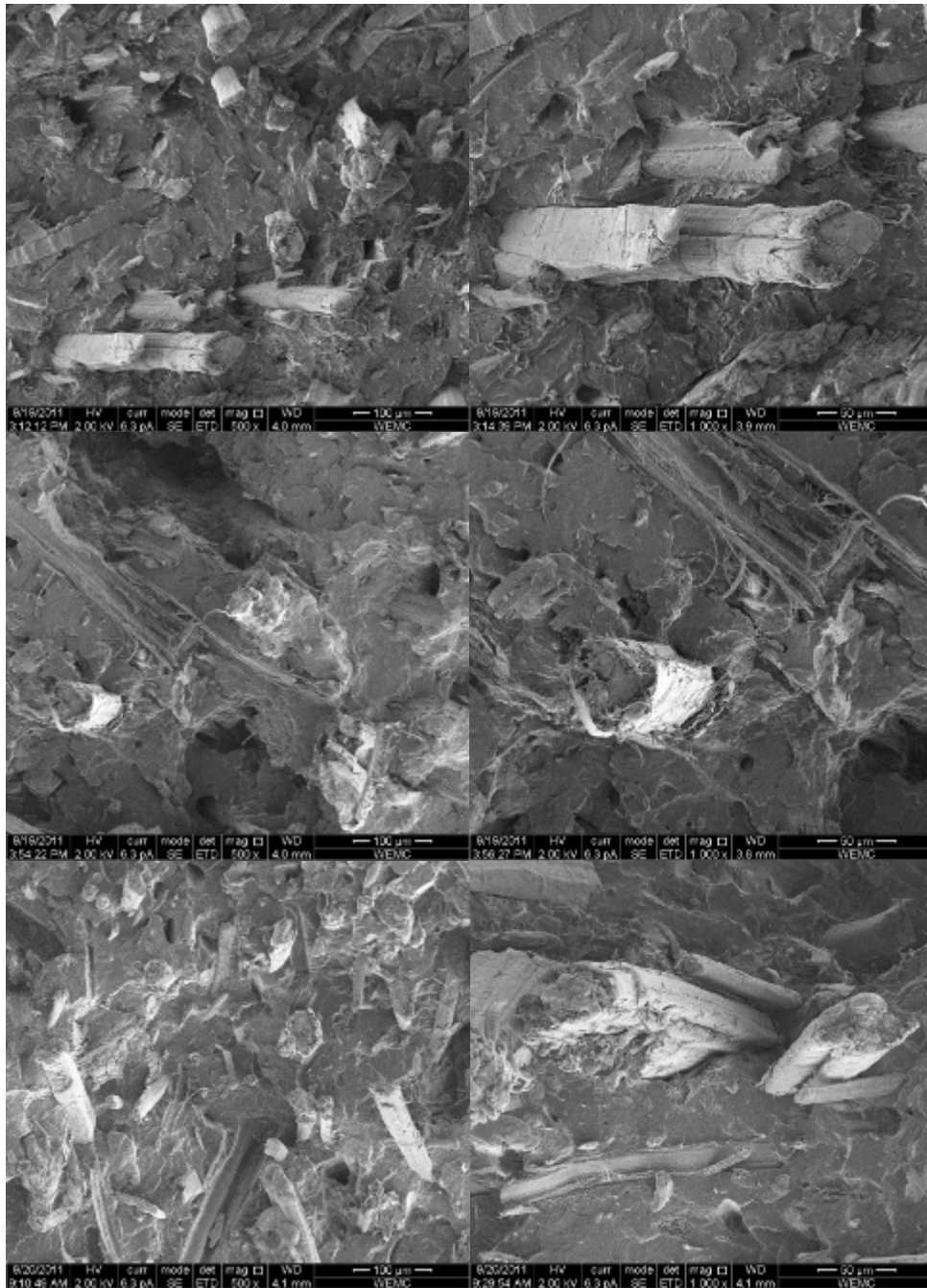for PP and PLA Matrices**

**Figure 12: SEM pictures of fracture surfaces of untreated hemp-PP (top), untreated hemp-MAPP (middle) and N$_2$ plasma treated hemp-PP (bottom) composites.**

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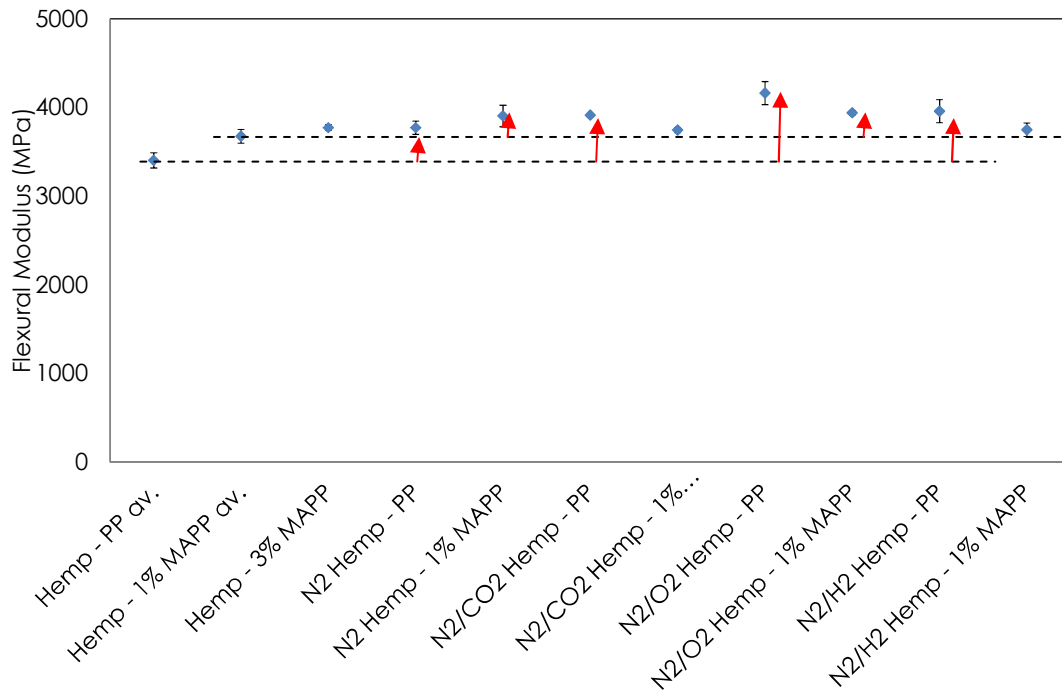for PP and PLA Matrices**

**Figure 13: Flexural modulus of PP/MAPP composites based on (refined) plasma treated hemp fibres and untreated (refined) references. Dashed lines represent levels of untreated fibres in PP and PP/1% MAPP, respectively.**

Hemp-PLA

Trends for 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 14). So far, no explanation has been found for the difference of performance of hemp-PP and hemp-PLA composites.

The 22% strength improvement in bending mode would allow a 10% thinner product having the same strength performance. Using $H_2$ as a dopant gas has no effect on composite strength (Figure 13) and a negative effect on stiffness (D5.2, Figure 44).

The increase in PLA composite performance due to atmospheric plasma treatment is similar to or exceeding improvements found for composites based on chemically treated fibres, which data were collected in the literature survey previously presented in D3.1, sections A2.3 and A3.5. In the literature survey, no data on plasma treatment for improved fibre-matrix adhesion were found for PLA polymer.

SEM pictures present hardly any difference in fibre-matrix adhesion for untreated and plasma treated flax and hemp-PLA composites (Figures 15 and

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16). Also, no difference is observed for $N_2 + H_2$ plasma treated hemp-PLA, which showed aberrant strength and stiffness values (Figure 15).

Charpy impact strength is not significantly affected by any plasma treatment applied.
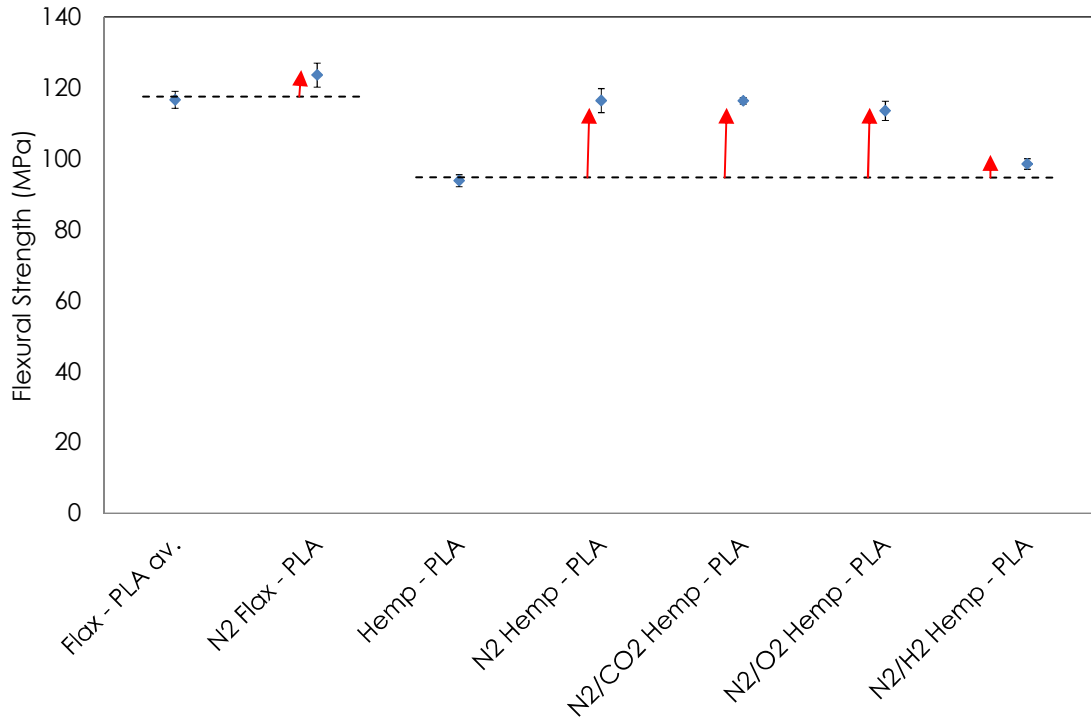


**Figure 14: Flexural strength of PLA composites based on (refined) plasma treated fibres and untreated references. Dashed lines represent levels of untreated fibre-PLA composites.**

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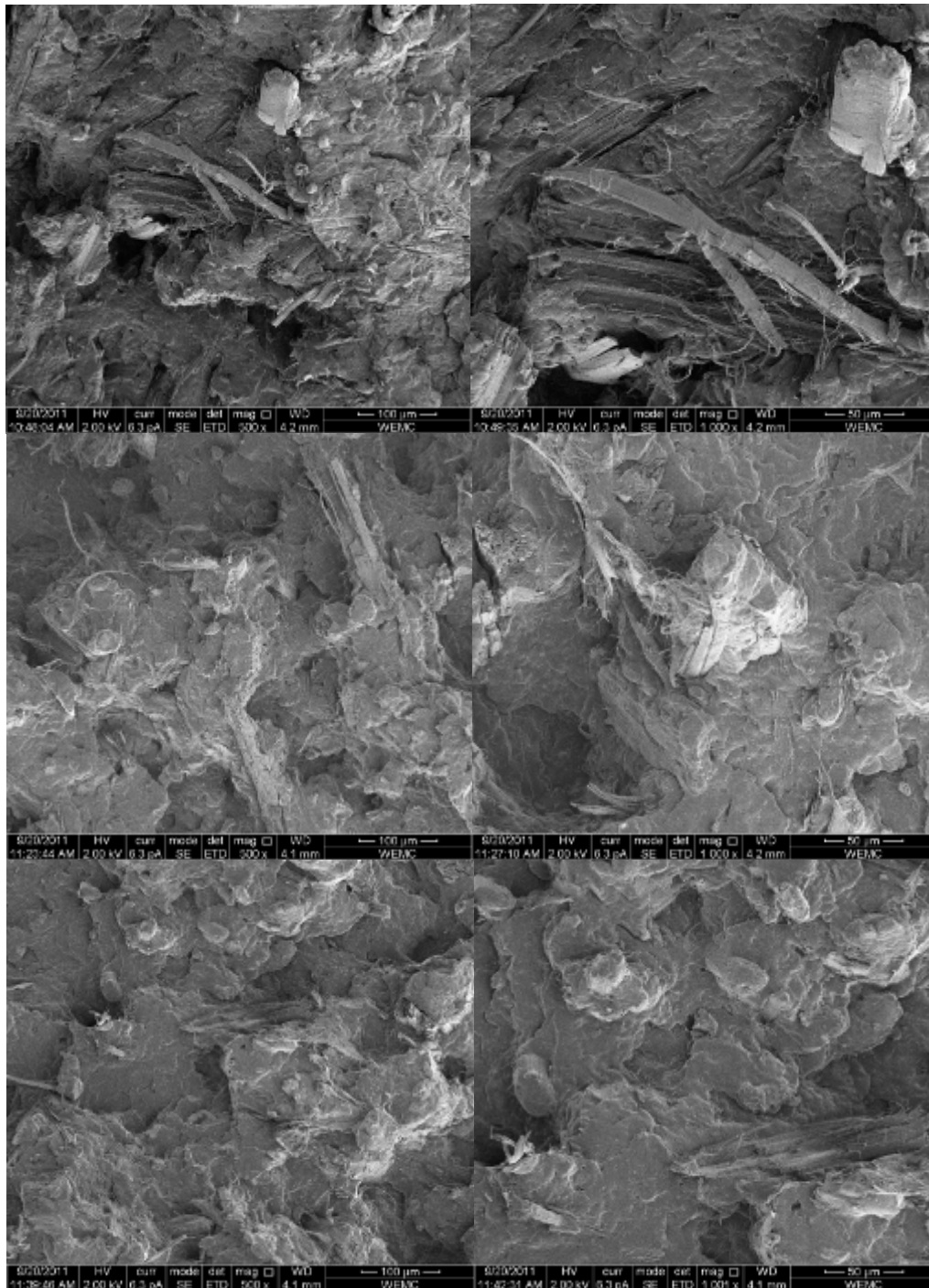of Flax and Hemp Fibres
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**Figure 15: SEM pictures of fracture surfaces of untreated hemp-PLA (top), $N_2$ plasma treated hemp-PLA (middle) and $N_2 + H_2$ plasma treated hemp-PLA (bottom) composites.**

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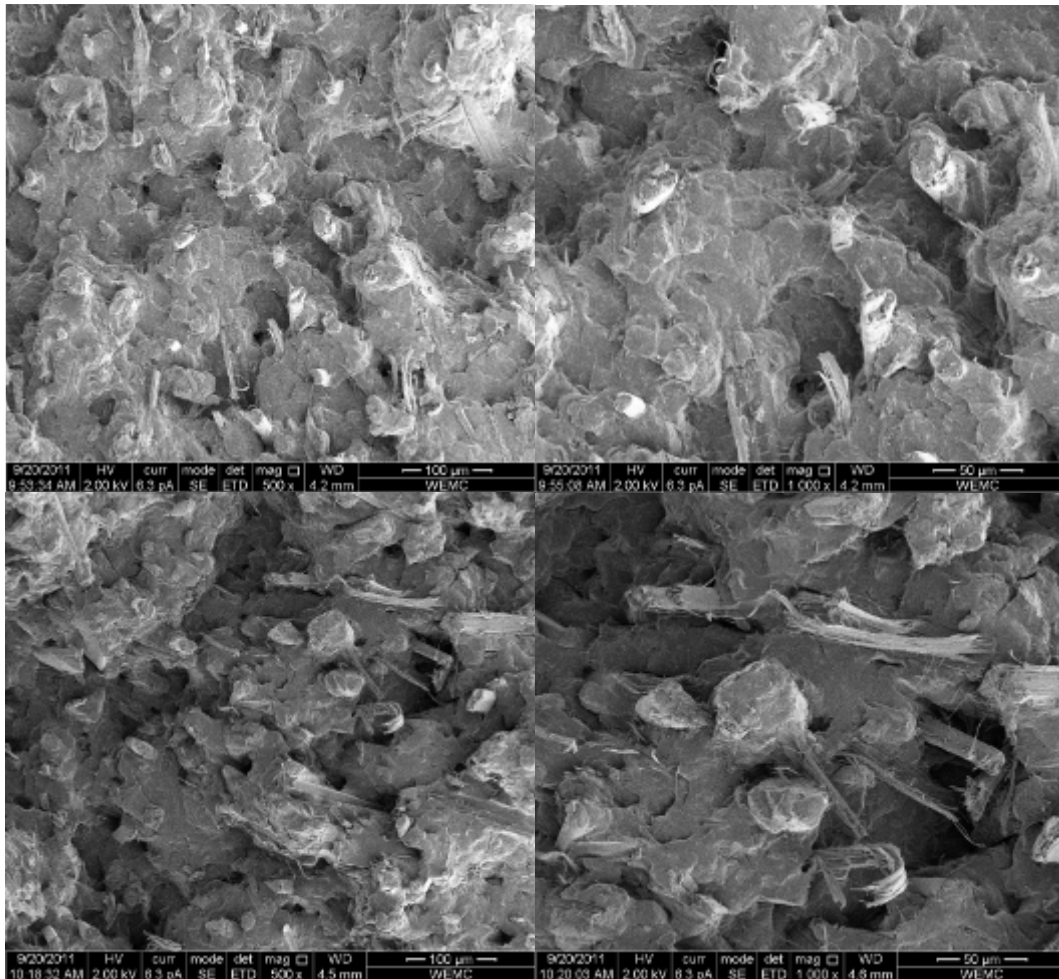for PP and PLA Matrices**

**Figure 16: SEM pictures of fracture surfaces of untreated flax-PLA (top) and N$_2$ plasma treated flax-PLA (bottom) composites.**

Conclusions on compatibilisation to PP and PLA

Effective plasma treatment requires that fibres do not refine during further processing. For extrusion compounds 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 upscaled 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, can not 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.

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## 2.4  Task 3.5 Process experimentation / optimisation for PP and PLA polymers

Results indicate that plasma treatment should be thorough in order to be effective (Figure 17:  6/2 passages versus 2/2 passages).

Once plasma treatment is applied, it seems rather durable. In figure 17, sample 4M, which was plasma treated at AcXys' facilities, was made into a composite full 4 months after plasma treatment, still showing a 12% increase in flexural strength compared to the untreated reference.
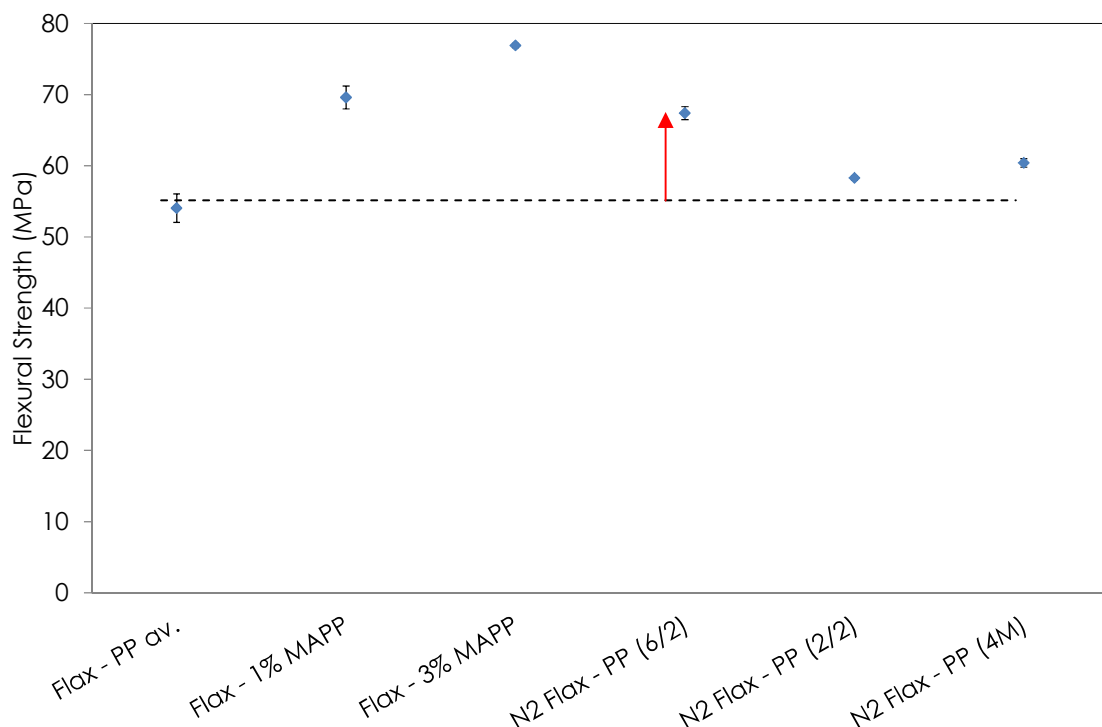


**Figure 17: Flexural strength of PP composites based on (refined) N$_2$ plasma treated flax fibres and untreated references. Dashed line represents level of untreated fibres in PP.**

Energy consumption

Energy consumption fluctuated ± 4 % during plasma processing. The average energy consumption for the 6 cm ULD plasma unit was about 1065 kW for following feed gas compositions: pure N$_2$, N$_2$ + O$_2$ and N$_2$ + CO$_2$, whereas for N$_2$ + H$_2$ energy consumption was about 1000 kW.

Emissions

Plasma treatment only uses electricity and gasses. There are no water emissions except for cooling water.

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Plasma can be considered a clean technology. Emissions mainly depend on the feed gases. 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 (NOx) emissions. Other emissions may be gaseous substances released from the fibre surface during plasma treatment, for instance $CO_2$, $H_2O$ and potentially methanol. However, so as to have a quantified evaluation of plasma emissions and in order to allow an LCA, AcXys has performed measurements on its R&D facilities.

In the following table, prescribed limitations concerning Ozone and NOx are described. Limitations references are given by the World Health Organisation and distinguish the maximum instantaneous limits and annual mean limits.

**Table 3: Risks and occupational limits for Ozone and NOx.**

|  | Ozone [$O_3$] | Nitrogen oxides [NO] / [$NO_2$] | |
|---|---|---|---|
| Can be detected by human | <0,01 ppm (Be careful, very fast habituation) | 0,05 ppm to 0,13 ppm | |
| Limits | 0,2 ppm / 15 min | 25 ppm NO / 15min | 3 ppm $NO_2$ / 15min |
|  | 0,1 ppm / 8h |  | 0,4 ppm $NO_2$ = WHO threshold (2005) for average annual exposure |
| Risks | Respiratory trouble after 6h > 0,2 ppm | Respiratory trouble 15 to 40 ppm NO during few hours |  |
|  | Vision trouble at 0,2-0,5 ppm. Many years (7 - 10) of exposition to >0,2 ppm can affect the brain (headaches, loss of memory) | Can produce nitric acid which is toxic | Can produce nitric acid which is toxic |

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In order to quantify the ozone and NOx emissions, a GASTEC pump and colorimetric probes (see Figure 18) were used to collect target gas samples. Samples were collected a few centimeters from the plasma source. The colorimetric probes contain a particular reactant which changes colour when in contact with the target gases ozone and NOx. The obtained colour indicates which amount of the target gas is present in the sample taken.



**Figure 18: Gastec calorimetric probes.**

In the following table, measurements achieved by AcXys on its own R&D ULD source are presented in Table 4.

**Table 4: Levels of Ozone and NOx detected near a ULD plasma source.**

|  | Ozone [$O_3$] | Nitrogen oxides [NO]/ [$NO_2$] |
|---|---|---|
| Nitrogen plasma | <0,05 ppm | Not detected, detection threshold is 0.04 ppm |
| $N_2$ + 400 ppm $O_2$ | 0,2 ppm | 0,3 ppm |
| $N_2$ + 2000 ppm $O_2$ | 0,75 to 1 ppm |  |

At regular plasma operating conditions, a very limited amount of oxygen in the feed gas leads to critical emissions of ozone. Extraction is consequently a necessary safety precaution for such plasma processing. Ozone is a greenhouse gas as well, however, also very unstable, and so far there no legal pressure to reduce ozone production.

Concerning Nitrogen oxides, we can observe that emissions are not overpassing safety limits. At the same time, NOx will be extracted together with the ozone.

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The levels of NOx detected can be extrapolated to evaluate the emissions of a plasma source along one year. Based on data from Table 4, annual NOx emissions for a 1 m ULD plasma unit operated for 225 days, 16 hours/day, 10 L/cm.min of $N_2$ or $N_2 + O_2$ consumption are calculated to be 16.2 – 122 g NOx (based on 0.04 and 0.3 ppm). This is similar to NOx emissions of a car travelling 160 – 1200 km at an average emission of 0.1 g/km. This calculation shows that NOx emissions of such an industrial scale plasma unit are relatively small.

Conclusions on process optimization and emissions
Surface modification resulting from plasma treatment is quite durable, however, under the 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 NOx may need to be extracted to protect operators, depending on concentration of $O_2$ dopant to the feed gas. Once in air, ozone quickly decomposes and there are no legal regulations. NOx emissions in principle pose a greenhouse gas issue, however, annual emissions of an industrial scale plasma unit are calculated to be in the range of a car traveling 160 – 1200 km. Emission data for ozone and NOx were collected for LCA purposes.

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## 2.5  Techno-economic evaluation for PP and PLA composites

After completion of a full optimization cycle of plasma treatment of flax and hemp for PP and PLA based extrusion compounds, an initial techno-economic evaluation was performed. 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 $N_2$ in tank and dopant gasses 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 95 and 290 g/m$^2$ for flax and hemp as for current lab trials, or 500 and 1000 g/m$^2$ as estimated upper limits. Hemp m2-weight was higher than for flax because of the coarser nature of the hemp fibres after refining.
- 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.
- 3 % MAPP in a composite costs 0.20 €/kg composite. Assuming a saving potential of 1.5 % of 3 % MAPP in the final composite, costs savings would be 0.10 €/kg of composite or 0.33 €/kg of fibre for a 30 wt.% fibre composite.

From the assumptions indicated above, plasma treatment costs can be calculated as presented in Figures 18 – 21 below. Conclusions are:

- Translation of applied plasma processing parameters to industrial scale production shows a cost level much higher than savings made by requiring 1.5% MAPP less in extrusion compounds (Figures 18 and 19).

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- Optimisation of processing in terms of production hours/day (8 → 16 h) and gas consumption (60 → 30 L/min) shows that the plasma process can only be economically feasible for fibre mats of high m² weight and at high processing speed (Figure 20 and 21). Costs for refining the fibres prior to plasma treatment is actually not taken into account. This means that plasma processing in more profitable for composites based on coarse fibre mats like SMC and NMT. The fact that the gas consumption potentially may be lowered further to 15 or 10 L/min by using a particular ULD design, will not alter this conclusion.

- Since there is no regular commercial coupling agent available for PLA composites, cost savings could 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 22% as 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 2.5 €/kg, cost savings are 0.25 €/kg of composite or 0.83 €/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. At the same time, it must be mentioned that similar performance can be obtained by using untreated flax-PLA.
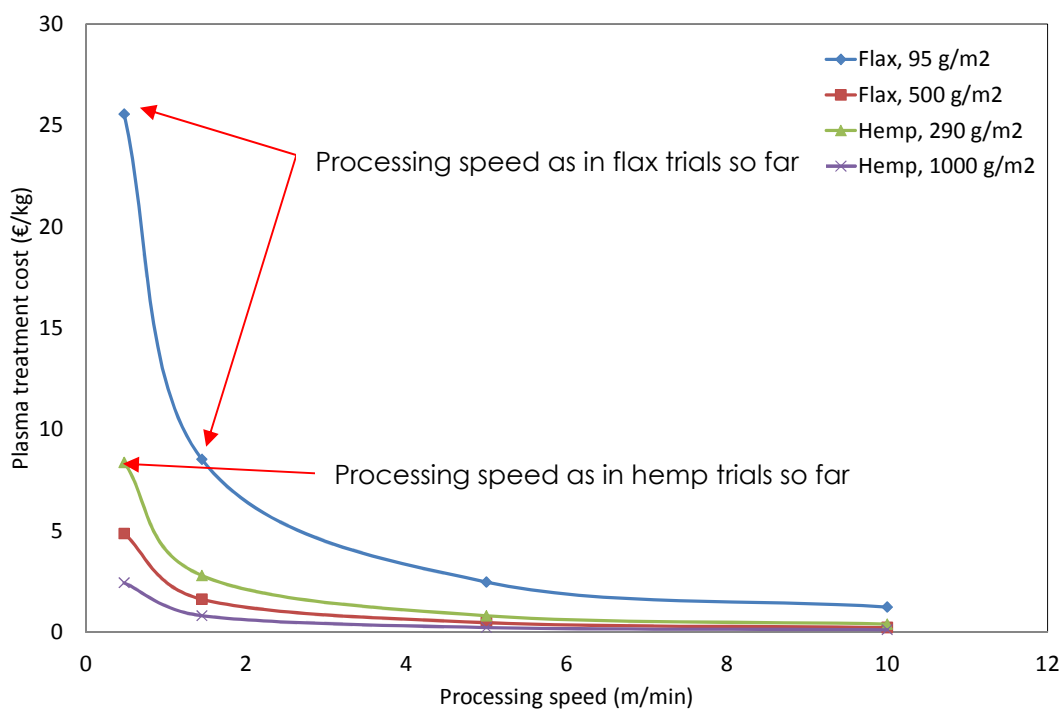


**Figure 19: Plasma treatment cost per kg of fibre based on assumptions summarized above.**

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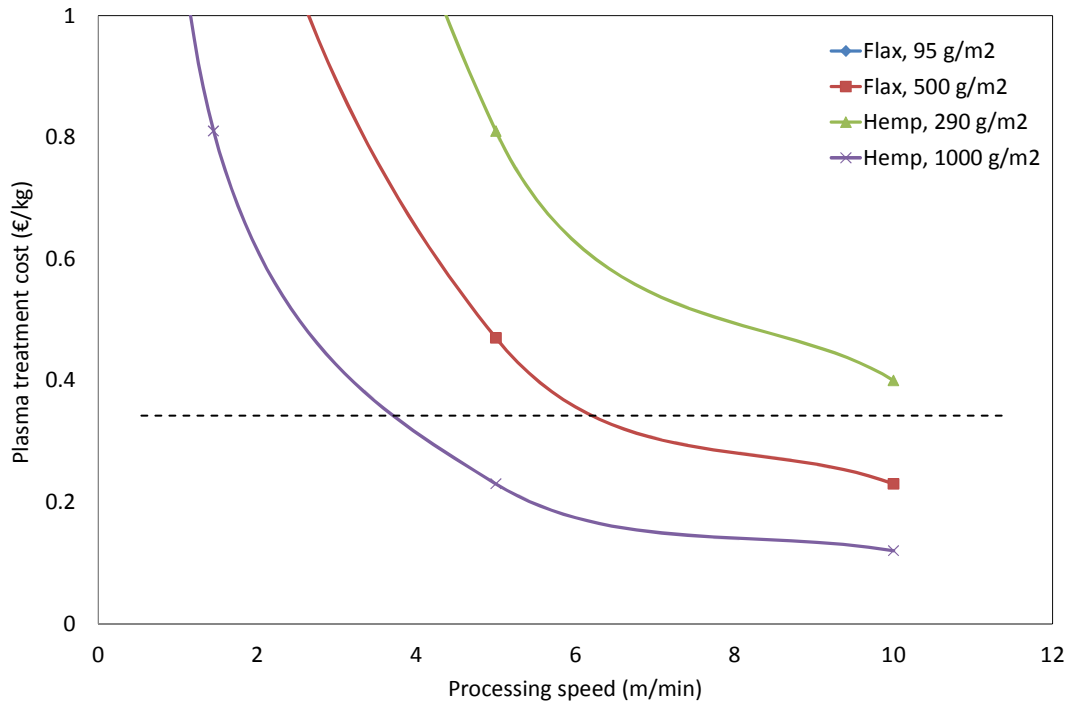for PP and PLA Matrices**

**Figure 20: Plasma treatment cost per kg of fibre based on assumptions summarized above (Zoom of Figure 9.4). Dashed line represents MAPP cost savings level of 1.5 wt% (of 3%).**
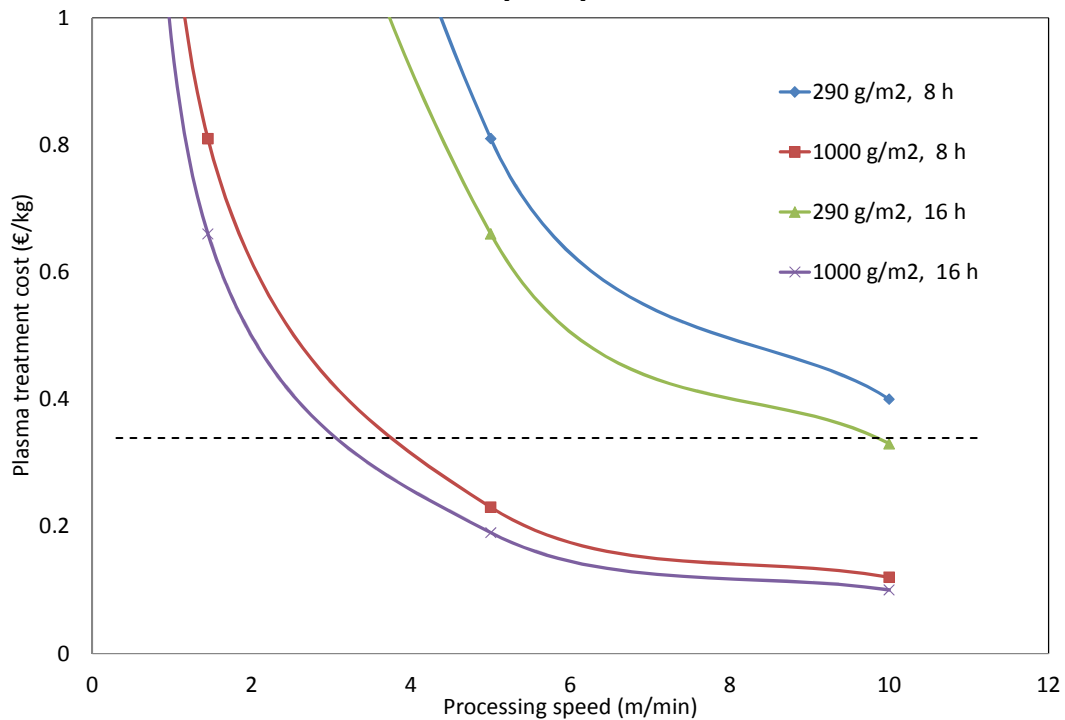


**Figure 21: Plasma treatment cost based on assumptions summarized above, including costs when operating 16 h/day instead of 8 h. Dashed line represents MAPP cost savings level of 1.5 wt% (of 3%).**

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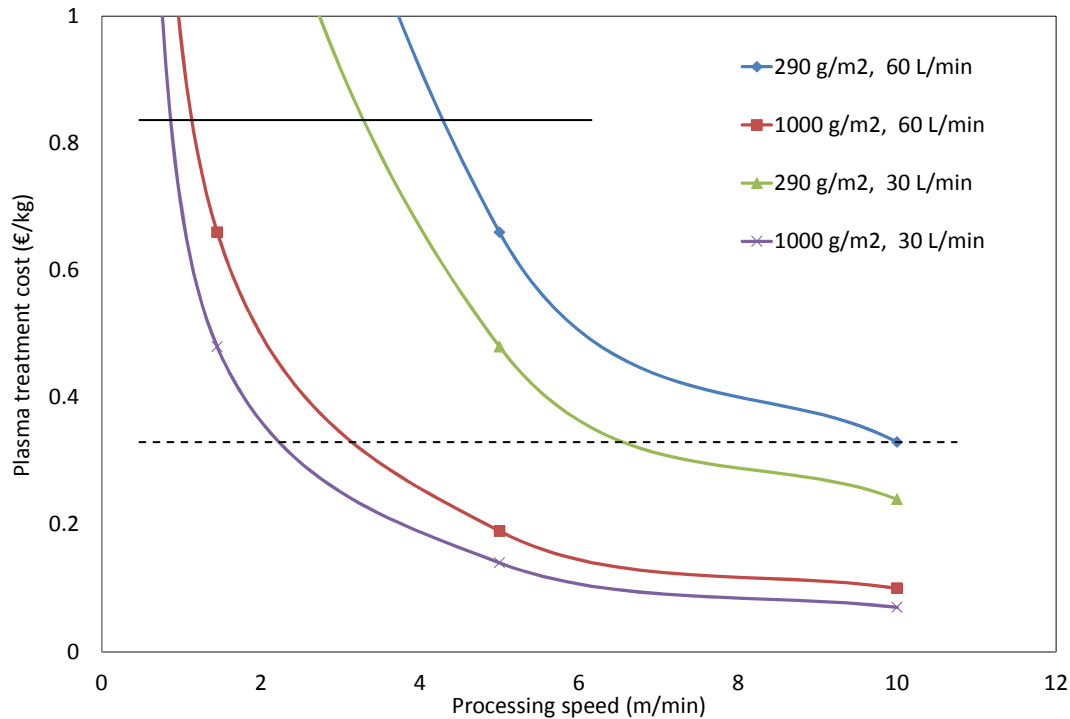for PP and PLA Matrices**



**Figure 22: Plasma treatment cost based on assumptions summarized above, except for operating 16 h/day instead of 8 h, and having a gas flow of 30 L/min instead of 60 L/min. Dashed line represents MAPP cost savings level of 1.5 wt% (of 3%). Solid line represents material cost savings level for hemp-PLA composite.**

<u>Conclusions and discussion on techno-economic analysis</u>
Effective plasma treatment requires that fibre diameter does not refine during further processing. For extrusion compounds this means that fibres need to be refined prior to plasma treatment. Considering the plasma conditions applied so far, the maximum effective plasma treatment rate for refined fibres is low, meaning that processing costs are high. Therefore, plasma treatment seems more profitable for composites, which are made by processes not exhibiting fibre refining such as SMCs and NMTs. As a consequence coarser fibres may be used for these types of composites, allowing higher plasma treatment rates. At the same time, the use of chemical reactants may be considered to improve the effect of plasma treatment on fibre-polymer matrix adhesion.


## 2.6 Issues and solutions

From the literature search results, extensively addressed in D3.1, it was concluded that natural fibres exhibit good bonding to furan resin already. Therefore, it was proposed to focus plasma treatment on improved adhesion to the other target polymers PP, PLA and UP.

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A techno-economic evaluation indicates that, after a first optimisation cycle, plasma treatment of flax and hemp for PP and PLA based extrusion compounds is not economically feasible. In section 2.5 it is indicated why composites based on coarser fibres like SMC are expected to give a higher profitability. Therefore, at the partner meeting in November 2011, it was decided to focus further plasma work on unsaturated polyester based SMC composites. After an experimental plan has been developed and prepared in Months 24-26, actual plasma development work for SMC composites will be performed in Months 27-30. It is foreseen that completion of this WP may require 2 additional months, so up to M32. The results will be described in an additional report D3.4.

One of the aims of the project was to modify the fibre-handling machine configuration in such a way that the plasma treatment process may be integrated into the ultrasonic process. It appears that the ultrasonic process has to be applied under wet conditions, and that fibres have to be dried prior to further processing, either direct manufacturing into composites or application of plasma treatment. Therefore, it is concluded that atmospheric plasma treatment cannot be fully integrated into the ultrasonic process. Processing in series, however, is possible.

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# 3.    Summary of results and Conclusions

- Different levels of fibre surface modification have been 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 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 NOx may need to be extracted to protect operators, depending on concentration of $O_2$ dopant to the feed gas. Once in air, ozone quickly decomposes and there are no legal regulations. Annual NOx emissions of an industrial scale plasma unit are calculated to be in the range of a car traveling 160 – 1200 km.
- 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.
- Plasma emission data of most critical components, ozone and NOx, were collected for LCA purposes.

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# 4. Future Work (Months 25 to 32)

- Plasma surface treatment of hemp for application in unsaturated polyester resin based SMC composites. The set-up of this development work will be determined in joint consultation with Movevirgo, RAPRA and AcXys.
- Evaluate possibilities to apply suitable chemical reactants directly after plasma treatment in order to enhance adhesion to PP/MAPP, PLA or UP, or which allow higher plasma processing rates.
- The effect of ultrasonic fibre processing prior to plasma treatment for application in unsaturated polyester SMC will be evaluated.
- The results will be described in an additional Deliverable report D3.4, suggested to be due in Month 32.
- Plasma treatments for scaled up trials in WPs 6/7 will be defined and planned in close co-operation with AcXys, Movevirgo, RARPA and DLO-FBR and performed at a partner of AcXys.