Lire
la première partie
de la thèse
IV Pressure and heat catalyzed esterification for the hydrophobation of compressed cellulose materials

Early in the research progress of project HYPMOBB was born the wish of working on increasing the water resistance of the specimens with the idea of grafting fatty side chains on the cellulose backbone (Peydecastaing et al. 2011) during the molding process, using heat and pressure as reaction catalysts. Preliminary results were performed on a bowl produced from miscanthus, which was re-processed after having coated the inside of the bowl with oleic acid. Steam was generated after this second processing and a quick water test was conducted, comparing one bowl that received oleic acid with another treated in the same conditions but without the fatty acid. The treated bowl did retain water for a few hours although the control swelled and let water leak after about one minute.

From this experiment, it was not clear what was responsible for the waterproofing because the basic adsorption of any fatty compounds on the surface of the object and in the porosity of the material would have been a satisfactory explanation. Nevertheless, a first set of trials were performed in order to test different fatty materials on cellulose, and the water drop angle was measured over time (kinetically).

Secondly, the grafting was more precisely studied on a case study and investigated with use of the analytics skills available in the LCA. This second part IV.2 was submitted for publication in Bioresources.

IV.1 Preliminary results, mapping of fatty compounds

Control conditions were defined for the evaluation of fatty compounds for hydrophobating cellulose samples, a control mass of 10 g was selected for a 50x50 mm plate shape; fatty compounds were added in proportions of 2, 5 and 10 %. Stearic acid, linoleic acid, sebacic acid, magnesium stearate, sodium stearate, highly oleic sunflower oil, and 95/5 mixtures of stearic acid and magnesium/sodium stearates were evaluated (Table IV.1).

Table IV.1: Summary of experimental conditions for fatty compounds evaluation for the hydrophobation of cellulose samples

<table>
<thead>
<tr>
<th>Cellulose (g)</th>
<th>Additive</th>
<th>Additive addition (g)</th>
<th>Additive content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>none</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>9.8</td>
<td>Stearic acid</td>
<td>0.2</td>
<td>2%</td>
</tr>
<tr>
<td>9.5</td>
<td>Stearic acid</td>
<td>0.5</td>
<td>5%</td>
</tr>
<tr>
<td>9</td>
<td>Stearic acid</td>
<td>1</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>Mg stearate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na stearate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stear. ac./Mg - 95/5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stear. ac./Na - 95/5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sebacic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Linoleic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sunflower oil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 25 modalities (8 fatty compounds . 3 percentages + 1 control) were prepared, molded in 50x50mm squares in duplicate at 200 MPa, 150°C for 2 minutes, and equilibrated 2 weeks at 60% RH 25°C before testing. For each of the 2 plates per modality, 5
measurements were performed according to Figure IV - 1 in order to obtain satisfactory representativeness of the whole surface and counter heterogeneity. The 10 curves of the water drop penetration on the surface were not repeatable, but the representation of the 10 curves together allows comparison. The complete results are presented in Figure IV - 2, Figure IV - 3 and Figure IV - 4.

![Figure IV - 1: 50x50 mm cellulose samples with fatty compound after 5 drop angle measurements](image)

An adequate way of proceeding is to compare each modality of additivation with the control condition. There are three factors to consider in the analysis of the penetration curves:

- Initial drop angle
- Absorption length
- Curve’s shape

The addition of stearic acid produced materials with initial angle significantly over the control and begun with a small slope indicating that after sitting the drop on the surface of the materials it stayed quite stable whatever the additive content. This last point was comparable to the control. The absorption length was about 50% higher for 2% stearic acid, about 100% higher for 5% but about 50% lower for 10% showing a limit of the fatty compounds addition. It seemed that too much additive produced excessive porosity that made the drop penetrate the material quicker than the control, even if initial drop angle was higher.

The addition of magnesium stearate produced materials with a higher initial drop angle compared to the control (and comparable to stearic acid) but the shape of the curve was quite different as, during the first seconds of the test, the drop angle decreases brutally to retrieve values comparable with the control (especially 2 and 5%). The adsorption length was about 50% higher for 2% addition but comparable to the control for 5 and 10%.

The addition of sodium stearate was very different: the initial drop angle was comparable to the control but the penetration curve showed the same trend than magnesium stearate with a brutal decrease of the drop angle during the first seconds of the test. Consequently, the drop angle was rapidly lower and absorption time lower than the control. Possibly, the addition of sodium stearate was hindering the cohesion mechanism and generated porosity which provoked higher water sensitivity than without the additive. The effect of the counterion Mg or Na was very drastic. Some differences exist between these two, Mg is divalent although Na is monovalent, which modifies the counterion / sterate ratio, and the ionic strength. Mg is also known to have a more diffuse charge than Na which creates reactivity differences.

The addition of the 95/5 mixture of stearic acid and magnesium stearate had a behavior comparable to pure stearic acid modality at 2% but 5 and 10% additions were
producing very water sensitive materials with shorter absorption length and a brutal drop of the drop angle at the beginning of the curve. Quite consistent results were observed on the 95/5 mixture of stearic acid / sodium stearate with a rapid decrease of the drop angle at the beginning of the curve and much quicker penetration of the drop into the material.

The addition of sebacic, linoleic acid and sunflower oil produced materials with much higher water sensitivity, with initial drop angle comparable or higher than the control condition, but a very quick penetration of the drop in the material, which could be explained by a higher porosity of the material and which gave much lower absorption lengths. The stearic / linoleic acid showed drastic difference which could be explained by the U and linear conformation of these acids.

These experiments showed the possible interest of stearic acid (short and linear fatty acid) and magnesium stearate for hydrophobation of cellulose samples but the behavior of the different fatty compounds rose issues about whether the increased water resistance was produced by an effective grafting or a simple surface adsorption. Water properties were also sometimes decreased with the addition of several compounds which was concluded to be because of a lack of cohesion of the samples. Possibly the addition of these compounds prevented the establishment of the hydrogen bonding network but the reason for this and why these compounds remained unanswered.

In order to investigate about the possibility of having an esterification reaction occurring during the molding, a short fatty acid was selected (octanoic acid) and a analytical protocol was set up.
Figure IV - 2: (1/3) Evaluation of fatty compounds for hydrophobation, water drop penetration, x axis time (s), y axis drop angle (°)
Figure IV - 3: (2/3) Evaluation of fatty compounds for hydrophobation, water drop penetration. 
- x axis time (s), y axis drop angle (°)
Figure IV - 4: (3/3) Evaluation of fatty compounds for hydrophobation, water drop penetration, x axis time (s), y axis drop angle (°)
IV.2 High-pressure driven solvent-free heterogeneous phase esterification of cellulose

Classically, the esterification of cellulose required solvents, involving reactors, solvent recycling, and phase separation, all of which are material- and time-consuming processes. A different approach was studied in this part: the use of high pressure at elevated temperatures as the contact method and energy supply to initiate the reaction.

IV.2.A List of Experiments

Eleven different experimental conditions were tested to evaluate the possibility of grafting octanoic acid (OA) and anhydride octanoic (OAn) onto cellulose and miscanthus under heterogeneous phase conditions at high pressure.

The first experiment involved standard compressed alpha cellulose, without additives, and was coded “Alpha_c.” The second made use of standard compressed miscanthus powder, without additives, and was coded “Mis.”

Six pretreatment conditions were used to test the efficacy of grafting OA onto cellulose. An emulsion pretreatment using OA, water, and cellulose, as described in the Experimental section, was coded “Emul.” Three different solvent exchange pretreatments were implemented. The first solvent exchange, as described in the Experimental section, involved washing with OA and was coded “OA_exch.” A variant of this procedure, in which the pH of the water exchange was adjusted to 2 (Pantze et al. 2007) was coded “OA_exch_pH.” A second variant was coded “OA_exch_pH_6,” in which cellulose was left to stir in OA for 6 h at the end of the contact step.

A high-pressure homogenizer pretreatment in water, followed by a solvent exchange step, was coded “OA_homo_exch.” Another high-pressure homogenizer pretreatment, in which water was replaced by OA in the apparatus, was coded “OA_homo.” The material did not show the same gel-like appearance in OA as it did in water. To graft OAn onto cellulose, a solvent exchange pretreatment was conducted with water, solvent, and OA, then one additional rinsing with OAn; this method was coded “OAn_exch.” Grafting of OA onto miscanthus was performed using a high-pressure homogenizer pretreatment; 20 g of miscanthus powder was introduced into the high-pressure homogenizer, along with 2 L of OA, and this procedure was coded “Mis_OA_homo.” Grafting of OAn onto miscanthus involved a high-pressure homogenizer pretreatment, in the same way as that of the “Mis_OA_homo” experiment, with an additional filtering and suspension in OAn; this experiment was coded “Mis_OAn_homo.”
Table IV · 2: Summary of results, investigation of the esterification reaction during molding

<table>
<thead>
<tr>
<th>Experiment code</th>
<th>Material</th>
<th>Pretreatment</th>
<th>Graft</th>
<th>Molding Temp</th>
<th>Molding Time</th>
<th>Drop angle</th>
<th>Absorb time</th>
<th>IR peak 1724 cm⁻¹</th>
<th>GR (mEq/kg)</th>
<th>DS (MPa)</th>
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<tbody>
<tr>
<td>Alpha_c</td>
<td>α Cellulose</td>
<td>none</td>
<td>none</td>
<td>165</td>
<td>2</td>
<td>49°</td>
<td>7 s</td>
<td>0.03</td>
<td>0.02</td>
<td>5.3E-05</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>N/A</td>
<td>N/A</td>
<td>0.03</td>
<td>0.02</td>
<td>5.1E-06</td>
</tr>
<tr>
<td>Ermul</td>
<td>α Cellulose</td>
<td>OA-water emulsion</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>57°</td>
<td>12 s</td>
<td>2.7</td>
<td>0.2</td>
<td>4.3E-04</td>
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<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>N/A</td>
<td>N/A</td>
<td>5.1</td>
<td>0.4</td>
<td>6.3E-04</td>
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<td>OA_exch</td>
<td>α Cellulose</td>
<td>Solvent exchange</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>50°</td>
<td>16 s</td>
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<td></td>
<td></td>
<td>190</td>
<td>1</td>
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<td>N/A</td>
<td>48°</td>
<td>0.2</td>
<td>N/A</td>
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<td>190</td>
<td>1</td>
<td>48°</td>
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<td>78°</td>
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<td>OA_exch_pH_6</td>
<td>α Cellulose</td>
<td>Solvent exchange at pH2 (water) + 6h in OA</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>64°</td>
<td>12 s</td>
<td>170</td>
<td>0.2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>67°</td>
<td>39 s</td>
<td>171</td>
<td>3.0</td>
<td>1.3E-02</td>
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<td>OAAn_exch</td>
<td>α Cellulose</td>
<td>Solvent exchange</td>
<td>OAAn</td>
<td>165</td>
<td>2</td>
<td>77°</td>
<td>208 s</td>
<td>265</td>
<td>1.0</td>
<td>4.3E-02</td>
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<td>190</td>
<td>1</td>
<td>77°</td>
<td>452 s</td>
<td>297</td>
<td>1.0</td>
<td>4.8E-02</td>
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<tr>
<td>OA_homo</td>
<td>α Cellulose</td>
<td>HP-Homogenizer (in OA)</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>58°</td>
<td>65 s</td>
<td>160</td>
<td>0.4</td>
<td>2.6E-03</td>
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<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>41°</td>
<td>17 s</td>
<td>12.8</td>
<td>0.7</td>
<td>2.1E-03</td>
</tr>
<tr>
<td>OA_homo_exch</td>
<td>α Cellulose</td>
<td>HP-Homogen. (in water) + Solvent exchange</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>63°</td>
<td>102 s</td>
<td>207</td>
<td>0.2</td>
<td>1.2E-03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>73°</td>
<td>88 s</td>
<td>241</td>
<td>0.1</td>
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<tr>
<td>Mis</td>
<td>Miscanthus</td>
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<td>none</td>
<td>165</td>
<td>2</td>
<td>81°</td>
<td>5 s</td>
<td>2.1</td>
<td>0.3</td>
<td>4.2E-03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>77°</td>
<td>17 s</td>
<td>4.4</td>
<td>0.7</td>
<td>3.9E-07</td>
</tr>
<tr>
<td>Mis_OA_homo</td>
<td>Miscanthus</td>
<td>HP-Homogen. (in OA)</td>
<td>OA</td>
<td>165</td>
<td>2</td>
<td>70°</td>
<td>11 s</td>
<td>16</td>
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<td>1</td>
<td>72°</td>
<td>2 s</td>
<td>24</td>
<td>0.3</td>
<td>N/A</td>
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<tr>
<td>Mis_OAAn_homo</td>
<td>Miscanthus</td>
<td>HP-Homogen. (in OA) + OAn suspension</td>
<td>OAn</td>
<td>165</td>
<td>2</td>
<td>83°</td>
<td>153 s</td>
<td>21.9</td>
<td>0.3</td>
<td>3.7E-03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td>1</td>
<td>81°</td>
<td>106 s</td>
<td>39</td>
<td>0.3</td>
<td>3.9E-07</td>
</tr>
</tbody>
</table>

ND: non determined, N/A: Not applicable
IV.2.B Results

Table IV.2 summarizes the results of all the experiments. Each line in the first column contains three lines as sub-elements: the first line corresponds to the pretreated material without the molding step, while the second and third lines describe the compression molding experiments at 165 °C for 2 h and 190 °C for 1 h, respectively.

The IR peaks of ester bands were detected, and the DS was measured according to the technique of Peydecastaing et al. (2009). This technique confirmed the esterification reaction with the unique conditions of an unstirred, solvent-free solid-liquid heterogeneous phase medium at high pressure and elevated temperature.

A GR value greater than 60 mEq kg\(^{-1}\) (i.e., a DS value greater than 0.01) was measured for a group of cellulose experiments, including OAn_exch, OA_homo_exch, OA_exch_pH_6, and OA_exch_pH, in decreasing GR order. The other experiments, including every experiment performed on miscanthus, obtained a lower GR value. The GR results obtained in OA_homo and Mis_OA_homo were quite low and comparable.

The detection limit of the IR setup was between GR values of 16 and 34 mEq kg\(^{-1}\) (i.e., a DS value between \(2.6 \times 10^{-3}\) and \(5.5 \times 10^{-3}\)), as seen in the results of OA_homo_165_2h (GR=16 mEq kg\(^{-1}\) with no ester peak) and OA_exch_190_1h (GR=34 mEq kg\(^{-1}\) with an ester peak detected).

The two pressing conditions, 190 °C for 1h or 165 °C for 2 h, did not influence the results, and no significant difference was observed between these two conditions.

Solvent exchange was the key pretreatment that affected the performance of the reaction. Without it, no reaction was significantly observed (based on preliminary experiments; unreported data).

The use of OAn in “OAn_exch” produced the best GR values (266 and 297 mEq kg\(^{-1}\) under the two different pressing conditions), which were tremendously higher than the GR values of 48 and 34 mEq kg\(^{-1}\) obtained with OA under the same conditions (OA_exch). With OA, only the combination of the high-pressure homogenizer and solvent exchange pretreatments permitted a GR value close to those obtained with OAn (GR values of 207 and 241 mEq kg\(^{-1}\) were obtained in the OA_homo_exch experiment).

On the contrary, the high-pressure homogenizer by itself did not make much difference, considering the low GR value obtained in the OA_homo experiment. The emulsion pretreatment was very unsuccessful and produced a low GR value and poor mechanical properties. The adjustment of pH to 2 during the water step of the solvent exchange was beneficial and facilitated a higher GR value (OA_exch_pH), as did the 6-h stirring step with OA in a similar experiment (OA_exch_pH_6); the explanation for this phenomenon would require further investigation, as these conditions were quite different from those of the work reported by Pantze et al. (2007).

Every pretreated powder that was not compression-molded (deemed the “standards”) had a very low GR value, which confirmed that the reaction occurred during the molding step. The use of OAn was the only exception (producing a GR value of 274 mEq kg\(^{-1}\)), which showed that the reaction did not need the molding step to occur and confirmed the much higher reactivity of OAn over OA. The standard samples were stored for about 1 week before analysis in a closed container (at room temperature), which, in the case of the OAn_exch experiment, allowed the reaction to occur.

Mechanical results showed that all experiments on cellulose produced lower bending moduli and strength than the non-grafted standard (Alpha_o). For miscanthus, the mechanical properties of the compressed specimens were comparable between the standards and the Mis_OA_homo results, but lower properties were measured in the Mis_OAn_homo experiment.
IV.2.C Discussion

A satisfactory correlation ($R^2 = 0.92$) was observed between the water drop angle and the GR value for cellulose experiments with a GR value greater than 60 mEq kg$^{-1}$ (i.e., a DS value greater than 0.01), as seen in Figure IV - 5. The extrapolation of the linear regression curve indicated that hydrophobicity (evidenced by an angle $> 90^\circ$) would have been obtained at a GR value of 370 mEq kg$^{-1}$ (DS value of $6 \times 10^{-2}$).

Figure IV - 5: Correlation between GR value and initial water drop angle of recompressed specimens

For comparison, Peydecastaing et al. (2011) performed the esterification of C18 and C2 fatty acids in a reactor with a solvent medium and observed that a DS value of $5 \times 10^{-3}$ (C18 basis) was sufficient to induce hydrophobicity (after 60 s). A difference in chain length, the presence of two types of grafts on the chain, the time of measurements, and the porosity of the recompressed specimens for the water drop experiments are some possible explanations as to the differences observed compared to the results of Peydecastaing et al. (2011). Also, changes in the DP of cellulose after pretreatment and molding would have been an interesting parameter to study for a better understanding of the relationship between macroscopic water properties and the GR value of the specimens.

In the miscanthus experiments, quite low GR values were observed, and the cellulose-miscanthus equivalent experiments produced comparable results (OA_homo: 16 and 13 mEq kg$^{-1}$; Mis_OA_homo: 16 and 24 mEq kg$^{-1}$), which was surprising considering the higher reactivity of lignin and hemicellulose than cellulose (Hon 1995). The other experiment on miscanthus added an OAn suspension step, which did improve the grafting yield significantly (GR values of 32 and 39 mEq kg$^{-1}$), but the reaction also occurred on the standard (non-compressed) specimen just as it did on cellulose. Due to the quite drastic conditions of pressing, the probability of degrading hemicellulose and lignin was high (Takahashi et al. 2010). There was thus a possibility of consuming OA and OAn in the esterification reaction of hemicellulose and lignin before these parts were further degraded, made soluble, and rinsed out during the washing step. The only experiments under the same conditions with cellulose and miscanthus are OA_homo and Mis_OA_homo, which obtained comparable but low GR values. The water-ethanol-OA-OAn solvent exchange (tested on cellulose OAn_exch) was not tested on Miscanthus, thus the comparison between cellulose and miscanthus in terms of reactivity cannot be established. Also an experiment comparable
to Mis_OAn_homo on cellulose would have permitted to impute more certainly to the solvent exchange the majority of the effect on increasing the grafting.

A comparison of the absorption times was made in Figure IV.6, confirming that higher GR values were correlated with a longer absorption time.

![Figure IV.6: Starting material, grafted material, and comparison of the water drop absorption time on recompressed specimens.](image)

However, there was no correlation between the initial drop angle and absorption time (Table IV.2) although these two parameters are supposed to describe the hydrophobicity of the material. In other words, specimens with long absorption times could nevertheless have quite low initial drop angle values associated with low GR values. Thus, it seems that the nature of the reactant actually had a high impact: the four experiments conducted with OAn on cellulose and miscanthus (the red points in Figure IV.6) produced longer absorption times than any other OA experiment.

From extrapolation of the data in Figure IV.6, a limit would appear (infinite absorption time, or hydrophobicity) for GR values around 350 mEq kg\(^{-1}\), which would be consistent with the value obtained upon extrapolation in Figure IV.5 (370 mEq kg\(^{-1}\)). A trend is observable from the same group of data on the mechanical properties with DS values greater than 0.01 displayed in Figure IV.7 (correlation between the bending modulus and the GR value).

Through this correlation, it was concluded that the more the material is grafted, the lower the modulus. A similar trend existed for the bending strength at break (Table IV.2): an explanation for this phenomenon probably lies in the consideration that the side chains grafted on the cellulose backbone prevented the establishment of a strong hydrogen bond network (Pintiaux et al. 2013). Therefore, it was concluded that bulk esterification under high-pressure conditions required a compromise between water properties and mechanical properties. A better approach and a better use of this technique would consist of producing specimens with two layers, a core of pure α-cellulose powder (or other plant material) covered by a layer of pretreated powder compressed together. Such a biocomposite should be capable of high mechanical properties, with a hydrophobic skin to protect it against water.
Conclusions

1. High-pressure compression molding was successfully used to perform the esterification of octanoic acid on commercial α-cellulose powder. However, pretreatment of the powder was necessary to improve its reactivity and obtain a significant grafting yield.

2. The use of octanoic anhydride instead of octanoic acid produced higher grafting yields. A direct prospect of this study would be the combination of the high-pressure homogenizer and solvent exchange pretreatments applied to the reaction with octanoic anhydride, which should provide higher grafting yields.

3. Water properties were measured on ground and recompressed specimens in order to eliminate the possible effect of adsorbed but non-grafted fatty compounds on cellulose. The water resistance should be tested directly on the washed compressed specimens first, then again without the washing step. The good surface effect that would be imparted by the thermo-compressed specimens combined with fatty acids adsorbed onto the α-cellulose powder would probably increase the water resistance. Investigations are also needed in order to explain the low grafting yields obtained with miscanthus.

4. The decrease of the mechanical properties was undoubtedly correlated to the grafting yield, which implied that prospective water-resistant, compression-molded α-cellulose specimens would necessarily have weak mechanical properties. Considering a “sandwich” structure, with a skin of pretreated materials covering a core of non-treated powder, would be a natural continuation of this present work.

5. Further study would be needed to understand the water properties of the specimens. For instance, investigation into the dynamic vapor sorption properties of the materials, the measurements of the degree of polymerization and its influence on the water properties, and establishment of the recovery yield would be interesting. The influence of the thermo-compression parameters would also need to be investigated.
V The processing of native plant materials

One of the primary objectives of this thesis was to evaluate the possibility for compaction molding to produce objects from raw plant materials as opposed to refined materials like cellulose. Following the surprising results obtained on cellulose, many experiments were performed around the understanding of the parameters effect and mechanisms of cohesion. The best properties obtained were a bending strength of 70 MPa and a tensile strength of 31 MPa, associated to moduli of 8 and 2 GPa in bending and tensile respectively.

After these quite high mechanical properties, the burning question was about the influence of the chemical composition and physical properties of the starting materials on the properties of the molded specimens. According to the literature (Chapter I) the presence of lignin, hemicelluloses, proteins and polyphenols in the starting material had a great chance to impact the bonding ability and flowability.

23 different materials were thus collected from different other projects of the laboratory and kindly provided by colleagues. The 23 plant materials were first ground to smaller particles (2 mm screen) because some materials’ particle size would not be compatible with the molds. It also permitted to obtain materials of comparable particle size and not generate too much effect from this parameter. Physical characteristics and chemical composition were measured on the starting plant materials (results available in Table V D 1), and specimens were processed in the same conditions in order to evaluate the properties of the corresponding materials. At first, flow tests were performed, and compaction molding was performed on 50 x 50 mm squares, and finally dog-bone specimens and 45 x 10 mm DMA specimens.

V.1 Physico-chemical analyses of the native plant materials

At first, the physical analyses were run on the 23 plant materials. The apparent (tapped) density, the particle size distribution (in mm, < 0.12, [0.12 – 0.25[, [0.25 – 0.5[, [0.5 – 0.8[, [0.8 – 1[, [1 – 1.25[, [1.25 – 1.6[, [1.6 – 2[, > 2 mm), and the form factor distribution (=1, ]1 – 2[, ]2 – 3[, ]3 – 5[, ]5 – 10[, >10) were analyzed.

The apparent density of two materials (Carded hemp and Cellulose wadding) was very different from the rest of the specimens. Carded hemp already had a density lower than average but the grinding treatment produced an even more fluffy material as well as upon the grinding of cellulose wadding. As a consequence, the particle size analysis of these two specimens was biased because the particles could not be separated one from the others and the form factor distribution could not be measured for the same reason.

Olive kernels flour is an industrial micronized flour which thus had a very marginal particle size distribution. For this reason, the form factor distribution could not be measured because of the small size of the particles.

As far as cellulose is concerned, the form factor distribution could be analyzed for the same reason as Olive kernels flour and the particle size was set to 100% < 0.12 mm because of the SEM pictures of the powder (Chapter III, Figure III D 26).

Secondly, the chemical composition of these plant materials was studied: moisture, ashes, lipids, hemicelluloses, cellulose, lignin, proteins and polyphenols contents were measured. The complete results are available in Table V D 1. Some remarkable elements have been highlighted thereafter:

The ashes content of cellulose wadding was the highest (16%) probably because of the additives and inks used onto paper. High values were also obtained for wheat straws (7 to 10%) probably because of the silica content. The value of the extruded wheat with NaOH was also marked by this treatment and a high value of 11 % was measured.
### Table V - 1: Physicochemical analyses of the native plant materials

<table>
<thead>
<tr>
<th>Moisture content (%)</th>
<th>Ashes content (%)</th>
<th>Tapped density (g/cm³)</th>
<th>Particle size distribution (%)</th>
<th>Form factor distribution %</th>
<th>Lipid content (%)</th>
<th>ADF NDF - Fiber content analysis (%)</th>
<th>Protein content (%)</th>
<th>Total polyphenols (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>Dev.</td>
<td>Mean</td>
<td>Dev.</td>
<td>Mean</td>
<td>Dev.</td>
<td>Mean</td>
<td>Dev.</td>
<td>Mean</td>
</tr>
<tr>
<td>AC</td>
<td>8.01</td>
<td>0.00</td>
<td>0.30</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS2</td>
<td>8.7</td>
<td>0.04</td>
<td>0.16</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS3</td>
<td>8.6</td>
<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WE1</td>
<td>10.12</td>
<td>0.07</td>
<td>0.16</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS2</td>
<td>8.7</td>
<td>0.04</td>
<td>0.16</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS3</td>
<td>8.6</td>
<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WE1</td>
<td>10.12</td>
<td>0.07</td>
<td>0.16</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS2</td>
<td>8.7</td>
<td>0.04</td>
<td>0.16</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS3</td>
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<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
</tr>
<tr>
<td>WE1</td>
<td>10.12</td>
<td>0.07</td>
<td>0.16</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS2</td>
<td>8.7</td>
<td>0.04</td>
<td>0.16</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WS3</td>
<td>8.6</td>
<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WE1</td>
<td>10.12</td>
<td>0.07</td>
<td>0.16</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
The lipid content was somehow binary: Most of the materials had very low lipid content, inferior to 0.5 %. Then, poplar bark and Sunflower seed cake had a value of 2.6 %, Olive kernels flour had a value of 3.5 %, Sugarcane bagasse 4.9 % and the maximum value was reached with Coffee waste (19 %).

The protein content was overall low, except for Sugar beet pulp (7.9 %), Coffee waste (14 %) and Sunflower seed cake (34 %).

V.2 Evaluation of the flowability of the different materials

The idea of trying to improve the flowability of cellulose appeared early in the project, and tests were performed with addition of magnesium stearate in cellulose (2%) which conducted to the destruction of a dog-bone mold. After the experiments in Nagoya, where it was impossible to run flow tests correctly on cellulose (Chapter III part 8), it seemed too much investment (on time and equipment) to try to run true viscosity tests. Nevertheless an empiric scale was desirable (and necessary) to evaluate the flowability and at least obtain a comparison of the different materials between them in order to predict and avoid the damages to the molds. Every 23 plant materials and cellulose were extruded through a (4,10) die at 175°C and 3 bar/s of pressure increase using the transfer molding equipment designed in Toulouse.

The value at which the material started to flow was retrieved from these experiments that were run in triplicates. The experiment was stopped at 140 bar of hydraulic pressure which corresponded to 500 MPa in the compression chamber for minimizing damages on the equipment. Results are presented in Table V - 2, sorted by decreasing flowability.

<table>
<thead>
<tr>
<th>Plant material</th>
<th>Code</th>
<th>Hydraulic pressure at flow mean (bar)</th>
<th>st. dev (bar)</th>
<th>Chamber pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee waste</td>
<td>Cof</td>
<td>26</td>
<td>0.7</td>
<td>94</td>
</tr>
<tr>
<td>Beet pulp</td>
<td>SBP</td>
<td>45</td>
<td>0.7</td>
<td>162</td>
</tr>
<tr>
<td>Sunflower seed cake</td>
<td>SSC</td>
<td>51</td>
<td>14.1</td>
<td>194</td>
</tr>
<tr>
<td>Barley straw</td>
<td>BS</td>
<td>54</td>
<td>5.5</td>
<td>194</td>
</tr>
<tr>
<td>Sweet maize residue</td>
<td>SCR</td>
<td>57</td>
<td>15.7</td>
<td>205</td>
</tr>
<tr>
<td>Extruded wheat straw</td>
<td>WE1</td>
<td>65</td>
<td>0</td>
<td>234</td>
</tr>
<tr>
<td>Poplar bark</td>
<td>Pop</td>
<td>64</td>
<td>0</td>
<td>230</td>
</tr>
<tr>
<td>Wheat straw &lt;0.5 mm</td>
<td>W31</td>
<td>70</td>
<td>3.1</td>
<td>262</td>
</tr>
<tr>
<td>Vine prunings</td>
<td>Vin</td>
<td>72</td>
<td>0.7</td>
<td>259</td>
</tr>
<tr>
<td>Wheat straw 0.5,1 mm</td>
<td>W32</td>
<td>73</td>
<td>0.6</td>
<td>263</td>
</tr>
<tr>
<td>Extruded wheat straw H0 100</td>
<td>WE3</td>
<td>78</td>
<td>4.2</td>
<td>281</td>
</tr>
<tr>
<td>Wheat straw &gt;1 mm</td>
<td>W33</td>
<td>86</td>
<td>3.5</td>
<td>310</td>
</tr>
<tr>
<td>Eucalyptus wood</td>
<td>Euc</td>
<td>86</td>
<td>3.5</td>
<td>317</td>
</tr>
<tr>
<td>Extruded wheat straw H0 70</td>
<td>WE2</td>
<td>90</td>
<td>2.8</td>
<td>324</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>Bca</td>
<td>101</td>
<td>0.7</td>
<td>304</td>
</tr>
<tr>
<td>Chenevotte</td>
<td>Che</td>
<td>105</td>
<td>20.5</td>
<td>378</td>
</tr>
<tr>
<td>Pinenne</td>
<td>Pin</td>
<td>109</td>
<td>1.4</td>
<td>393</td>
</tr>
<tr>
<td>Olive kernels flour</td>
<td>FNO</td>
<td>110</td>
<td>8.7</td>
<td>396</td>
</tr>
<tr>
<td>Agave bagasse</td>
<td>Bag</td>
<td>110</td>
<td>6.1</td>
<td>306</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>Mis</td>
<td>120</td>
<td>n/a</td>
<td>432</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Bee</td>
<td>123</td>
<td>0</td>
<td>443</td>
</tr>
<tr>
<td>Carded hemp</td>
<td>Car</td>
<td>130</td>
<td>6.6</td>
<td>468</td>
</tr>
<tr>
<td>Cellulose wadding</td>
<td>CVWa</td>
<td>no</td>
<td>n/a</td>
<td>no</td>
</tr>
<tr>
<td>o-Cellulose</td>
<td>AC</td>
<td>no</td>
<td>n/a</td>
<td>no</td>
</tr>
</tbody>
</table>

The pressure needed to make the material flow permitted to initiate a ranking of flowability between the different materials, the lower the pressure of extrusion (flow) the higher the flowability. Thus, during the molding of dog-bone specimens, in order to prevent damages to the mold, the materials will be tested by increased flowability order starting with.
the material with the poorest flowability and so on. For the realization of 3D molding, this flowability ranking is of high interest because it indicates what materials will preferentially flow and permit to mold 3D shapes, or can orientate towards mixing a poor flowing material with another easy flowing one. Some tests were performed following this idea and are presented in the perspectives of this work.

α-cellulose and cellulose wadding were the only two that did not flow at all. This confirmed the poor flowability of cellulose and the benefits of other components in increasing the flowability, at least in these conditions of moisture and temperature. The correlation between the cellulose content and extrusion pressure was drawn (Figure V - 1) which shows that a link exist between these two parameters but also that the correlation is not perfect and could be further refined by adding other composition factors. For instance, SBP and SSC are the two matters with the highest NDF extractives value, Euc has the highest lignin content and Car was defibrated which could lower its flowability.

![Figure V - 1: Correlation between cellulose content and extrusion pressure](image)

The extrudates were very much influenced by the material’s origin. Most of them were not continuous, and very fragile. It seems the easy flowing materials had extrudates with better cohesion and continuity. The extrudate continuity was much influenced by the pressurization speed during the flow test. This parameter was unfortunately not further studied.

Nice patterns of orientated fibers following the material’s flow could be observed on materials left in the compression chamber at the end of a test (Figure V - 2). A close look at the extrusion sprue left in the die indicated that the discontinuity observed on the extrudates was initiated right at the beginning of the die when materials was leaving the compression chamber to enter the die. The high shear taking place in this area probably induces the discontinuous extrusion, what could be a subject of further studies.

At the end of these tests, the punch and dies of the equipment were severely damaged and had to be replaced which shows how much work is still needed on the technological part...
V.3  The influence of the volume/surface ratio

V.3.A  50 x 50 mm square molding as a preliminary study

At first, the square mold was used because it is the most versatile tool, which suffers less from blockades than the highly justified and thus fragile dog-bone mold. The 23 materials and cellulose were first tested in the reference conditions for cellulose, i.e. at 175°C and moisture equilibrated to 60% RH. Other parameters were: 200 MPa of molding pressure (maximum), 50 bar/s of pressure increase, 30 seconds of molding time. Three 50 x 50 mm squares were first molded.

Surprisingly, although these conditions produced sound dog-bone specimens, i.e. without cracks or being delaminated, as well as perfect 50 x 50 mm squares for cellulose, the molding of a many other materials led to delamination. Only Poplar bark, Vine prunings, Beech wood, Pinsotte and Agave bagasse produced satisfactory specimens. All the others were more or less delaminated. The molding results were collected in Table V - 3. It was difficult to quantify delamination, even though it was certain that different degree of damages existed, from slight and discrete cracks to the complete opening of the specimen which usually let steam audibly escape from the mold upon releasing pressure: levels of delamination were reported in table V - 2 from very slightly delaminated “cracks”, mildly delaminated samples “delam.”, and highly delaminated samples, that led to the splitting of the specimen, noted “delam. +”.

Following these deceiving results, another condition that was producing sound dog-bone specimens on cellulose (Chapter III) was tested on the 50 x 50 mm square mold: 250°C and equilibrium to 60% RH. Cellulose was successfully molded into squares without delamination. On the other native plant materials, consistent results were obtained compared to the previous condition: a majority of the square specimens were delaminated, and most of the time, the delamination was even worse at 250 than 175°C. Also, extrusion occurred which was noted “extr.” in Table V - 3 when a significant part of the material was lost by extrusion.

Because dog-bone specimens and squares could be produced at 60% RH and 175 and 250°C and because the same conditions applied on native plant materials let to the delamination of most of the samples, it was concluded that native plant materials could not be molded in the same conditions than cellulose and that delamination was also affected by the chemical composition and probably other physical parameters (e.g. particle size).
Table V - 3: Compaction molding results comparing 50 x 50 mm squares and dog-bone shape

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Shape time - pressure</th>
<th>50 x 50 mm</th>
<th>dog-bone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature - RH</td>
<td>30 s - 200 Mpa</td>
<td>30 s - 264 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>175°C - 60%</td>
<td>175°C - 60%</td>
<td>250°C - 0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250°C - 60%</td>
<td>250°C - 0%</td>
<td></td>
</tr>
<tr>
<td>Cellulose wadding</td>
<td>CWa</td>
<td>ok</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Wheat straw &lt;0.5 mm</td>
<td>WS1</td>
<td>delam. +</td>
<td>delam. +</td>
<td>n/a</td>
</tr>
<tr>
<td>Wheat straw [0.6, 1] mm</td>
<td>WS2</td>
<td>delam. +</td>
<td>delam. +</td>
<td>ok but cracks</td>
</tr>
<tr>
<td>Wheat straw &gt; 1 mm</td>
<td>WS3</td>
<td>delam. +</td>
<td>delam. +</td>
<td>ok but cracks</td>
</tr>
<tr>
<td>Extruded wheat straw NaOH</td>
<td>WE1</td>
<td>delam. +</td>
<td>delam. +</td>
<td>ok but cracks</td>
</tr>
<tr>
<td>Extruded wheat straw H2O</td>
<td>WE2</td>
<td>delam. +</td>
<td>delam. +</td>
<td>ok but cracks</td>
</tr>
<tr>
<td>Extruded wheat straw H2O</td>
<td>WE3</td>
<td>delam. +</td>
<td>delam. +</td>
<td>ok but cracks</td>
</tr>
<tr>
<td>Barley straw</td>
<td>BS</td>
<td>delam. +</td>
<td>delam. +</td>
<td>sticking effect</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>Mis</td>
<td>delam. delam.</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Carded hemp</td>
<td>CHa</td>
<td>delam. delam.</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Chenevotte</td>
<td>Che</td>
<td>delam. +</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Sugar beet pulp</td>
<td>SBP</td>
<td>delam. delam.</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Sweet maize residue</td>
<td>SCR</td>
<td>delam. extr.</td>
<td>extr</td>
<td>extr</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>BCa</td>
<td>delam. delam.</td>
<td>delam. ok but cracks</td>
<td></td>
</tr>
<tr>
<td>Agave bagasse</td>
<td>BAg</td>
<td>ok</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Pine</td>
<td>Pin</td>
<td>ok</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Sunflower seed cake</td>
<td>SSC</td>
<td>delam. extr.</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Olive kernels flour</td>
<td>FNO</td>
<td>delam. delam.</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Coffee waste</td>
<td>Cof</td>
<td>delam. extr.</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Bee</td>
<td>ok</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Eucalyptus wood</td>
<td>Euc</td>
<td>delam. delam.</td>
<td>ok</td>
<td>ok</td>
</tr>
<tr>
<td>Vine prunnings</td>
<td>Vin</td>
<td>ok</td>
<td>extr</td>
<td>ok</td>
</tr>
<tr>
<td>Poplar bark</td>
<td>Pop</td>
<td>ok</td>
<td>delam. &amp; extr.</td>
<td>ok</td>
</tr>
</tbody>
</table>

V.3.B Dog-bones specimen molding from the native plant materials

Molding in reference conditions (175°C – 60 % RH equilibrium)

Dog-bones specimens were even produced in the control conditions (175°C equilibrium 60 % RH, 264 MPa of molding pressure, 50 bar/s pressurization and 30 seconds holding time), beginning with the materials which did not experience delamination in the 50 x 50 mm square mold. Then, materials with the lowest delamination damages were tested, which surprisingly produced sound specimens. It was decided to try to mold dog-bone specimens from all materials, from the lowest flowability to the highest and significant differences were observed between results obtained on squares and on dog-bones. The results have been assembled in Table V - 3: many specimens that produced delaminated 50 x 50 mm squares ended-up producing sound dog-bones specimens, showing the important effect of the molded shape, and more precisely, the surface volume ratio, which is much higher in the dog-bone than on the square shape.

Additional troubles were encountered upon the molding of Carded hemp and Cellulose wadding: because having much too low apparent density, the volume of 7.5 g of these two materials was much too high for the mold, and filling had to be done in several steps, required to pre-compress the material between two steps, and ended up having very poor homogeneity (Figure V - 3) and potential danger for the mold as it was not possible to guarantee a sufficient homogeneous filling of the mold in the longitudinal. These two materials were abandoned and noted “n/a” in Table V - 3.

Extrusion burr started to appear on the sides of the molded specimens. The extruded wheat straw with NaOH (WE1) was the first to exhibit significant burr and demolding started to be difficult (Figure V - 4).
Figure V - 3: Heterogeneity upon filling cellulose wadding because of its very low apparent density, the specimen is presented next to the 7.5g of origin material.

Figure V - 4: WE1 sample with significant burr on the side.

Figure V - 5: Barley straw specimens exhibited burr and a surprising sticking effect.

WE1 specimens were successfully molded, but it seems this material had a limit flowability for the molding of dog bone specimens because the next one on the flowability list (Table V - 2) which was sweet maize residue was extruded between the punches and die of the dog-bone mold, after what the experiments had to be stopped. Barley straw was also tested, which also produced burrs on the sides of the specimens, in addition to a surprising
sticking effect: the removal of the punches from the die was difficult and the molded specimen stuck to both punches (Figure V - 5). While demolding some materials remained on the surfaces of the molds and some specimens were damaged upon demolding. Barley straw was the only material with such a behaviour, it was also abandoned (“sticking effect” is noted in the BS line of Table V - 3).

The mold was not too damaged by these experiments, but none of the materials with higher flowability were tested (i.e. coffee waste, sugarbeet pulp and sunflower seed cake were not tested). The reduction of molding pressure would probably have solved the problem of burr / extrusion, but then the comparison between the different samples would be impossible. Compaction molding can be concluded a not suitable technique for molding highly flowing materials and probably transfer molding would be more appropriate.

Inspired by the work of Jallabert with the PVT apparatus, a test was performed by the introduction of perfectly adjusted dog-bone teflon gaskets, which led to the extrusion of the gaskets and the blockage of the mold.

As a summary, the materials with a too low apparent density were discarded (Cellulose wadding and Carded hemp) as well as specimens with too much flowability (Coffee, Sugar beet pulp, Sunflower seed cakes, Sweet maize residues) and Barley straw which produced a sticky effect on the metal of the mold. The remaining plant materials after removal of the later cited ones was defined as the “compaction molding set”. The complete results are presented in Table V - 4. Following the dog-bone specimens production, the materials of the “compaction molding set” were molded into 6 DMA specimens in order to perform the water resistance tests. Consistent results were obtained upon molding DMA specimens compared to dog-bones.

**Molding in alternative conditions (250°C – 0% MC)**

Considering the lack of results under the first condition, another condition was desirable to increase que volume of data for interpretation and also start the investigation of the influence of molding conditions on these materials processed from native plant materials, similarly to what was done with cellulose in Chapter III. Because of the number of specimens to test which was taking a considerable time to process, the other condition had to be chosen carefully. Because of the results obtained on squares at 250°C and equilibrium with 60% RH (Table V - 3), a reduced moisture content was preferrable. A condition giving increased properties to cellulose samples was also of high interest. 250°C and 2% was giving the best results on cellulose samples, but the reduction of moisture to 2% for each plant sample was quite difficult to manage and would have taken much time. On cellulose, a surprising conclusion appeared in the molding of dry material (103°C dried), this condition was thus selected (250°C – 103°C dried) as the second molding condition on the 23 native plant materials. Other parameters were the same than the reference condition. These experiments were performed on the possible-to-mold materials as defined with the first condition, i.e. the “compaction molding set”.

Table V - 4: Properties of compaction-molded specimens from native plant materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Bending Strength 175°C 60% RH (MPa)</th>
<th>Bending Modulus 175°C 60% RH (GPa)</th>
<th>Tensile Strength 175°C 60% RH (MPa)</th>
<th>Tensile Modulus 175°C 60% RH (GPa)</th>
<th>Water Immersion Test 175°C 60% RH WA (%)</th>
<th>TS (%)</th>
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<tr>
<td>AC</td>
<td>34.8 5.9 175°C 60% RH</td>
<td>1.2 0.1 175°C 60% RH</td>
<td>1.2 0.1 175°C 60% RH</td>
<td>1.9 0.1 175°C 60% RH</td>
<td>0.7 0.2 175°C 60% RH</td>
<td>3</td>
</tr>
<tr>
<td>WS1</td>
<td>4.4 0.6 175°C 60% RH</td>
<td>1.8 0.1 175°C 60% RH</td>
<td>0.6 0.1 175°C 60% RH</td>
<td>0.6 0.1 175°C 60% RH</td>
<td>7.5 0.7 175°C 60% RH</td>
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</tr>
<tr>
<td>WS3</td>
<td>6.6 1.0 175°C 60% RH</td>
<td>3.1 0.4 175°C 60% RH</td>
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<td>1.1 0.1 175°C 60% RH</td>
<td>370 41 175°C 60% RH</td>
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<tr>
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<td>WE2</td>
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<td>-</td>
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<th>Mean</th>
<th>St. dev</th>
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<td>0.7</td>
<td>1.2</td>
<td>0.1</td>
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<td>15</td>
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</tbody>
</table>

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The first effect of this alternative condition was a higher number of valid specimens, i.e. not delaminated. In fact, Olive kernels flour, Extruded wheat straw 3 and Sugarcane bagasse, which produced delaminated samples under the first condition, produced sound specimens despite the small cracks on the sides of Sugarcane bagasse specimens. These specimens were tested under the second conditions which was not possible under the first condition. The quantity of information was then increased from the first to the second condition. 6 DMA specimens (water resistance evaluation) for each condition were also molded, and consistent results obtained (Table V - 4).

V.4 Analysis of “compaction molding set” results

V.4.A Summary of results

Missing values

In this part, only the plant materials that gave successful results in compaction molding i.e. which was defined as the “compaction molding set” are considered.

A first look at the mechanical properties results showed that none of the native plant materials was able to produce values close to cellulose which remained way over. Under the two conditions of molding, cellulose specimens had strengths at break in bending and tensile about two folds higher than the best native plant specimens (Eucalyptus). As for the moduli, the gap was much less than two folds but cellulose still had the maximum values.

Under the first molding condition, Extruded wheat straw 3, Sugarcane bagasse and Olive kernels flour produced delaminated specimens which were not tested mechanically.

The consideration of the water resistance values led to consistent conclusions: cellulose had by far the best water resistance under the first molding condition with about twice lower swelling (TS) and water absorption (WA) than the more water resistant specimen from the other plant materials (Poplar bark). The specimens molded under the first condition were overall very sensitive to water, none of them could have been tested mechanically except cellulose and several specimens (WS2, WE2 and Bee) were not tested because they could not be taken out of the frame used for the 24 hours of swelling (Figure V - 6).

Figure V - 6: Example of results of the swelling tests under the first condition
Yet, under the second condition of molding (250°C – 0% MC), the results were overall improved: all the specimens were successfully produced and none of them was delaminated. It was thus possible to perform mechanical tests and obtain values in the whole “compaction-molding set” without any missing values. The mechanical properties were overall improved under the second molding condition but not as much as the water resistance which was drastically increased: no specimens returned to its original powder shape like it did for some specimens under the first condition (Figure V·6).

The complete results are presented in Table V·4 for the mechanical and water properties, and the physicochemical analysis in Table V·1.

Inspection of variable ranges

A summary of the results is presented in Table V·5, Table V·6 and Table V·7 which also present the coding of the variables that was used on the graphs and tables for the statistical analysis part.

Table V·5: Summary of results for the chemical composition of the “compaction molding set” plant materials

<table>
<thead>
<tr>
<th>Plant material composition</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Median</th>
<th>Unit</th>
<th>Code</th>
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<td>Moisture content</td>
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<td>4.48</td>
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<td>Lipid content</td>
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<td>0.34</td>
<td>%</td>
<td>Lip</td>
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<td>Cellulose content</td>
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<td>96</td>
<td>50.1</td>
<td>45.7</td>
<td>%</td>
<td>Cell</td>
</tr>
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<td>Lign</td>
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<td>Pphe</td>
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Table V·6: Summary of results for the physical characteristics of the “compaction molding set” plant materials

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<td>Tapped density</td>
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<td>g/cm³</td>
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<td>%</td>
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<td>%</td>
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<td>%</td>
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<td>45.8</td>
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Table V - 7: Summary of results for the molded specimens properties of the “compaction molding set”

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<td>2458</td>
<td>GPa</td>
<td>DM_1</td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
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<td>17.2</td>
<td>5.24</td>
<td>3.99</td>
<td>MPa</td>
<td>TS_1</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>616</td>
<td>1880</td>
<td>1220</td>
<td>1171</td>
<td>GPa</td>
<td>TM_1</td>
<td></td>
</tr>
<tr>
<td>Water absorption</td>
<td>74.8</td>
<td>391</td>
<td>273</td>
<td>275</td>
<td>%</td>
<td>WA_1</td>
<td></td>
</tr>
<tr>
<td>Thickness swelling</td>
<td>96.5</td>
<td>420</td>
<td>272</td>
<td>288</td>
<td>%</td>
<td>SWE_1</td>
<td></td>
</tr>
<tr>
<td>Bending strength</td>
<td>7.48</td>
<td>51.7</td>
<td>16.4</td>
<td>14.3</td>
<td>MPa</td>
<td>BS_2</td>
<td></td>
</tr>
<tr>
<td>Bending modulus</td>
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<tr>
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<td>8.00</td>
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<td>MPa</td>
<td>TM_2</td>
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<tr>
<td>Young’s modulus</td>
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<td>2000</td>
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<td>1318</td>
<td>GPa</td>
<td>TM_2</td>
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</tr>
<tr>
<td>Water absorption</td>
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<td>153</td>
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<td>%</td>
<td>WA_2</td>
<td></td>
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<tr>
<td>Thickness swelling</td>
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<td>160</td>
<td>179</td>
<td>%</td>
<td>SWE_2</td>
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</table>

The restriction to the “compaction molding set” led to the reduction of the diversity in the chemical composition especially for the lipids and protein contents that were in narrow ranges (0 – 4.89 % and 0 – 3.62 % respectively). These parameters that have a low variability are probably to consider with care in the analysis, because enlarging the range could led to drastic changes on the conclusions. The mean and median values for the chemical composition appearing in Table V - 5 provides the portrait of the typical “compaction-moldable” materials, with high cellulose content, low extractives ashes protein and polyphenol contents.

When looking at the summary of physical characteristics results (Table V - 6), some variables also appear very centered, for instance the particles with size over 1.6 mm are very rare (max value for P>2 and P1.6 are 0.88% and 1.9% respectively), which is consistent with the values on F>10 (=0.45%). Such particles are not well represented, thus the analysis should not consider these results with too much weight.

As far as the compacted specimens are concerned (Table V - 7), the first observation was the quite low values observed for the mechanical properties and quite high WA and TS on the native plant materials compared to cellulose. The median was also systematically lower than the mean for mechanical properties and higher for water resistance which means a disbalance within the specimens. All the maximum values of the mechanical properties and minimum values for the water resistance belonged to the cellulose samples. Considering that the conditions defined here are based on cellulose study (Chapter III), this result is not so surprising. The second condition, however appears to significantly improves all the specimens properties as it did for cellulose.

V.4.B Statistical analysis

The main objective of this chapter was to establish links between the characteristics of plant materials and the parameters of the resulting compaction molding parameters. Due to the number of variables, statistical analysis (linear cross correlation and PCA, see Materials and Methods VI.3.D) was used in order to summarize the information.

First considering the whole “compaction molding set”, the cross correlation table was established between the starting plant material’s variables (columns) in one hand and the compressed specimen properties (lines) in the other hand (Table V - 8). The figures in the table indicates the correlation between the variables, values close to -1 means a negative correlation (and +1, positive), values close to 0 means the independency of the two variables.
A color scale was used in order to graphically observe the significant correlations either positive (red) or negative (blue).

Table V - 8: Cross correlation table “compaction molding set”

<table>
<thead>
<tr>
<th></th>
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<td>0.35</td>
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<td>0.59</td>
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<td>0.27</td>
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<td>0.98</td>
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<td></td>
</tr>
<tr>
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<td>-0.29</td>
<td>0.31</td>
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<td>0.47</td>
<td>0.90</td>
<td>0.70</td>
<td>0.66</td>
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<td>0.22</td>
<td>0.17</td>
<td>0.30</td>
<td>0.04</td>
<td>0.20</td>
<td>0.28</td>
<td>0.91</td>
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<td>0.55</td>
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<td></td>
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<tr>
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<td>0.11</td>
<td>0.11</td>
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<td>0.30</td>
<td>0.10</td>
<td>0.92</td>
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<tr>
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<td>0.05</td>
<td>0.65</td>
<td>0.52</td>
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<td>0.44</td>
<td>0.12</td>
<td>0.13</td>
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<td>0.10</td>
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<td>0.04</td>
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<td>0.00</td>
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<td>0.16</td>
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<td>0.07</td>
<td>0.09</td>
<td>0.07</td>
<td>0.90</td>
<td>0.81</td>
<td>0.32</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
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</tr>
<tr>
<td>BS_2</td>
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<td>0.43</td>
<td>0.07</td>
<td>-0.23</td>
<td>-0.39</td>
<td>-0.22</td>
<td>-0.35</td>
<td>0.31</td>
<td>0.39</td>
<td>0.50</td>
<td>0.52</td>
<td>0.62</td>
<td>0.32</td>
<td>0.31</td>
<td>0.14</td>
<td>-0.15</td>
<td>0.00</td>
<td>0.09</td>
<td>0.69</td>
<td>-0.42</td>
<td>0.56</td>
<td>-0.51</td>
<td>-0.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BM_2</td>
<td>0.27</td>
<td>0.43</td>
<td>0.03</td>
<td>0.13</td>
<td>0.01</td>
<td>0.06</td>
<td>0.18</td>
<td>0.05</td>
<td>0.20</td>
<td>0.50</td>
<td>0.72</td>
<td>0.51</td>
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<td>-0.64</td>
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<td>-0.25</td>
<td>-0.44</td>
<td>0.02</td>
<td>0.94</td>
<td>-0.85</td>
<td>0.60</td>
<td>-0.81</td>
<td>-0.23</td>
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<tr>
<td>TS_2</td>
<td>0.18</td>
<td>0.33</td>
<td>0.25</td>
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<td>0.30</td>
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<td>-0.11</td>
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<td>0.43</td>
<td>-0.61</td>
<td>-0.38</td>
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<td></td>
</tr>
<tr>
<td>WA_2</td>
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<td>0.73</td>
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<td>0.20</td>
<td>0.63</td>
<td>0.49</td>
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<td>0.40</td>
<td>0.26</td>
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<td>0.07</td>
<td>0.03</td>
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<td>0.95</td>
<td>0.55</td>
<td>-0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YVE_2</td>
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<td>-0.24</td>
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<td>0.77</td>
<td>0.82</td>
<td>-0.18</td>
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<td></td>
</tr>
</tbody>
</table>

This first analysis showed that some parameters were remarkably correlated: the 8 mechanical properties appeared correlated positively with the cellulose content, in the same time water properties were negatively correlated. The particle size < 0.12 followed a similar trend, and on the opposite, the other particle sizes parameters, the hemicelluloses content, the NDF extractives content, protein content and ashes content were correlated positively with the water properties and negatively with the mechanical properties. These parameters are precisely those for which cellulose has the min / max values of the set, far from the average, i.e. the highest mechanical properties and cellulose content by far, the highest proportion of particles < 0.12, the lowest WA, TS, the lowest proportion of the other particle sizes, lowest hemicelluloses, NDF extractives, protein, and ashes contents (Table V - 1). The values of the cellulose sample are too different from the rest of the materials and also have properties that are much better than the plant materials, which influences a lot the correlation.

When performing the PCA analysis of this set of experiments, the first principal component had 41% of the explained value, which went down to 16% for PC2. 9 principle components would have been needed to explain 95% of the variance, which is a lot compared to the number of variables and the last PCs contained a very low proportion of the information.

The analysis was performed on the 2 first principal components (PC1 and PC2, 57% of the variance: Figure V - 7) and results were not much different from the cross correlation table: there is a first group on that has high correlation loading along the PC1 which includes the 8 mechanical properties (BM, BS, TM, TS for the 2 molding conditions), Cell (cellulose content), P<0.12 (% of particle < 0.12 mm) and F1 (% of spherical particles). AC has a very high score on PC1 and is the only one in this case which confirms the particular behaviour of this material.
On the opposite on the PC1 axe, WA_1 and SWE_1 form a group with hemi, P0.12, P0.25, P0.5, P0.8, P1 (part of particles size between 0.12 and 1 mm), and F2-3, F3-5, F5-10, F>10 (part of particles with form factor between 2 and 10 and over). No specimens presented low scores on the PC1 axe, so this group is likely to be much influenced by the cellulose results which had the lowest values in this group within the whole set of samples. With high scores on PC1 and PC2, another group is formed by SWE_2, WA_2 and Prot (protein content), Ash (Ashes content) and NDF (NDF extractives) but no specimens was related to this group. On the opposite of the PC1/PC2 diagonal is the specimen FNO which had particularly low values on these variables.

On the score plot, cellulose appeared circled which meant it is considered as an outlier for this set of experiments and except cellulose, none of the other materials had significant scores to join one or the other group of variable. Cellulose was seen to influence too much the results which led to biased conclusions of this PCA about the influence of the chemical composition / physical parameters of the native plant materials; thus the analysis was run again without the cellulose sample in the calculation (Figure V - 8).

It can be observed on PCA2 that upon the removal of cellulose, the variables are much more separated, with an appreciable amount of variable being significant (outer ellipse). The 2 first PCs contained 52 % of the variance which is again low. Again, many PCs were necessary to explain 90% of the variance and PC3 and next had a very low proportion of the variance explained; the analysis was thus made on PC1/PC2 only. FNO was detected as an outlier which can be explained by its very particular particle size and missing results on form factor.
Results were analyzed whatsoever: there are variables forming two groups on the PC1 axe, and specimens are disposed along the PC1 axe which is a good conformation for the analysis of the results. At the positive correlation loadings on PC1, a first group is formed by the bending moduli BM_1 and BM_2, the tensile modulus TM_1, the tensile strength TS_1 and the lignin and cellulose contents (Lig, Cell). On a lower extent, along to the PC1 axe but inside the first ellipse (50% variance), a group is formed by the rest of the mechanical properties BS_1, TM_2, BS_2 TS_2 (and P 1.25). On the opposite (on PC1), another group is formed with WA_2, SWE_2, and Ash, NDF, Prot, P0.12, F>10 and hemi. The conclusion is that plant materials with high cellulose content (even without the cellulose samples in the calculation), high lignin content, low ashes, NDF, proteins, hemicelluloses contents will produce compressed materials with the highest mechanical properties and best water resistance (under the second molding condition). Eucalyptus wood, Miscanthus and Chenevotte are examples of plants fitting these requirements and which produced specimens with improved properties. Wheat straw, Sugarcane bagasse are examples of plants which had the wrong characteristics, and thus produced compressed materials with lower properties.

The water properties under the first condition (i.e. SWE_1 and WA_1) were highly correlated with the PC2 axe, forming a group together with P0.5, P0.8, P1, and opposed to F1-2, P<0.12Pphe (polyphenols content). Lipids content, apparent density, P<0.12. This opposition on PC2 tend to show a correlation between water resistance under the first condition and a high lipids and polyphenols content, a high proportion of the smallest (and spherical) particles (P<0.12, F1, F1-2) and a higher apparent density. On the PC2, FNO had
particularly low scores and precisely had the best water properties SWE_1 and WA_1 and high values of lipid and polyphenols contents, smaller particles etc. As FNO is considered an outlier in this PCA, and that few specimens had particularly high or low scores on PC2, this result is to consider with a lot of precaution.

Table V.9: Cross correlation table “compaction molding set” except cellulose

<table>
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<tr>
<th></th>
<th>Moist</th>
<th>Ash</th>
<th>deng</th>
<th>P+2</th>
<th>P1.6</th>
<th>P2.5</th>
<th>P1.8</th>
<th>P0.5</th>
<th>P2.5</th>
<th>P15.12</th>
<th>P0-2.1</th>
<th>F1-2</th>
<th>F2-3</th>
<th>F3-5</th>
<th>F5-15</th>
<th>P10</th>
<th>Lip</th>
<th>Cell</th>
<th>hems</th>
<th>Lig</th>
<th>NDF</th>
<th>Prot</th>
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<tbody>
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<td>0.1</td>
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<td>-0.4</td>
<td>-0.2</td>
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<tr>
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<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>0.3</td>
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<tr>
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<td>0.1</td>
<td>0.4</td>
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<tr>
<td>SW_1</td>
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</tbody>
</table>

The cross correlation analysis was run again without the cellulose sample in order to visualize and confirm some of the results from PCA2 (Table V.9): compared to the previous cross correlation table (Table V.8), much more values are close to zero (and coloured in white) which means no linear correlation between the two variables in the table. Some results in accordance with previous results can yet be retrieved, for instance, a significant correlation exists between the water resistance under the second molding condition (WA_2 and SWE_2) and the apparent density, high particle sizes, lipids, cellulose, lignin and polyphenols contents and negatively with the ashes, NDF extractives, protein and hemicelluloses contents. The particular behaviour of the water resistance under condition 1 is also marked with a negative correlation with the apparent density, proportion of smallest particles and lipids content. Finally, the mechanical properties consistently appeared correlated to the cellulose and lignin content, and negatively with protein hemicelluloses and protein contents.

Considering the very low part of variance explained by the PCA plots, these results have to be carefully considered: there is a lot of variance which is not explained by the statistical tests and for which no explanation was found. This variance could be either a mis-evaluation of the true properties of the compressed samples (reliability and regularity of the molding process, especially the mold-filling step), experimental error during the evaluation of these properties (measurements during the water resistance tests for instance), experimental error during the measurements of the plant material chemical composition and properties (sampling, analytical methods not always perfectly adapted, limited repetitions) or noise generated by other parameters that were not taken into account. All these reasons probably participate together in lowering the reliability of these analyses which can be considered as first steps toward the explanation of the correlation between the plant materials properties and the performances of the resulting compressed specimens.
V.5 Transfer molding or compaction molding: The perspectives of a promising processing route?

V.5.A The limitations of compaction molding

The conclusions drawn upon the analysis of the performances of materials molded from the different biomass in the last part are also specific to the 2 molding conditions that were tested. It is probable that the composition and physical properties of the starting material also influences the reaction of the material to variations of the molding conditions (pressure, temperature, moisture, time). Probably a huge experimental design would be needed in order to satisfactorily analyze the link between the plant material’s parameters, the operating conditions and the resulting performances of the compressed specimen. A supermodel could be created to make all these variables interact in order to deliver the desired plant properties and processing conditions to achieve the best possible material, or match certain industrial specifications, or predict the potential applications of any kind of plant materials based on its physic-chemical properties. That was an idea of this thesis at the beginning but the objectives had to be trimmed down.

The main reasons behind the complexity of this work are related to the technological limits of compaction molding:

- the achievement of the equal distribution of material in the mold remained random due to manual operations
- low density material would require pre-compression to avoid an over-sizing of the molds
- delamination is always a limit that is to be considered carefully when working on the effect of temperature and moisture
- last but not least, as soon as one plant material exhibits significant flowability (which should be desirable for molding), extrusion occurs which either blocks the molds or destroys it.

Compaction molding can be then considered a fragile technique, dependent on many parameters that bring limitations. A lot of conditions (plant’s or processing conditions) can lead to a lack of values because specimens cannot be molded or tested which is highly problematic for the construction of a model.

One potential alternative is the use of transfer molding which should allow to mold a higher diversity of materials (with higher flowability), would solve the problem of homogeneous filling, thus improving reproducibility and measurements reliability and could possibly partly solve the problem of delamination. Of course more parameters would be entering the model, with the effect of shear being another constraint that would complicate a bit the experiments, but also bring new possibilities.

Most of all, the difference of properties between specimens processed by compaction molding and transfer molding should be carefully compared, which could lead to materials being more suitable for compaction, and others more suitable for transfer. With this comparison in mind, a prototype was designed (materials and methods, Figure VI · 12 and Figure VI · 13) during this thesis in order to mold tensile and bending tests specimens using the technique of transfer molding. Due to technical troubles, only a few experiments could be run (WS1, 2 and 3).

V.5.B Exploratory results on the mechanical properties evaluation of extruded materials

Principle
The idea here was to use the transfer molding apparatus to produce dog-bones specimen and bending specimens. Due to the size of the apparatus, only the 5B dog-bone described in EN ISO 527-2 was suitable. This transfer molding module was designed with aim to produce at the same time (i.e. in one press cycle) 2 bending tests specimens of 34.5 x 5 mm and 2 tensile tests specimens of matching ISO 527-2 (see Materials and Methods Figure VI - 12).

![Figure V - 9: WS1 injected in the mechanical properties specimens' module](image)

![Figure V - 10: Demolding of the transferred specimens using an aluminum punch](image)

The procedure is the same as for flowability evaluation, plant materials is precompressed, loaded in the chamber and the cycle is run from 0 to 140 bar with a 3bar/s increase of pressure. One some point, the pressure brutally drops a few bars, and comes back to normal, i.e. the material has been injected. The pressure is let to increase to the max in order to apply the same final force on material’s which would have different flowability (thus different values of injection pressure). The apparatus is put apart and the material is molded (Figure V - 9). A tool was machined in order to remove the specimen from the module which is performed by pushing gently the module on the tool which pushes the specimen out of the die (Figure V - 10). The molded specimens are retrieved with the transfer sprue still on, they exhibited a smooth and shiny surface, the molded shape is very precise does not look like the
original material (Figure V.11). Each experiment was run in triplicate in order to obtain 6 specimens for the tensile and bending tests. They can be separated one from the others using a cutting wrench, and after 2 weeks of equilibrium at 60% RH and 25°C, the mechanical tests were performed.

![Demolded specimen, burr has been partially removed](image)

**Figure V.11:** Demolded specimen, burr has been partially removed

**Results**

The results are presented in Table V.10: the first element is that delamination which was occurring during compaction-molding of WS1 did not occur in transfer molding. The high shear during transfer test probably explains a better homogeneity and water diffusion thorough the material in transfer although in compaction, it was shown that water was accumulated and imprisoned in the core layer of the material.

| Table V.10: Mechanical properties of transfer molded wheat straw specimens compared to compaction-molded |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Transfer molding | Compaction molding |
| Tensile test (20.5mm) | Bending test (22 mm) | Tensile test (60 mm) | Bending test (80 mm) |
| | | | | | | | | | | | |
| Modulus (GPa) | Strength (MPa) | Modulus (GPa) | Strength (MPa) | Modulus (GPa) | Strength (MPa) | Modulus (GPa) | Strength (MPa) |
| Mean | St. dev | Mean | St. dev | Mean | St. dev | Mean | St. dev |
| WS1 | 0.24 | 0.62 | 4.4 | 1.0 | 2.1 | 0.1 | 12.0 | 1.0 |
| WS2 | 0.28 | 0.03 | 3.5 | 0.9 | 1.9 | 0.5 | 11.9 | 3.4 |
| WS3 | 0.28 | 0.01 | 6.8 | 1.1 | 2.0 | 0.2 | 11.0 | 1.0 |

The strengths at break in bending and tensile were approximately doubled comparing transfer to compaction. The bending moduli were comparable but the tensile moduli were drastically reduced in transfer compared to compaction molding. The orientation of the fibers was not observable on the transferred specimens although it was obviously on the compacted ones. But, due to the design of the apparatus, flow occurs in the direction of the specimens which should orientate the fibers about the same way than in compaction. The destructuration of the fibers due to high shear in transfer molding may be part of the explanation. However, these results have to be considered with care because of the difference
of sizes between the specimens used in transfer / compaction, especially in tensile for which the results on 1A and 5B dog-bones cannot be compared directly.

In compaction, WS3 had higher properties than WS2 which was also the case in transfer molding. In transfer WS1 had higher properties (in tensile) than WS2 which again should be considered with care due to the low number of replicates and considering that the apparatus was in testing phase. An hypothesis can anyway be formulated to explain the better properties obtained for WS3: the higher shear undergone by particles of higher size when going through the die in transfer could lead to more destructuration and matrix effect as reported in the literature (Chapter I).

Even though the mechanical properties were increased by the use of transfer, they remained low compared to what was observed on cellulose in compaction molding. A direct perspective of this work would be to continue in this direction and perform the same analysis of the links between the results of the transfer molded materials and the composition of the plant materials they are made of.

Conclusions

1. Compaction molding is not suitable for producing specimens from materials that would express too much flowability. A too low apparent density also made it impossible to mold the specimens. This conducted a major reduction of the number of plant materials successfully processed, which a consequence on the diversity in the plant characteristics which was reduced, reducing the significance of the analysis.

2. Many troubles were encountered with delamination, which was already the case with cellulose in Chapter III. The surface/volume parameter was revealed to impact the delamination. The design of the experiments was to process a high number of specimens in the reference conditions determined for cellulose. The main parameters of this study were based on results from Chapter III. None of the specimens reached half of the mechanical strengths obtained on cellulose, which remained by far the best specimen. Probably the molding parameters that were optimized on cellulose were not optimal for the other plant materials, and the study of the impact of the parameters should be done on some typical materials which could probably lead to much better properties (like reported in the literature).

3. The properties of the cellulose samples were so high that the analyses were distorted. The analyses were run again without the cellulose sample which permitted to obtain some interesting conclusions: The cellulose and lignin contents were the two variables that significantly influenced the mechanical properties positively. On the opposite, the protein, ashes, NDF extractives, hemicellulose contents and the fine particles were negatively correlated with the mechanical properties. The water properties were also well correlated to the mechanical properties.

4. These results provide the portrait of the materials that would provide the best possible properties in compaction/molding under these conditions. But, these results are probably very impacted by the molding conditions that were optimized on cellulose, thus, the fact that high cellulose content was desirable for better mechanical properties was actually quite obvious. The impact study of the operating conditions should thus be performed on the raw plant materials, which would require a lot of work due to the immense number of experiments needed. Experimental designs could be used, but as they rely on models, missing values (extrusion, delamination or other incapacity to mold) can seriously hinder the reliability of the analyses.
5. The technological part also had a high impact on the results, due to the experimental conditions, some specimens were not molded, which reduced the field of investigation. It is highly probable that with a better control on the technological part, the results could have been different. Much work is needed on reducing the results’ dependency on the technology.

6. Transfer molding was considered a potential alternative to avoid the technological difficulties encountered with compaction molding. The objective of this chapter was to evaluate the difference between compaction and transfer on the properties of the molded specimens, and find the correlation to the plant compositions in both cases. This objective was not completed again because of technological failures.
General conclusion

In the context of worldwide plastic pollution and fossil resources depletion, this thesis provides an exploratory work towards the evaluation of a one-step thermo-compressive process for the production of bio-based (and hopefully biodegradable and eco-compatible) objects from lignocellulosic materials without pretreatment nor binders. It is included in a longer ANR (French National Research Agency) project of the laboratory (HYPMOBB) which purpose is to investigate thermo-compressive molding of renewable resources for producing agromaterials. The project has been organized in two workpackages, a first one dedicated to the study of the pressure-volume-temperature relationships and the associated microstructural changes of model carbohydrates, and a second one dedicated to the technical application, and study of the properties of the processed materials. The first workpackage was completed during a first thesis defended by Bastien Jallabert at the end of 2014. The second workpackage which comprised a lot more technological investigations was completed through the present thesis work: a CIFRE thesis with the young company The Green Factory, partially supported by the ANRT (French National Agency for promoting Research and Technology). Although during the first workpackage different model polymer were studied (i.e. cellulose, native starch, gelatinized starch) the present work focused on lignocellulosic materials and took cellulose as a model polymer.

At first the available literature in the field of self-bonded lignocellulosic materials was closely examined. The majority of the reports concerned the molding of lignocellulosic materials (crop residues and wood) into binderless boards, i.e. at low pressure (a few MPa) for a long time (5 to 20 minutes). The optimal conditions were collected and temperature was already considered the most important parameter. The problem of delamination was also a concern in binderless particle boards pressing. One of the major differences between the available literature and the present thesis was the molding pressure which was a hundred times higher. The difference of pressure control was also major, as boards pressing has thickness (and thus density) control and pressing pressure adjusted to match the requirements of thickness in the case of boards. During this thesis, the pressing machine was pressure controlled and density could not be adjusted, it was a consequence of operating conditions. A tight link was actually reported between density and the mechanical properties of binderless boards.

Much data were available with pretreatments involving steam. The chemical changes occurring during these pretreatments were examined and compared to those reported to occur during hot-pressing and many common elements were found. Additional data from other fields of research were collected (wood welding, polymer science) in order to gather the knowledge about the mechanisms of cohesion of self-bonded materials. It appeared that the majority of the reports did not concern much about the mechanisms of cohesion. Some elements were still available which permitted to formulate hypotheses of two different mechanisms: a “thermoplastic mechanism” which would take place bellow 200°C, and which would rely on crossing the Tg of the lignocellulosic polymers in order to produce sufficient deformability of the polymers and provide a matrix effect. Above 200°C, another mechanism would start and it was called “thermoset mechanism”. This second mechanism would rely on heavier degradation of polymers, autohydrolysis and the formation of reactive compounds and new complexes.

Naturally, these two mechanisms were addressed to polymers which exhibited a true Tg, lignin and hemicelluloses mostly, and proteins, starch secondly. However, some reports were available about the molding of pure cellulose, and it was decided to start the experimental work of the present thesis by this model polymer.

The properties of compacted cellulose were surprising, and a method was designed to mold dog-bone specimens for measuring properly the mechanical properties in tensile and
bending, and the influence of the parameters was investigated. Some parameters with low influence were concluded to be secondary: the molding time, and the pressurization speed. The most important parameter was temperature, which was consistent with the literature. A minimum of moisture was observed to be necessary for the self-bonding, which made it an important parameter. The temperature/moisture couple was then identified as a priority for the study of the delamination phenomena and the research of improved mechanical properties. The reduction of moisture and increase of temperature were successful in avoiding delamination and increasing the mechanical properties which reached 31 and 70 MPa of stress at break in tensile and bending, with moduli values of 2 and 8 GPa, in tensile and bending, for 2% moisture and 250°C.

Thanks to the data produced in this thesis and within the whole project HYPMOBB, a discussion was proposed about the structure/property relationship of the compacted cellulose materials. Hypotheses are made about the effect of uniaxial high-pressure thermocompression on cellulose and the mechanical properties of the compacted specimens: Most of the strength of the material comes from the skin, and most of all from the Tg of cellulose in the conditions of molding, i.e. in regard to the moisture of the sample and molding temperature. The higher above the Tg, the higher the deformability and possibilities for the hydrogen bonding network to be established. In this model, pressure acts as a catalyst and provides a deconstructing effect, breaking the fibers' original structure and with an effect on the amorphization of cellulose. Temperature and moisture are responsible for the self-bonding effect and the mechanical properties obtained through hydrogen bonding and possibly co-crystallization at different particles interface.

Yet, the role of water is contradictory, a minimum of moisture is necessary in order to lower the Tg of cellulose, but free water also seemed to accumulate in the inner layers of the material, hindering the establishment of fiber-fiber hydrogen bonding, and building up steam pressure, which in case provoked the delamination of the samples.

Some additional data were collected to complete the evaluation of the compacted cellulose materials, ageing tests were performed for 2 months without modification of the mechanical properties after 10 days, the water resistance properties were measured and the sensitivity of the material to moisture and water was confirmed.

Experiments were thus run in order to investigate the possibility of adding fatty compounds to cellulose prior to molding which would provide a hydrophobating effect. After a quick mapping of the potential usable fatty compounds, a deeper study was run on the grafting of octanoic acid (using the acid and the anhydride) on cellulose during the molding process. Pretreatments (high pressure homogenizer and solvent exchange) were necessary to improve the contact between the grafts and cellulose, and the grafting was finally confirmed by CPG analysis. Degree of substitution of $4.8 \times 10^{-2}$ and $3.9 \times 10^{-2}$ were obtained under the best conditions with respectively the anhydride and the fatty acid. The grafted cellulose powder exhibited a more hydrophobic character which hopefully could widen the application field for this kind of materials.

A good correlation was obtained between the grafting yield and the decrease of the mechanical properties. An hypothesis for this was that the grafting of side chains on the cellulose backbone provoked distortions in the establishment of a hydrogen bonding network, which consequently lowered the mechanical properties.

Based on the cellulose results, a panel of raw lignocellulosic materials (crop residues and by products of crop agroprocessing) were processed into test specimens and the influence of the plant composition and physical properties (particle size, form factor, apparent density) on the mechanical properties and water resistance was investigated using cross correlation and principle component analyses. In addition, flow tests were conducted in order to start the investigation about the rheological behavior of the raw plant materials. The equipment used in this thesis that were validated for cellulose molding showed limits in processing raw plant materials: too much flowability conducted to extrusion of materials between the punches and die, which conducted to the blockage of the mold. Materials with a too low apparent density
were also not possible to mold because of impossible charging and heterogeneity. About 1/3 of the desired plant materials were discarded which drastically reduced the diversity of compositions and physical properties. Besides, none of the specimen was able to exhibit mechanical properties close to what was obtained on cellulose.

Nevertheless, the statistical analysis was computed on the moldable materials, and the significance was not very high i.e. a lot of variance was not explained. Some correlations were detected between cellulose and lignin contents, water resistance and mechanical properties positively, and extractives, ashes, proteins and hemicelluloses negatively. This draws the profile of the desirable plant materials candidate for obtaining improved results in compaction molding.

In order to cover the limits of compaction molding, an alternative process was proposed based on the flow test apparatus: transfer molding. Some 3D parts were successfully produced, and a tool was designed in order to mold tensile and bending specimen but unfortunately too much technical troubles arose and these experiments could only be started.

Technological mastery was confirmed to be a key point all along this work. Despite all the trials, which led to significant improvements on the molding equipment, a lot of work would still be required: on a scientific point of view because the technique should not impact the results as it did in this work, on an industrial point of view, because major improvement are required before considering industrial applications.

The major part of this thesis was dedicated to cellulose, which provided mind-blowing results and conducted to significant scientific research and discussions on the mechanisms of cohesion at stake during compaction under high temperature.

In a second time, it was highly desirable to study the influence of the chemical composition of the plant materials and other physical properties on the molded specimens. The choice about the molding parameters was made when it came to switching from the cellulose to the native plant materials and it naturally was based on cellulose results. These conditions, as well as the technological limits majorly influenced the conclusion which provided mixed results.

3D molding were performed in the early stages of this work, flowability was rapidly noticed to influence the possibility of molding, and mixing plants with high flowability (like sunflower seed cake) with low flowability plants (like miscanthus or wheat straw for instance) improved the results. The use of coffee waste in small proportion was observed to provide a desirable lubricant effect. The improvement of the overall flowability was also made with temperature, which was concluded to majorly influence the molding results and strength of the 3D specimens. Unfortunately, steam delamination came in, and was observed to be a result of material composition and molding parameters. The concomitant influence of all these parameters is at the heart of the problematic of this whole project, which could occupy the work of a whole thesis. Hopefully, this thesis work provides a strong basis for the future developments of these innovative molding technique and materials.

Prospects

Despite the high volume of data generated during this thesis, a lot of grey zones still remained, which on investigations would make an obvious continuum to this thesis work. The prospects can be sorted in 3 ordered levels: at first, (1) technological improvements can be made for the high-pressure molding process to become more reliable and versatile, which will permit to improve the (2) quality of the scientific data and increase the knowledge about the physico-chemical phenomena involved in the consolidation process. Technological
mastery and knowledge about the material could then be used towards (3) the improvement of the material properties, aiming at an industrialization.

**Technical prospects needed to improve the process of uniaxial high-pressure thermocompression molding:**

* Much troubles were encountered because of heterogeneity in the samples while charging the material in the mold (Figure II · 9). Most of the scattering probably came from this manual step that was highly operator dependent and not very reproducible. The possibility of performing reproducible and reliable homogeneity of the specimens would be a major improvement of the technique. In the field of board processing, automatic processes exist that spread the material evenly in the frame / mold. This problem of homogeneous filling was also encountered some time ago in the processing of pharmaceutical tablets: automatic feed hopper were used for even repartition, but then the flowing properties of the powder was problematic, partially solved with the employment of lubricants like stearate magnesium, or by precompacting the excipient to pellets which increased drastically the hopper flow but caused additional troubles in tablets cohesion.

* There could be a possibility of precompressing the material before entering the mold (especially useful for the low density materials like Carded hemp or Celullose wadding).

* The extrusion occurring between the punches and dies of the molds was a serious limit to the technique. Reducing the mechanical slack in order to prevent extrusion conducted to another limit: the seizing of the molds (Figure II · 22). Some work was made on the mechanical slack needed and different alloys tested, the employment of gaskets was tested but none of these investigations allowed to mold materials with high flowability (Chapter II).

* Delamination was another important limit of the technique, which was partially solved upon moisture reduction (Table III · 7). Yet, the density patterns acquired in X-ray tomography (e.g. Figure III · 34) suggested the existence of a porus core (assumed containing more water, Figure II · 15). An apparatus could be designed in order to proceed to the degasing of the interior of the material during the molding using microperforation for instance. Such a capacity would be particulary useful in 3D molding where water would probably be needed to guarantee flow ability and steam thus being highly problematic.

* These technological improvements (and others) should be directed towards the capacity of producing results independently from the technique. In other words, being able to form test specimens under uniaxial high pressure thermo compression from whatever starting materials.

**Scientific prospects for the increase of knowledge about the physico-chemical phenomena occurring during molding and explaining the consolidation process:**

* The better qualification of the delamination process is desirable. A quantitative scale should be found in order to study the correlations between materials parameters and operating conditions. The water sorption isotherms could be used to quantify the water / polymer interactions according to the temperature, using for example the parameters of Guggenheim–Andersen–de Boer (GAB) like presented in the materials and methods VI.2.C. An interesting experiment would be using materials (e.g. cellulose) of different moisture contents and spread them in layers along the thickness of the specimen, for instance, dry material in the core layer, and moist materials on the outside.
General conclusion and prospects

* The delamination could be linked with the thickness of the material and also the volume / surface ratio of the molded parts in order to better understand this phenomenon. These results would participate in validating the hypothesis formulated in Chapter III concerning the strength of the material being mostly coming from the skin and the disappearing of delamination under 8% and 250°C conditions.

* The second hypothesis formulated concerned the mechanisms of cohesion, being based on the establishment of hydrogen bonding, which to a high extent would be responsible for crystallization of the cellulose samples at the surface preferably. A method for systematic analyses of the samples crystallinity should be used and the crystallinity changes within the thickness of the samples measured under different operating conditions and compared to X-ray tomography porosity patterns. There is a high possibility that these two parameters would not be directly correlated (III.7).

* There is still a research quest for measuring the Tg of cellulose, because the whole concept of amorphous phase for cellulose remains quite uncertain. The influence of pressure on the Tg was thought to be explaining the densification process in the work of Jallabert (PhD thesis, 2014) and gave satisfactory explanations for the mechanisms of cohesion and the mechanical properties obtained in this thesis. Yet, many experiments could be run in order to validate the hypotheses formulated in these two thesis. For instance, experiments close to those found in the literature (applied to board molding and concerning the Tg of lignin) for measuring the local temperature within the compacted material during the molding and correlation of the T-Tg gradient to the local strength of the material would be major.

* Data collected by the CERMAV showed the destructuring effect of high pressure molding of cellulose crystallinity, for which some reports were consistent in the literature. The DP might also probably be altered and could be an interesting parameter to measure, and to put in relation to the mechanical properties (even though the evaluation of the molecular mass distribution of cellulose is already is challenge by itself).

* In the context of the hydrophobation studies, much work is needed in explaining the effect of the different fatty compounds added to cellulose (IV.1). In IV.2, the grafting was confirmed but on drastic conditions of molding, which needs to be varied again, it is probable that such long processing time is not needed to perform the reaction. The influence of the molding time (i.e. reaction time) would be interesting to study.

* The functional properties of hydrophobated materials observed in some experiments could be further studied in order to evaluate the part of responsibility of adsorbed fatty compounds and grafting respectively. For instance, in IV.2, the hydrophobation effect was measured on the powder but not on the material itself which needs to be done. The water properties of modified compacted specimens could be tested right out of the pressing machine, then washed for rinsing unreacted materials, tested again etc.

* There is much hope in working on layered material (grafted materials on the outside and non-grafted in the inside) for solving the problem of the loss of the mechanical properties due to the grafting. Such a method could be problematic as we demonstrated that most of the strength comes from the skin of the material, and that grafted materials had mechanical properties lowered in the proportion of the grafting yield. To avoid this problem, there could be a possibility of molding specimen and further coat it either with modified powder, or make the reaction on the surface of a premolded specimen.

* Transfer molding was supposed to be a promising technique, prototyping made in this thesis were almost successful in providing tools for studying the flow ability and transfer molding of raw plant materials. These analyses should be carried on, studying the influence of extrusion dies length and diameters, angles, and establishing the link between extrusion
conditions, the other parameters (temperature, moisture) and the composition / morphology of the raw plant materials processed.

**Prospects directed towards the improvement of the bio-based, simple and elegant material obtained:**

With improved technological mastery and knowledge about the cohesion mechanisms and impact of the composition and morphology of the plant materials used, an enormous model could be designed. The entry variables would be the plant materials composition, morphology, operating conditions (extrusion or compaction) and output variables would be the properties of the molded materials (mechanical, morphology, water resistance, ageing behavior etc.). Actually two models could be established, one for compaction and one of transfer. This model would be able to predict and optimize the properties of materials obtained from a known biomass, but also using the opposite approach, based on industrial specifications (in terms of strength, water resistance, colour, etc.) the model could predict what materials and conditions should be used to fulfill the requirements.

The collaboration of scientists and industrials from different fields (ceramic, pharmacy, board processing, metal sheets stamping etc.) would probably be a necessary condition to the future development and hope for industrialization.
Scientific contributions

Open access publications

* High Pressure Compression-Molding of α-Cellulose and Effects of Operating Conditions
  Thibaud Pintiaux, David Viet, Virginie Vandenbossche, Luc Rigal and Antoine Rouilly
  In: Materials 2013, 6(6), 2240-2261.
  Submitted: 22 January 2013 / Revised 12 March 2013 / Accepted 21 May 2013 / Published 30 May 2013.

* Binderless Materials Obtained by Thermo-Compressive Processing of Lignocellulosic Fibers: A Comprehensive Review.
  Thibaud Pintiaux, David Viet, Virginie Vandenbossche, Luc Rigal and Antoine Rouilly
  In: Bioresources 2015, 10 (1)
  Submitted: August 4, 2014 / Revised September 4, 2014 / Accepted December 11, 2014 / Published: January 16, 2015.

* High-Pressure Driven Solvent-Free Heterogeneous Phase Esterification of Cellulose
  Thibaud Pintiaux, Feriel Laourine, Guadalupe Vaca-medina, Antoine Rouilly and Jerome Peydecastaing
  In: Bioresources.
  Submitted: November 17, 2014, under review.

International conferences

* High pressure compression molding of pure cellulose as a potential way towards the production of biomaterials: pressure-volume-temperature behavior, mechanical properties, microstructure changes and operating conditions study.
  Thibaud Pintiaux, Antoine Rouilly, Bastien Jallabert, Guadalupe Vaca-medina

Posters

* Effects of a high pressure compression-molding process and its parameters on the mechanical properties of compressed α-cellulose
  Thibaud Pintiaux, Guadalupe Vaca-medina, David Viet, Luc Rigal, Antoine Rouilly

* Effect of pre-treatment in thermo-mechanico-chemical reactor on self-bonding capacity of lignocellulosic materials.
  Assad Mogni, Thibaud Pintiaux, Joël Albet, Antoine Rouilly, Pierre-Yves Pontalier
  9th International Conference on Renewable Resources & Biorefineries (RRB9), June 5 – 7, 2013, Antwerp (Belgium).

* Valorization of palm date by-products as self-bonded materials
  Nabila Saadaoui, Antoine Rouilly, K. Fares, Thibaud Pintiaux, Luc Rigal
  8th International Conference on Renewable Resources and Biorefineries (RRB8), June 8 – 10, 2011, Bruges (Belgium).
Acknowledgments

I would like to sincerely thank the jury’s members for their participation in judging my work and make it improve, especially the referees for their meticulous examination. The ANRT and The Green Factory (Grégoire, Martin, David) who made this work possible with the financial support and collaboration. For the warm welcome, professional skills, comfortable everyday work experience and cheerfulness, I would like to thank all the LCA staff members that I have been seeing during these 4 years. Thanks to the HYPOMOBB team, Bastien, Lupita, Jerome, Virginie. Particular thanks to Carlos, for the sympathy, contact easiness and freedom of speech, support and wise advises. I could not have produced all that scrap metal during this thesis without the help of the INP mechanic workshop: I would like to express my sincere thanks to all the staff there, Gilles, Alain, Rafik, Vincent and the others. Thanks for all the advices, good and funny times and of course tools and molds machining. This was such a great opportunity to work with you as we did, and be sure that you put on some serious bricks to assemble this work. For the work that was not possible at the INP workshop especially when electro erosion was needed, I have found awesome skills and professionalism from CEE and its CEO Christian who greatly contributed to the comprehension on the seizing that we were facing. For their hard work and adaptability, Mathieu, Feriel and Floréal, the three interns I have had under supervision. Thanks to Manuel from IMFT for the X-ray tomography, Laurent from the CERMAV for the RMN crystallinity measurements. Many thanks to the JSPS (Japan Society for the Promotion of Science), Miki-san, Kanayama-sensei and all the AIST staff members (Aishi Institute of Science and Technology – host laboratory in summer 2013 in Japan) for their unbelievable kindness, the inspiration and this great opportunity of discovering this awesome country. Thanks to Luc for his precious advice all along the thesis. Last but not least Antoine, thank you so much for the continuous support, ideas, freedom in my research, for the trust that you put in me since the first day.

Remerciements

Je souhaite sincèrement remercier les membres du jury pour leur participation à juger mon travail et contribuer à le faire grandir, et particulièrement les rapporteurs pour leur travail minutieux. Merci à The Green Factory (Grégoire, Martin, David) et à l’ANRT pour le soutien financier indispensable à tout travail de recherche. Merci à toute l’équipe du LCA pour l’accueil chaleureux, les compétences et leur contribution à maintenir un environnement de travail confortable dans la bonne humeur durant ces 4 ans. Merci à toute l’équipe HYPMOBB, Bastien, Lupita, Jérome, Virginie. Merci particulièrement à Carlos, pour la sympathie, la facilité de contact, le franc-parler, le soutien et les bons conseils. Merci au personnel de l’atelier de l’INP sans qui il m’aurait été impossible de réaliser autant de « presse-papiers », Gilles, Alain, Rafik, Vincent, merci pour les bons moments et pour tout le soutien « technologique » sur la création des outils et moules. Mes travaux de thèse ont en partie été possibles grâce à vous, et ça a été une véritable aubaine de pouvoir travailler avec vous comme nous l’avons fait. Pour tout ce qui n’était pas possible de réaliser à l’atelier (notamment l’électro-érosion) j’ai trouvé auprès de CEE un complément idéal, merci également au directeur de CEE Christian qui a contribué à la compréhension sur les problèmes de grippage rencontrés tout au long de la thèse. Merci aux stagiaires, Mathieu, Feriel et Floréal pour leur travail acharné et leurs facultés d’adaptations. Merci à Manuel de l’IMFT pour la tomographie rayon X, et Laurent du CERMAV pour les données de cristallinité en RMN. Merci à la JSPS (Japan Society for the Promotion of Science), Miki-san, Kanayama-sensei, et les autres membres de l’AIST (Aishi Institute of Science and Technology - laboratoire d’accueil lors du stage doctoral effectué au Japon à l’été 2013) pour la gentillesse, l’inspiration et cette immense opportunité de découvrir ce merveilleux pays. Merci à Luc pour les précieux conseils tout au long de la thèse. Et enfin, merci à Antoine, pour le soutien que tu m’as apporté tout au long de ce travail, les idées, la liberté que tu m’as laissé, pour avoir cru en moi dès le début.
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VI  Materials and methods

VI.1  Starting materials and chemicals

VI.1.A  Cellulose

In chapter III, IV and V, α-cellulose, 96% purity according to the provider, with 4% insoluble hemicelluloses (French et al. 2000) was purchased from Sigma-Aldrich (St Louis, MO, USA) under the reference “bulk cellulose”, this product was extracted from aspen trees. The crystallinity index has been measured at 62%. The crystallinity index of starting material was measured using X-ray diffraction. It was performed on a quartz-lead sampler loaded with the α-cellulose powder using a MiniFlex II Desktop X-ray Diffractometer with Cu Ka radiation (Rigaku, Tokyo, Japan). Scans were obtained from 5 to 50 degrees 2θ in 0.05 degree steps for 15 seconds per step. The crystallinity index was evaluated according to the method of Segal et al. (Segal et al. 1959).

VI.1.B  Hydrophobating agents (Chapter IV, part IV.1)

Stearic acid, linoleic acid, sebacic acid, magnesium stearate, sodium stearate were purchased from Sigma Aldrich (St Louis, MO, USA) and highly oleic sunflower oil was provided by La toulousaine des céréales (Toulouse, France).

Stearic acid was melted, stirred and 5% of sodium and magnesium stearate were added in order to generate 95/5 mixtures of the acid and corresponding salts (Mg and Na). These two mixtures were cooled down and added to the cellulose under their solid state.

A ceramic mortar bowl and pestle were used in order to mix the additives to cellulose powder in proportions of 2, 5 and 10% and used the day of preparation for molding. The mixing of solid material was quite easy and uniform (magnesium stearate, sodium stearate, stearic acid, mixtures of those and sebacic acid) whereas for sunflower oil and linoleic acid (liquids at room temperature) the homogeneity has been difficult to obtain especially for low additive contents.

VI.1.C  Esterification reagents (Chapter IV, part IV.2)

Octanoic acid (OA) with purity over 98% was purchased from Alfa Aesar (Schiltigheim, France). Anhydride octanoic (OAn) with purity over 95% was purchased from TCI (Zwijndrecht, Belgium). Potassium laurate was produced from mixing of lauric acid heated to 80 °C with a 1.59.10⁻² M potassium hydroxide aqueous solution, and successive vacuum drying at 50°C. Potassium laurate is described as a catalyst for the esterification of cellulose (Peydecastaing et al. 2006). 2% of potassium laurate was added to the OA, consequently, for the purpose of this work OA will refer to the 98% OA / 2% potassium laurate mixture.

VI.1.D  Native plant materials

In chapter IV, miscanthus (Miscanthus sinensis, purchased from Burlerrow Farm, Bodmin, UK) was ground on a 250 µm screen in a Pulverisette 15 grinder from Fritsch (Idar-Oberstein, Germany) and manually sieved at 150 µm to obtain a fine and homogeneous powder.
In chapter V, diverse raw plant materials were processed, most of them were collected in the laboratory from other research projects:

- Wheat (Triticum sp.) straw was obtained from Arterris (Castelnaudary, France) and ground with a VS1 hammer mill from Electra (Podenas, France) with 2 mm grid and separated in 3 fractions, >0.5 mm · [0.5,1] mm · <1 mm using an automatic industrial sieving machine from RITEC (Toulon, France). The three fractions were coded WS1, WS2 and WS3 respectively.
- Olive (olea europaea) kernels flour was given by Bardon Ets (Le Muy, France) and was coded FNO.
- Cellulose wadding (CWa) (Univercell®) was collected from SOPREMA (Strasbourg, France).
- Sweet corn (SCR) (Zea mays saccharata) co-products came from industrial corn grain canneries and were provided, dehydrated, by SARL Soupro+ (Castelmoron sur Lot, France).
- Agave (Agave tequilana) bagasse is the fiber residue from the manufacture of Tequila. It was air dried, and kindly provided by the PATRON Spirits Company in Mexico (Atotonilco, State of Jalisco). Agave bagasse was coded Bag.
- Oil palm (Elaeis guineensis) empty fruit bunch (pinsotte) is the residue after separation of the fruits in the production of palm oil. It was air dried before being sent from Costa Rica (Palma Tica grupo NUMAR). Pinsotte was coded Pin.
- Barley (hordeum vulgare) straw (BS) came from Spain and was provided by the Centre for the Development of Renewable Energy Sources (CEDER – Soria, Spain).
- Sugarcane bagasse (saccharum) came from Brasil and was coded BCa. Eucalyptus wood came from Uruguay and was coded Euc. The vine prunings (vitis vinifera) came from Chili and was coded Vin. No more information were available about these materials as they were used in a no more active research project. Originally these 7 later materials were studied for their hydrolysis ability and evaluated for the production of 3rd generation ethanol (Vandenbossche, Brault, et al. 2014).
- Miscanthus (miscanthus sinensis) which normal use is animal bedding has been provided by The Green Factory and purchased from Burlerrow Farm (Bodmin, UK). Micanthus was coded Mis.
- Chenevotte, coded Che is the center part of hemp (cannabis sativa) and is normally used as ecofriendly wall coating (hemp and lime for instance) or hemp concrete construction material. It was collected from Agrofibre SAS (Cazères, France).
- Sunflower (helianthus annuus) seeds cake (SSC) pellets and sugarbeet (beta vulgaris) pulp (SBP) were obtained from an agricultural cooperative: La toulousaine des céréales (Toulouse, France).
- Carded hemp (cannabis sativa) was collected from AGROMAT (Tarbes, France) and coded Car.
- Coffee (cofnea) waste (Cof) was collected at the laboratory employees cafeteria and air dried.
- Beech wood (fagus sylvatica) and Poplar bark (populus) were obtained from the FCBA (Forêt Cellulose Bois construction Ameublement, Grenoble, France). They were coded Bee and Pop, respectively.

VI.2 Preparation methods

VI.2.A Thermo-mechanical refining

Even though the thermomechanical refining was not investigated as a priority, some preliminary trials were performed pushed by scientific curiosity, and good results obtained. Thus, the thermomechanical refining of wheat straw was performed in 3 different conditions, in order to evaluate its impact on the molded materials.
The thermo-mechanical refining was conducted using a Clextral (Firminy, France) BC 45 co-penetrating and co-rotating twin-screw extruder. It comprises 7 modular barrels induction-heated and thermoregulated (The wheat straw is introduced in the extruder using a volumetric hopper screw feeder set to 15 kg/h. A piston pumps with power control (Clextral DKM K202 PP32) was used to inject water at a controlled flow. Water was injected in the extruder as to maintain a liquid solid ratio of 0.7 (L/S = 0.7).

The screw profile (Figure VI - 1) is a very important parameter, it was inspired by other works conducted in the laboratory, for which a paper was published recently by Vandenbossche et al. (Vandenbossche, Doumeng, et al. 2014). In Figure VI - 2 each set of screws is indicated by a type (T2F: trapezoidal double-thread, C2F: conveying double-thread, BB: bilobe paddle screw, C1FT: reverse pitch simple-thread screw) followed by a number indicating the pitch except for the BB type for which number indicated the length of the screw module.

3 different conditions were tested, in the first one, water was added with 3% sodium hydroxide and the pretreatment was conducted at 100°C. This experiment was called WE1. In the second and third trial, the extrusion was performed with water only and at 100 and 70 °C which resulted in materials called WE2 and WE3 respectively.
VI.2.B  Grinding

In Chapter IV, in order to increase the contact surface area, the Miscanthus was ground on a 250 µm screen in a Pulverisette 15 grinder from Fritsch (Idar-Oberstein, Germany) and manually sieved at 150 µm to obtain a fine and homogeneous powder.

In Chapter V, because the 23 materials had very different particle size and some of them not compatible with the size of the molds, they were all ground using a VS1 hammer mill from Electra (Poudenxas, France) fitted with a 2 mm grid. No sieving was performed but the particle size distribution and form factor distribution were measured in order to evaluate the influence of these parameters on the molded specimens’ properties.

VI.2.C  Moisture conditioning and dynamical vapor sorption

Two different methods were used to get starting materials to the desired values of moisture content. First and most used method was the equilibrium of one material to air calibrated to specific RH. For example, in chapter III, cellulosics with different moistures were conditioned in a climatic chamber (Fisher Scientific, Bioblock Scientific, Illkirch, France) tuned at 45% - 60% - 75% RH and 25°C which produced cellulosics with 6.1, 8.0, 10.8 % MC respectively. In this case, materials were let to equilibrate in said atmospheres for at least 15 days. The relationship between RH and MC of cellulose samples was verified on the sorption/desorption graph (Figure VI - 3) made on a Dynamic Vapor Sorption (DVS) apparatus from Surface Measurements System Ltd (Alperton London, UK).

![Figure VI - 3: Water uptake against atmosphere Partial Pressure of alpha cellulose](image)

From the water sorption desorption isotherms, the parameters of Guggenheim–Andersen–de Boer (GAB) were calculated which permitted to obtain the mole number of water monomolecular coverage (first GAB parameter) at $2.8 \times 10^{-3}$ mol/g. The monolayer is thus reached at 5 % moisture content.

As atmosphere below 30% RH are difficult to obtain in climatic chambers, a second method was used to generate lower moisture content cellulose in chapter III: cellulose
equilibrated to control conditions (60% RH 25°C – with known MC) was let to dry in a 70°C vented oven while kinetically measuring the weight loss in order to reach a specific value. For example, for generating 4% MC cellulose, 8.0 % MC cellulose was dried until a 4.0% weight loss weight loss was measured etc. Dry samples were generated by letting them 48 hours in a 103°C oven.

VI.3 Methods of analysis for physic-chemical properties of plant materials

VI.3.A Physical parameters

Apparent density of the powder (tapped density)

In this work, the apparent density (g/cm$^3$) referred to the tapped density of the one starting material, uncompressed. The tapped density was measured by measuring mass and volume occupied by one analyzed material equilibrated with 60% RH 25°C atmosphere, after 750 hits (tap) using a Densitap apparatus from Granuloshop (Chatou, France). Several runs of 750 hits were performed sequentially until the variation of tapped density from the run n compared to the run n+1 was below 5% (usually 2 or 3 runs are needed).

Particle size distribution

Pre-weighted sieves with different opening (2.0, 1.6, 1.25, 1.0, 0.8, 0.5, 0.25 and 0.12 mm ) were used in a Retsch (Düsseldorf, Germany) model AS 200 basic automatic laboratory sieving machine in order to analyze the particle size distribution, as a result of the grinding treatment. About 100 g of the plant materials were put in the first sieve (2.0 mm) and the apparatus was let to vibrate at 75% of its amplitude for 45 minutes. After what the sieves were reweighted and material weight retained in each sieve was obtained. The different particle sizes were expressed in percentage: P>2 represented the percentage of particles retained in the 2.0 mm sieve, P1.6, P1.25, P1, P0.8, P0.5 P0.25 and P0.12 represented the particles retained in the corresponding sieve number. P<0.12 represented the bottom container of the sieves pile, i.e. the particles with size inferior to 0.12 mm. Although the grinding treatment was the same for all materials through a 2 mm screen the particle size distribution was quite different. This analysis being reliable and made on a significant quantity of material (about 100 g), only one measurement was made.

Form factor profile

An EPSON image scanner model G860B was used to obtain pictures of plant materials powder spread on either a mat white or black sheet of paper. An image analyser software (Lucia from Laboratory imaging s.r.o., Prague, Czech Republic) was tuned in order to measure for each particle the minimum and maximum Feret’s diameter (respectively minferet and maxferet). The form factor is classically the ratio of the minferet to the maxferet. In this work, in order to work on finite numbers, the term F was used, and defined as the inverse of the aspect ratio. F is thus calculated from the ratio of the maxferet to the minferet.

F1 was defined as the percentage of particles with aspect ratio (or F) equal to 1. Fx:y was defined as the percentage of particles with a ratio strictly superior to x and inferior or equal to y. The distribution was analysed using F1, F1:2, F2:3, F3:5, F5:10 and F10 variables, F10 representing the percentage of particles with F>10.

3 different images were analysed and the F factors were expressed with the mean of the triplicates ± standard deviation.
VI.3.B Chemical composition

Moisture content

Moisture content (MC) evaluation was performed on materials after at least 15 days of equilibrium with atmosphere under known conditions. The MC measurement was performed by difference of weight between an equilibrated sample (\(m_{\text{moist}}\)) on its dry mass \(m_{\text{dry}}\) obtained with 2 days drying at 103°C, in triplicates.

\[MC = \frac{m_{\text{moist}} - m_{\text{dry}}}{m_{\text{moist}}} \times 100\%\]

Mineral matter

Ashes content was evaluated after MC evaluation by ashes weight (\(m_{\text{ashes}}\)) after calcination at 550°C for 3 hours using a Nabertherm Gmbh oven (Lilienthal, Germany). This analysis was performed in triplicate.

\[\text{Ashes content} = \frac{m_{\text{ashes}}}{m_{\text{dry}}} \times 100\%\]

Total lipids

The total lipids content was measured by weighting the result of a Soxhlet extraction using a 125 mL Soxhlet apparatus for 6 hours in cyclohexane on one plant material (\(m_{\text{initial}}\)) powder imprisoned in a paper filter cartridge. At the end of the extraction time and final solvent draining, the content of the balloon was evaporated using a rotative evaporator in order to obtain the extracted mass (\(m_{\text{extracted}}\)). This analysis was performed in triplicate.

\[\text{Total lipids} = \frac{m_{\text{extracted}}}{(1 - MC/100) \times m_{\text{initial}}} \times 100\%\]

Protein content

The protein content was evaluated using the total nitrogen content analysis or Kjeldahl procedure assisted by a Tecator Kjeltec 2000 apparatus from Foss (Nanterre, France). This analysis relies on first the mineralization of the proteins and other sources of nitrogen of the analyzed sample into ammonia by acid hydrolysis (98.5% sulfuric acid) catalyzed by hydrated copper sulfate for 2 hours at 400°C. Secondly sodium hydroxide is added which converts the ammonium ions into ammonia, the solution is distilled and vapor (ammonia gas) trapped in a flask containing a 4% boric acid solution, methyl red and bromocresol indicators. Hydrochloric acid is finally added to the flask until neutralization of the remaining ammonia, and the calculation of the ammonia distilled from the mineralized solution can be made (Kjeldahl 1883). A blank control is made in order to ease the calculation and avoid titration troubles with the boric acid.

The protein content is then evaluated by multiplying the equivalent nitrogen content given by the Kjeldahl procedure by 6.25. The factor of 6.25 for the conversion of N values to protein is known to be varying from one protein source to another, but has been the most widely used since despite its obscure origins (Hiller et al. 1948). In this work, it was sufficient to use the classical protein factor for comparison purpose between the different plant materials.
Lignocellulosic constituents

The ADF/NDF method of van Soest et al. (van Soest and Wine 1967) was used for determining the cellulose, hemicelluloses and lignin, using a Tecator Fibertec M1017 from Foss (Nanterre, France), in triplicates.

The analysis works with 2 initial sintered glass filters. First takes place the Neutral Detergent Fiber treatment with the first filter, at ebullition temperature and reflux in the NDF solution (sodium laurylsulfate, sodium ethylenediaminetetraacetic, sodium borate decahydrate) for 1 hour. This treatment solubilizes all the non lignocellulosic constituents (metabolites, proteins, fat, ashes etc.) thus after phase separation and rinsing with hot water, the solid remaining in the sintered glass filter would contain only lignin, cellulose and hemicelluloses which can be measured after drying (m_{NDF\ treatment}). This first sintered glass filter is calcined and weighted (m_{ashes}).

In parallel, another sintered glass filter is used and the Acid Detergent Fiber treatment takes place, at ebullition temperature using the ADF solution (hexadecyltrimethylammonium bromide 2% in 1N sulphuric acid) for 1 hour. This treatment solubilizes the hemicelluloses thus the remaining solid after rinsing with hot water contains only lignin and cellulose. After drying, the lignin and cellulose content can be measured by weight difference (m_{ADF\ treatment}).

Successively the oxidant treatment takes place using potassium permanganate at room temperature for 1 hour and a half which solubilizes the lignin. The solid is separated by filtration and a demineralizing solution (dehydrate oxalic acid, ethanol, hydrochloric acid, distilled water) which permits to bleach the fibers by elimination of the remaining permanganate salts (m_{permanganate\ treatment}). The sintered glass filter is finally calcined (m_{ashes2}).

By weight difference of the successive extractions summed up in Figure VI - 4, the cellulose, lignin and hemicelluloses content can be calculated:

\[
Cellulose\ cont. = \frac{m_{permanganate\ treatment} - m_{ashes}}{m_{2\ plant\ material}} \times (1 - MC/100) \times 100\% 
\]
Total polyphenols

The Folin-Ciocalteu method was used to analyze the total polyphenols content in the plant materials. This analysis relies on a reduction reaction of yellow colored ionic polymer complexes formed from phosphotungstic and phosphomolybdic acids into blue molybdo-tungstene complexes by the polyphenols in an alkaline media. First, extracts were made on the different plant materials, a known mass ($m_{plant\ material}$) of each plant material was added to a known volume ($V_{extract}$) of 30% distilled water 70% ethanol and left to stir together for 2 hours at room temperature (19°C) and finally filtered. The extraction was performed in triplicates and each extract was analyzed.

A known volume of extract was collected, diluted ($d$ times) when needed (colour observation) and added to 1 mL of sodium carbonate (20% w/w) and 0.5 mL of the Folin-Ciocalteu reagent, purchased from VWR (Fontenay sous bois, France) in a test tube (of V volume). Controls were prepared for the calibration by adding gallic acid. The test tubes were placed in a stirred water bath at 70°C for 10 minutes followed by the reaction being stopped by ice-quenching for 20 minutes. The absorbance at 700 nm was then measured using a UVS 1800 ultraviolet spectrophotometer from Shimadzu (Noisiel, France). The Beer-Lambert law permitted to retrieve the equivalent gallic acid concentration $C_{eq.\ gallic\ acid}$ (mg / L) in each sample, which was converted in mg$_{eq.\ gallic\ acid}$/g of raw plant material using the following equation:

\[
Total\ polyphenols: \frac{C_{eq.\ gallic\ acid} \times V_{extract} \times d}{m_{plant\ materials} \times (1 - MC/100)} \text{ (mg}_{eq.\ gallic\ acid}/g )
\]

Thermo-compressive molding

Pressing machines

The major part of the experiment have been performed in a MAPA 50 computer-controlled laboratory-scale hydraulic press (Pinette Emideceau, Chalon-sur-Saône, France), capable of 530 kN of effort (about 50 tons). The metal plates (50cm x 50cm) were thermo-regulated, and used to warm up the mold at least 30 m before each molding attempt.

In chapter IV (and only) a manual hydraulic press was used. It has a capacity of 10 tons and is from the same manufacturer than the MAPA 50 was used, and both plates (25 x 25 cm) are also thermo-regulated.

In chapter III, the pressing machine from AIST in Nagoya was used, it had a capacity of 200 kN and was manufactured by SAGINOMIYA (Tokyo, Japan).

2D molding

All the molds used in this work were custom made to produce different specimens: 1A dog-bone specimens:
50x50 mm square specimens: This first available mold was used to produce square plates, for numerous preliminary tests and in chapter IV (part IV.1) in order to perform water drop angle measurement tests in the evaluation of fatty compounds as hydrophobation agents. WA/TS experiments were initially designed to be performed on squares (in chapter V) but it had to be abandoned because of inconsistency between the results on 1A dog-bone in one hand, and squares. The difference probably came from a too different surface / volume ratio in 50x50 specimen compared to a 150x10 (dog-bone shape).

A mold (Figure VI.5) was machined (Cristin Electro Erosion, Grisolles, France) in order to produce 1A dog-bone tensile specimens according to ISO 3167 standard (ISO 3167 2002). The molds were machined in 55NCDV7 (given to 140-150 kg/mm² of strength) steel allow without further modification except for the 4th version of this mold for which lower and upper punches were hardened by quenching (Figure VI.6). Such apparatus has never been reported in the literature and tensile strength on compression molding tests is rarely reported. The production of ISO 1A dog-bone also haven’t been seen anywhere else.

Figure VI.5: NF EN ISO 3167 1A specimen compression mold: schematics, first version

Figure VI.6: Picture of the 4th 1A dog-bone specimen compression mold preheating in the MAPA 50 press
45x10 mm DMA specimens: This mold was designed in order to perform DMA analysis, for the other part of project HYPMOBB, and it was used for molding the WA/TS specimens (Chapter III, Chapter V) and also during the esterification study (Chapter IV). A first version was made out of 55 NCDV7 steel, and a second version used the same allow with hardened punches (Figure VI · 7).

In chapter IV, the specimens were pressed in the 10 tons press, at maximum force capacity and the resulting pressure in these conditions was about 220 MPa. For each molded specimen, 1 g of material (cellulose, miscanthus with a certain quantity of OA or OAn in it) was manually charged in the mold in the hot press with preheated mold, after 1 or 2 hours of experiment, the material was manually unloaded without a cooling step. Preliminary results based on IR measurement indicated that no grafting was detected unless quite drastic conditions of molding were used. Two conditions of molding were tested in each experiment for the need of comparison: First condition was a rather low temperature (165°C) and a long time of 2 hours, second condition was a higher temperature (190°C) and shorter time of molding (1 hour).

![Figure VI · 7: 45 x 10 mm DMA specimens used for molding water resistance and esterification specimens](image)

3D molding

A bowl-shape and a candle holder shape molds were available to produce 3D moldings. They have been described in Chapter II, in Figure II · 3 and Figure II · 11. Although many tests were performed on these molds, obtaining a perfect shape ended up to be very difficult. 3D molding appeared much more complicated than 2D molding because of the flow parameters playing a role in the resulting specimens. No scientific data were produced thanks to these molds.

Molding cycle

The pressing machine was preheated, and the initialization of the mold is made before each set of experiments so that the pressing machine integrates the position of the mold. The mold is preheated, laying on the hot plates, and at least 30 minutes were waited
between the time at which the plates were at temperature and the beginning of the experiments. The temperature of the mold was regularly verified using an IR temperature sensor, it was between 2 and 5 degrees below the temperature of the plates.

The material to compress is charged in the mold manually, using a laboratory spoon and looking directly in the die from over the mold (in the press). Attention was paid to first charge quickly in order to prevent moisture changes of the sample in contact to the hot mold (evaporation for moist samples, moisture uptake for dry samples) and secondly to fill up the mold as homogeneously as possible.

The mold is then closed (upper piston, or upper shape) put on the material and press cycle launched. Several parameters are programmed in the computer, temperature of the plates (°C), hydraulic pressure (bar), pressure increase slope (i.e. pressurization speed, bar/s), maintaining time (s) and depressurization speed (bar/s).

In chapter III and in the first published paper, the effect of the pressurization speed was investigated, which was performed by calculating an integral I on the control press cycle (Figure VI-8). Pressure rate was set up at 1 bar/s, 2 bar/s, 50 bar/s (hydraulic pressure) while adjusting time to maintain equal I. Therefore, the time was different for each experiment, but also the maximum pressure of 267 MPa was not obtained for the 1 bar/s experiments (Table VI-1) because the integral I was reached before.

![Figure VI-8: Description of the press cycle (Chapter III)](image)

| Table VI-1: Parameters for pressurization speed evaluation in chapter (Chapter III) |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| **Prate**                  | **I pressure increase phase (bar/s)** | **I plateau at max pressure (bar/s)** | **I (bar/s)** | **Time on pressure increase phase (s)** | **Time on plateau at max pressure (s)** | **Max hydraulic pressure reached (bar)** | **Max process pressure reached (Mpa)** |
| 10 bar/s                   | 4500                        | 36000                       | 40500          | 30                          | 120                         | 300                         | 267                         |
| 50 bar/s                   | 900                         | 29600                       | 40500          | 6                           | 132                         | 200                         | 267                         |
| 2 bar/s                    | 22500                       | 18000                       | 150            | 150                        | 60                          | 300                         | 267                         |
| 1 bar/s                    | 40500                       | 0                           | 285            | 285                        | 0                           | 285                         | 254                         |

**Molding pressure**

The calculation of the molding pressure was made by two different means, first by considering the hydraulic pressure gauge, which the pressing machine uses for controlling the pressure:
Secondly, a force sensor installed in the MAPA 50 press was used to confirm the calculations on pressure:

\[
P_{\text{specimen}} = \frac{P_{\text{hydraulic}} \times S_{\text{piston}}}{S_{\text{mold}}}
\]

For instance, the dogbone specimen mold has an area of 20.057 cm² \((S_{\text{mold}})\), the pressing machine (MAPA 50) piston has a surface of 176.7 cm² \((S_{\text{piston}})\) and maximum hydraulic pressure \((P_{\text{hydraulic}})\) on the pressing machine is 300 bar so the maximum pressure produced by this press on the dogbone mold was 2643 bar i.e. 264 MPa. With hydraulic pressure set up to 300 bar, the force sensor indicated 530 kN, which confirms a specimen pressure of 2642 bar.

**Flow test apparatus (Nagoya) – Chapter III**

![Flow test setup in Nagoya](image)

In Nagoya, the main elements of the molding and flow tests was a rectified and polished, nickel-chrome plated, hardened steel chamber with a 30 mm inner diameter. The very smooth and resistant surface provided a high durability of this equipment. Tungsten carbide dies were available with different diameters and lengths and were entered in the chamber. Several setup were possible, a foot to install bellow the chamber in order to let the material flow out for the extrusion tests, lower punches (flat or small pot shaped) for molding experiments, and a gear shape.

**Transfer molding and flow tests (Toulouse) – Chapter V**

In Toulouse, a versatile setup was also designed for performing the flow tests experiments and allows molding of several parts. The 2 main elements were the chamber (with inner diameter of 25 mm) and the punch machined directly in pre-hardened steel \((55NCDV7)\). The chamber was equipped with a heating band, a K-type thermocouple and a
PID regulator. Different dies were produced, but finally only one die (diameter 4mm, length 10 mm) was used.

Pre-compression was performed thanks to a manual 10 tons press in a 24 mm chamber which permitted to load the material in the 25 mm compression chamber with ease, and permitted to put on the punch and start the test right away.

A foot was machined for free flowing experiments Figure VI - 11, and several molding modules were machined to produce different objects: a small gear, an M10 bolt, an M10 screw and a 2 tensile 2 bending tests specimens module (Figure VI - 12, Figure VI - 13). These modules were barely used due to a lack of time and technical troubles.

Figure VI - 10: Flow test setup in Toulouse

Figure VI - 11: Example of flow test with the prototype made in Toulouse
VI.3.C  Thermo-compressed material specimens evaluation

SEM Observations

SEM pictures were taken using a LEO 435 VP microscope from Leo Electron Microscopy Ltd (Cambridge, UK) and sample silver plating before observation.
Specific Gravity and moisture equilibrium measurements

Six 2 cm long pieces were cut out of six different dog-bone specimens (from the mechanical tests) to measure specific gravity and moisture content of the materials. These six small pieces were first let to equilibrate in a 60% relative humidity 25 °C climatic device, room and moisture content was measured on 103 °C oven-dry basis (24 hours). The dried 6 pieces were then used for evaluation of specific gravity using an YDK01 density determination kit on a Sartorius MC210P precision scale (Sartorius AG, Goettingen, Germany). The specimen were weighted in the air, and then dipped into cyclohexane (Sigma Aldrich, St Louis, MO, USA, Chromsolv for HPLC purity > 99.7%) and the resulting Buoyancy \( (W_{\text{air}} - W_{\text{fluid}}) \) was measured. Specific gravity was measured using the following equation:

\[
\rho_{\text{sample}} = \frac{W_{\text{air}} \times (\rho_{\text{cyclohexane}} - 0.0012)}{0.99983 \times (W_{\text{air}} - W_{\text{cyclohexane}})} \quad (g/cm^3)
\]

wherein \( \rho_{\text{sample}} \) is the specific gravity of the materials tested; \( W_{\text{air}} \) and \( W_{\text{cyclohexane}} \) the weight of the tested specimen in the air and in the cyclohexane respectively; \( \rho_{\text{cyclohexane}} \) the specific gravity of cyclohexane at the measured temperature during the experiment: 0.0012 \( (g/cm^3) \) the specific gravity of air at 20 °C and 101.325 kPa; and 0.99983 a manufacturer’s correction factor related to the increase of the fluid level and immersion of the wires in the fluid when the specimen is dipped in the fluid.

Cyclohexane was chosen arbitrary, air bubbles were chased out of the material when immersing it in the solvent, but some of the porosity of the material might remain inaccessible to the solvent, so the specific gravity measured here may differ from real absolute value of density. However, it is thought to be close to the real density and significantly higher than the apparent density.

Measuring dried specimen was thought to prevent mismeasurement of specific gravity due to difference of water content between the specimens. On the control specimens (Chapter III), the measured specific gravity of the material equilibrated at 60% relative humidity and 25 °C was 1.485 ± 0.003 g/cm\(^3\), but the measured specific gravity of the dried same specimens was 1.503 ± 0.002 g/cm\(^3\). This analysis was done on the same specimens that were measured, dried and measured again, and confirmed on other specimens that were dried directly and measured. Same results were obtained and no modification was observed due to cyclohexane dump-in.

X-ray tomography

Manuel Marcoux from the IMFT (Fluids Mechanics Institute of Toulouse) offered the possibility to use 3-D X-ray tomography in order to evaluate the porosity distribution within cellulose samples (results presented in III.7). The principle is the scanning of a specimen by X-rays all along the rotation of the sample at 360°. A Skyscan 1174 tomograph model 1174 from Brucker (Kontich, Belgium) was used for acquisition at 0.5° of sampling rate, triplicates image were taken and averaged. 3-D reconstruction was performed using the Avizo software from FEI Visualization Sciences Group (Hillsboro, USA) and an 8 level colour scale of porosity was applied to the group of samples.

Tensile and 3 Points Bending Tests

Prior to testing, the specimens were let to equilibrate 2 weeks in the main climatic chamber available at the laboratory (60% RH, 25°C). The weight variation was seen to be stable after about 10 days of equilibration. The mechanical properties were later observed to
vary within the first 15 days, and to remain stable thereafter (Figure III · 25). Tensile and point bending tests were conducted according to ISO 527-2 (ISO 527-2 1993) and ISO 178 (ISO 178 2010) using a H5KT Universal testing machine (Tinius Olsen, Horsham, PA, USA) at 1mm/min speed. These standards are related to the evaluation of mechanical properties of plastics which was chosen on purpose. From the stress/strain curves, four variables were collected: The tensile modulus (Et), tensile strength at break (σt), bending modulus (Ef) and bending strength at break (σf).

Because the compacted specimens obtained in this thesis had a heterogeneous laminar structure, the Tensile modulus was calculated (and not the Young’s modulus). The basic expression of an elastic modulus E is (with σ the stress and ε the strain):

\[ E = \frac{\sigma}{\varepsilon} \]

The extensional strain ε is basically calculated from its derivate, with \( l \) the effective tested length of the specimens during the test:

\[ d\varepsilon = \frac{dl}{l} \]

Which, upon integration from 0 to \( l \), makes:

\[ \varepsilon_i - \varepsilon_0 = \ln \left( \frac{l_i}{l_0} \right) \]

With \( \varepsilon_0 = 0 \) and \( \Delta l = l_i \cdot l_0 \),

\[ \varepsilon_i = \ln \left( \frac{l_0 + \Delta l}{l_0} \right) = \ln \left( 1 + \frac{\Delta l}{l_0} \right) \]

The maximum deformation in tensile was usually less than 2 mm, which makes 2.5% of deformation (ε). Materials with ε < 10% are in the “small strain” domain which, using the limited development of ln (1+x), permits to simplify the previous equation to:

\[ \varepsilon_i = \ln \left( 1 + \frac{\Delta l}{l_0} \right) \approx \frac{\Delta l}{l_0} \]

Considering this approximation, and with the introduction of \( S_{\text{tensile}} \) and \( S_{\text{bending}} \), the test’s span in the apparatus (= \( l_0 \)) for the tensile and bending test, 80 mm for 1A dog-bone specimens, 38 mm for the smaller DMA-type specimens; \( W_{\text{specimen}} \) and \( T_{\text{specimen}} \) the width and thickness of the tested specimen respectively; \( F_{\text{break}} \) the force (in N) measured when the specimen broke (maximum force of the stress / strain curve); \( (\Delta F/\Delta l) \) the slope of the strain/stress curve, taken at the beginning of the deformation; the following equations were used in order to calculate the mechanical properties:

\[ Et = \frac{S_{\text{tensile}}}{W_{\text{specimen}} \times T_{\text{specimen}}} \times \frac{\Delta F}{\Delta l} \text{ (GPa)} \]

\[ \sigma_t = \frac{F_{\text{break}}}{W_{\text{specimen}} \times T_{\text{specimen}}} \text{ (MPa)} \]

\[ Ef = \frac{S_{\text{bending}}^3}{4 \times W_{\text{specimen}} \times T_{\text{specimen}}^3} \times \frac{\Delta F}{\Delta l} \text{ (GPa)} \]
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\[ \sigma_f = \frac{3 \times F_{\text{break}} \times S_{\text{bending}}}{2 \times W_{\text{specimen}} \times T_{\text{specimen}}^2} \text{ (MPa)} \]

Some specimens were presenting defects like cracks when compression molded (e.g. at 200 °C and 8% moisture), or sometimes heterogeneity marked by lighter spots where density seemed lower. These “low density” spots generated when charging the material in the mold inhomogeneously discarded these specimens from the tests.

VI.3.D  Statistical analysis (Chapter V)

The statistical analyses (Cross correlation and Principal components analysis · PCA) in chapter V were performed with The Unscrambler 9.5 software from CAMO AS (Oslo, Norway).

The cross correlation (“Statistics” in the software) is a 2 entry table (the plant materials characteristics in columns, the molded materials parameters in line) wherein correlation coefficients between -1 and +1 are presented. These coefficients are computed as the covariance between 2 variables divided by the square root of their variance. If values are close to 1 it means the 2 variables tend to increase simultaneously. If values are close to -1 it means that one of the variable increases when the other decreases. Values close to 0 means the 2 variables vary independently one from each other.

The PCA tool was used as a way to detect groups of variables, group of specimens and correspondences between significant variables and specimens, in a simplified way. Prior to this analysis, because of the differences of units and range of the variables, the data were standardized (i.e. values were divided by the standard deviation of the serie). This gives the variables the same chance to influence the estimation of the components as they get all the same variance.

The principle of the PCA (Principle Components Analysis) is the following: find the directions in space along which the distance between data points is the largest. In other words, find the linear combinations of the initial variables that contribute the most to making the samples different from each other. These directions or combinations are called principal components (PCs) computed iteratively in such way that the first PC (PC1) carries the most explained variance, the second PC carries the maximum share of the residual information, and so on. PCA produces an orthogonal bilinear matrix decomposition where components are obtained in a sequential way explaining the maximum variance.

The results of the PCA model are presented as 2 plots: the variable loadings and specimens scores. The loading plot (also called map of variables) displays information about the variables in the PCA model. A variable that has low loadings is badly accounted in the PC(s), which means it cannot be interpreted using this plot. A positive variable loading means that all samples with positive scores have higher than average values for that variable. When a variable has a negative loading, all samples with positive scores have lower than average value for this variable. The higher the positive scores of a sample, the larger its values for variables with positive loadings and vice versa. From the loadings, "correlation loadings" are computed for each variable for the displayed PCs and drawn in two ellipses: the outer ellipse is indicates 100% explained variance and the inner ellipse indicated 50% of explained variance. Thus, variables close to the outer circle will have most of their variance explained by the two plotted PCs.
VI.3.E Methods for performing and studying the esterification in high pressure molding conditions (Chapter IV part 2)

Liquid solid separation

A 6-16K Centrifuge equipped with a 12500 rotor from SIGMA Laborzentrifugen GmbH (Osterode am Harz, Germany) was used at 18°C, 10000 g for 15 minutes for liquid solid separation. A 100 microns nylon tissue, used as a filter, was wedged between the cap and the centrifugation pot, in order to retain the solid in the filter and collect the liquid in the pot. The state of the material after contact between cellulose/miscanthus and reactants after phase separation was a solid, slightly humid powder, which weight consisted of roughly 30 % of reactants adsorbed on the powder. The precise composition of material entering the mold was not measured due to the number of transfer steps during pretreatments. Also at the beginning of the compression step, liquid was extracted from the solid material and leaked onto the press plates. The liquid solid ratio, during the molding step was thus not determined.

Materials pretreatments for solid-liquid pre-contact

**Emulsion:** The solid material was emulsified with water and grafts (Peydecastaing et al. 2006) using a high shear mixer, L4RT from Silverson (East Longmeadow, USA) in order to increase water content of cellulose and test the emulsion contact method between cellulose and OA. 200 g of OA and water 5/12 were mixed together and emulsified at 7000 rpm for 15 minutes, then 10 g of cellulose were added.

**High pressure homogenizer:** 20 grams of cellulose was suspended in 2 L of distilled water and introduced progressively in the APV 1000 high pressure homogenizer from APV (Albertslund, Denmark). The first pass was performed at relatively low pressure (average 40 bar, not constant), on the second pass pressure was increased to 100 bar, the third pass pressure was increased to 400 bar, and then 3 more passes were performed at 800 bar. After the second of these three 800 bar passes, the suspension became stable in water with a gel-like appearance. After the 6 passes, the temperature was measured to be around 70°C.

**Solvent exchange:** Cellulose was left to swell in a large excess of distilled water for 12 hours, filtered and washed twice with ethanol (2 * 160 mL), stirred in ethanol for 5 minutes, and successively washed twice with the desired reactant (OA or OAn). Cellulose is left to stir in the last reactant bath for 5 minutes. The solvent exchanged cellulose is then filtered on a Buchner set up and centrifuged at 18°C, 10000 g for 15 minutes.

Reactant removal prior to analysis

Powders (generated using a small kitchen grinder) from molded specimens were washed using a Soxhlet for 8 hours in technical ethanol using small filter paper bags in order to get rid of the non-grafted reactants from the solid. After washing, the filter paper bags were left to evaporate for 24 hours at 70°C to remove the solvent and the washed powder recovered.

IR Analysis

A FTIR apparatus from Perkin Elmer (Courtaboeuf, France) was used for obtaining IR spectra, acquisition was performed from 400 to 4000 cm⁻¹. KBr tablets were produced with
a manual screw press. IR analysis has been used to track esters on early preliminary results (data not shown), and also on cellulose grafting experiments shown in this paper. As for miscanthus, the starting material showed ester bands as expected, which would overlap with ester resulting from grafting, thus, IR spectra were not performed on miscanthus grafting experiments (ND appears in corresponding lines in Table 1).

**Drop angle determination method**

A R&D Digidrop apparatus from GBX (Bourg de Péage, France) was used to perform the drop angle measurements with distilled water (Figure VI - 14). In IV.1, the measurements were performed directly on the compressed specimens and differences were observed within the results of one specimen, which was attributed to different surface porosity due to heterogeneity generated during filling of the mold. Thus, in IV.2, in order to avoid surface effect due to high pressure molding and also because homogeneity in the compressed material could not be guaranteed, the measurements were made on washed and ground powder recompressed in a basic IR tablet press. The analysis was kinetically measured thus initial water drop angle (\(t_0\)) and penetration time (\(t_{final}\)) were collected from the experiments and reported here.

![Figure VI - 14: Picture obtained with the Digidrop and used for drop angle measurements in chapter IV](image)

**Degree of substitution (cellulose) and grafting rate measurements**

The method was derived from Peydecastaing et al. (2009). The methylesterification transesterification was performed on a precise quantity of solid material (cellulose or miscanthus) by Trimethylsulphonium (TMSH) in Tertbutylmethyl (TBME). The reaction was carried out at 75°C for 1 hour in 2 mL vials stirred at 1200 rpm in a Vortemp 56 incubator from Labnet International (Edison, USA). After cooling and decanting, the supernatant was analyzed in a Varian 3900 gas chromatography from Agilent Technologies (Santa Clara, USA) and its FID detector. The separation is performed thanks to a CP select CB column. Helium as carrier gas had a flow of 1.2 mL/min. Injector temperature and detector were set to 260°C, oven temperature to 110°C stable for 4 minutes and a 15°C/min slope to 230°C and a final plateau at 230°C for 7 minutes. Detector gasses had flow rate of 25, 30 and 300 mL/min for helium, hydrogen and air respectively. 1 µl of supernatant sample is injected. For comparison and for the need of figure’s drawing, the grafting yield (GR) was first calculated as the millimole number of OA divided by the mass of tested grafted material (cellulose or miscanthus, in kg) using the following equation:
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\[
GR = \frac{10^6 \times C_{GC} \times V_{\text{standard}}}{m_{\text{specimen}} - C_{GC} \times V_{\text{standard}} \times (M - 18.02)} \text{(mEq\text{acetic acid}/kg)}
\]

wherein:
- \(C_{GC}\) is the concentration of OAME after transesterification determined by GC peak integration in mol.L\(^{-1}\).
- \(V_{\text{standard}}\) the internal standard volume added to the sample in L, 500 µL were injected in each vial,
- \(m_{\text{specimen}}\) the solid test specimen mass in g,
- \(M\) the molar mass of OA in g.mol\(^{-1}\) and
- 18.02 the molar mass of H\(_2\)O lost during the transesterification reaction.

Secondly, for cellulose samples, the degree of substitution (DS) was calculated using the following equation:

\[
DS = \frac{162.14 \times C_{GC} \times V_{\text{standard}}}{m_{\text{specimen}} - C_{GC} \times V_{\text{standard}} \times (M - 18.02)}
\]

wherein:
- 162.14 is the cellulose monomer molar mass.

Duplicate vials were prepared from the same sample and 2 injections were performed for each vial. The mean of 4 obtained values was made and the standard deviation was calculated to evaluate reproducibility.
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