Hydrophobic Cellulose-based Materials Obtained by Uniaxial High Pressure Compression: *In-situ* Esterification with Fatty Acids and Fatty Anhydrides

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High-pressure molding at an elevated temperature was investigated as a potential technique for performing the esterification of octanoïc acid and octanoïc anhydride on cellulose and miscanthus. Emulsion, solvent exchange, and high-pressure homogenizer pretreatments were performed on the reactants in order to improve liquid-solid contacts. After pretreatment, cellulose or miscanthus and octanoïc acid or octanoïc anhydride were molded at 220 MPa and an elevated temperature. The mechanical properties of the resulting compressed materials were measured, and the material was then ground and washed; the water drop angle was measured, and IR analysis was performed, as well as an accurate measure of the degree of substitution. The esterification reaction was confirmed, the water properties of the grafted cellulose were modified, and the mechanical properties of the modified materials were altered. From this pioneering work, a better understanding of the effect of the molding process on the reaction and production of water-resistant compressed cellulose materials was developed.

INTRODUCTION

The need for new materials from renewable origins is a rising concern for modern researchers. Cellulose, the most abundant polymer on the planet, is moldable using different techniques, *e.g.*, pulping and evaporation processes in the paper industry, solubilization processes (Fink *et al.* 2014) which are industrially viable, but also some processes still under development: nanofibrillation (Nogi *et al.* 2009) and high-pressure molding (Pintiaux *et al.* 2013). The interest in high-pressure molding is a result of the single thermo-compression step and the short processing times required (a few seconds) to turn cellulose powder without modification or additives into bulk objects of various shapes. Since the first stages of the research, the water resistance of the molded cellulose products was a huge obstacle for the development of this technique; therefore, the need for techniques to waterproof these kinds of materials is great. The grafting of hydrophobic side chains onto the cellulose backbone has been reported to modify its behavior against water, achieving hydrophobicity (Peydecastaing *et al.* 2011). The concept in the present research is to perform the esterification reaction at the same time that the cellulose is being molded during the thermo-compression step, *i.e.* in heterogeneous phase.

Cellulose chemical modification has been extensively studied in the last decades for various purposes: wood treatment (Hill 2006), composites reinforced with cellulosic fibers (George *et al.* 2001) or cellulosic nanocrystals (Espino-Pérez *et al.* 2014; Boujemaoui *et al.* 2015), membranes functionalization (Liebert and Heinze 2005), *etc*. Regarding esterification, cellulose can be esterified under homogeneous phase conditions, which require its solubilization and inevitably lead to some degradation, but this remains the most efficient method (Tkacheva *et al.* 2013). The most widely known application of such solution-phase esterification is cellulose acetate, a bio-based thermoplastic material (Steinmeier 2004). To achieve hydrophobation, the use of fatty compounds from vegetable oil makes it possible to produce fully renewable materials. A degree of substitution of 3 can be achieved and when the DS is about 1 and over, and by this means thermoplastic behavior is imparted to the modified cellulose (Vaca-Garcia *et al.* 2003; Crépy *et al.* 2011). Under heterogeneous phase condition, the esterification performed by acyl chloride associated to pyridine to capture the hydrochloric acid or the use of cyanates or anhydrides are reference methods (Bras *et al.* 2007). As far as the thermo-compression step is concerned, the focus was placed on keeping the process a single step without washing of the molded objects; thus, harmful chemicals cannot be used, and only the anhydride methods has been considered compatible. It was also decided to evaluate the possibility of grafting the acid directly despite its much lower reactivity.

This article thus reports the investigation of a one-step thermo-compression molding process applied to cellulose added with fatty acid and anhydride acid in order to mold objects from cellulose powder, perform the reaction during the molding step and finally produce increased hydrophobic properties. Because of the very specific scope of this research, the authors recommend reading about the thermo-compression molding process (Pintiaux *et al.* 2013).

EXPERIMENTAL

Materials

Lauric acid, α-cellulose, and potassium hydroxide were purchased from Sigma Aldrich (Saint Quentin Fallavier, France). Miscanthus (*Miscanthus sinensis*) was purchased from Burlerrow Farm (Bodmin, UK), ground on a 250-μm screen in a Pulverisette 15 grinder from Fritsch (Idar-Oberstein, Germany), and manually sieved using 150-μm mesh to obtain a fine and homogeneous powder. Octanoïc acid (OA) with a purity greater than 98% was purchased from Alfa Aesar (Schiltigheim, France). Octanoïc anhydride (OAn) with a purity greater than 95% was purchased from TCI (Zwijndrecht, Belgium). Potassium laurate was produced from the mixing of lauric acid heated to 80 °C with a $1.59 * 10^{-2}$ M aqueous potassium hydroxide solution, followed by vacuum drying at 50 °C. Potassium laurate has been described as a catalyst for the esterification of cellulose (Peydecastaing *et al.* 2005). 2% 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 for the rest of this paper.

Methods
Experimental scheme

Figure 1 presents a summary of the experiments run for the study reported in this paper, for which details are available in the rest of this section: Cellulose powder (or

miscanthus) was pretreated in order to increase the contact with OA / OAn following several methods that are presented later. The centrifuged cellulose powder added with OA / OAn was thermo-molded in order to obtain a solid material, which was tested in 3 points bending. The broken specimens are then ground, washed, and dried, which gives a potentially esterified powder that was analyzed in GC in order to measure the grafting yield, and recompressed in small tablets, whereon water drop penetration tests were run in order to qualify the hydrophobic behavior of the powder that had been grafted.
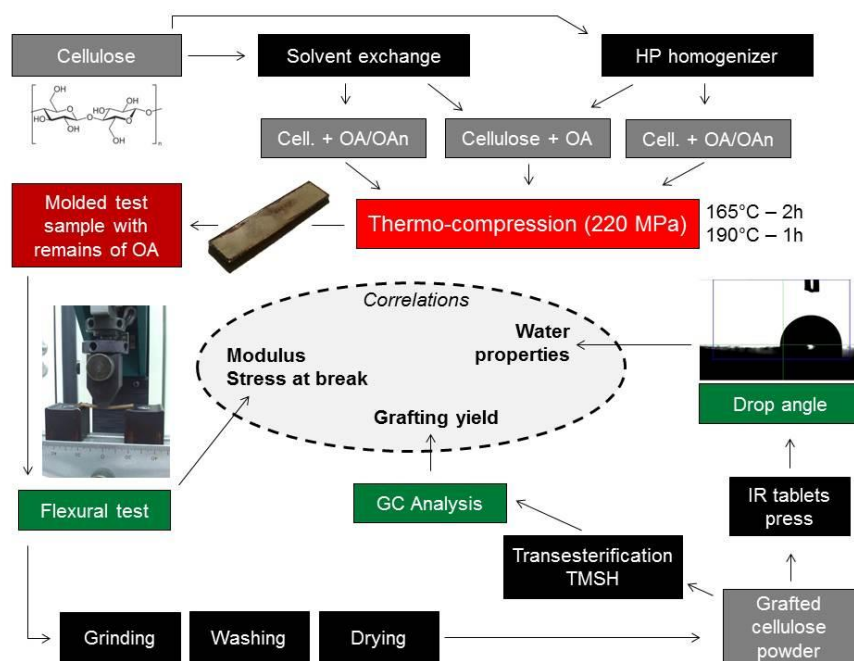

Fig. 1. Simplified experimental flowchart (only the most significant modalities are presented)

Miscanthus fibers analysis

The method used for determining the composition of cellulose, hemicellulose, and lignin in miscanthus was developed by van Soest and Wine (1967), and is better known as the ADF/NDF method (van Soest and Wine 1967). The fiber constituents of the miscanthus were determined to be 52.1% cellulose, 24.8% hemicellulose, and 15.4% lignin, on a dry weight basis.

Liquid solid separation

A 6-16K model centrifuge equipped with a 12500 model rotor from Sigma Laborzentrifugen GmbH (Osterode am Harz, Germany) was used at 18 °C and 10000 g for 15 min to enable liquid-solid separation. A 100-micron 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 the cellulose/miscanthus and the reactants after phase separation was a solid, slightly less pulverulent powder, the weight of which consisted of roughly 30% reactants adsorbed on the powder. The precise composition of material entering the mold was not measured due to the number of transfer steps during the pretreatments. In addition, at the beginning of the compression step, liquid was extracted from the solid material and leaked onto the press plates. Thus, the liquid-solid ratio during the molding step was not determined.

Emulsion pretreatments

The solid material was emulsified with water and grafts (Peydecastaing *et al.* 2005) using an L4RT high shear mixer from Silverson (East Longmeadow, MA, USA) in order to increase the water content of the cellulose and test the emulsion contact method between cellulose and OA. 200 g of OA and 83 g of water were mixed together and emulsified at 7000 rpm for 15 min, then 10 g of cellulose was progressively added.

High-pressure homogenizer

20 g of cellulose were suspended in 2 L of distilled water and introduced progressively into an APV 1000 high-pressure homogenizer from APV (Albertslund, Denmark). The first pass was performed at relatively low pressure (average 40 bar, not constant); the second pass pressure was increased to 100 bar, the third pass pressure was increased to 400 bar, and three 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 six 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 h, filtered and washed twice with ethanol (160 mL of ethanol were used per wash), stirred in ethanol for 5 min, and successively washed twice in about 80 mL of the desired reactant (OA or OAn). Cellulose was left to stir in the last reactant bath for 5 min. The solvent-exchanged cellulose was then filtered using a Buchner set-up and centrifuged at 18 °C and 10000 g for 15 min.

High-pressure molding

A 10-ton-force, thermoregulated manual pressing machine from Pinette-Emideceau (Chalon sur Saone, France) with a 45 * 10 mm custom-designed mold machined by Cristin Electro Erosion (Grisolles, France) was used to perform the high-pressure moldings. The pressure capacity of the press was at its maximum, so molding pressure in these conditions was about 220 MPa. For each molded specimen, 1 g of material (cellulose or miscanthus with a certain unknown quantity of OA or OAn in it) was manually charged in the mold in the hot press with a preheated mold; after 1 or 2 h of experimentation, the material was manually unloaded without a cooling step.

Preliminary results based on IR measurement (data not shown) indicated that no grafting was possible unless quite drastic molding conditions were used. Two molding conditions were tested in each experiment for comparison; the first condition was a rather low temperature (165 °C) and a 2 h duration, while the second condition was a higher temperature (190 °C) and shorter molding time (1 h).

Reactant removal prior to analysis

Powders (generated using a small kitchen grinder) from molded specimens were washed using a 1 L Soxlhet extractor from VWR (Fontenay sous Bois, France) for 8 h in technical ethanol using small filter paper bags in order to eliminate the non-grafted reactants from the solid. After washing, the filter paper bags were left to evaporate for 24 h at 70 °C to remove the solvent, and the washed powder was recovered.

IR analysis

A Fourier transform infrared (FTIR) spectrophotometer model Spectrum 65 from Perkin Elmer (Courtaboeuf, France) was used for obtaining IR spectra; acquisition was

performed from 400 to 4000 cm^{-1}. Grafted and washed cellulose powder tablets were produced using a manual screw press (without KBr). IR analysis was used to track esters in early preliminary results (data not shown) and for all the cellulose grafting experiments shown in this paper. Under adequate conditions (for instance OA_homo_exch_190_1 or OAn_exch_190_1), ester bands (1724 cm^{-1}) appeared on the spectra. Some examples are presented in Fig. 2. As for miscanthus, the starting material already showed ester bands, as expected, which would overlap with esters resulting from grafting. Thus, IR spectra were not performed in the miscanthus grafting experiments (ND for non-determined appears in the corresponding lines in Table 1).
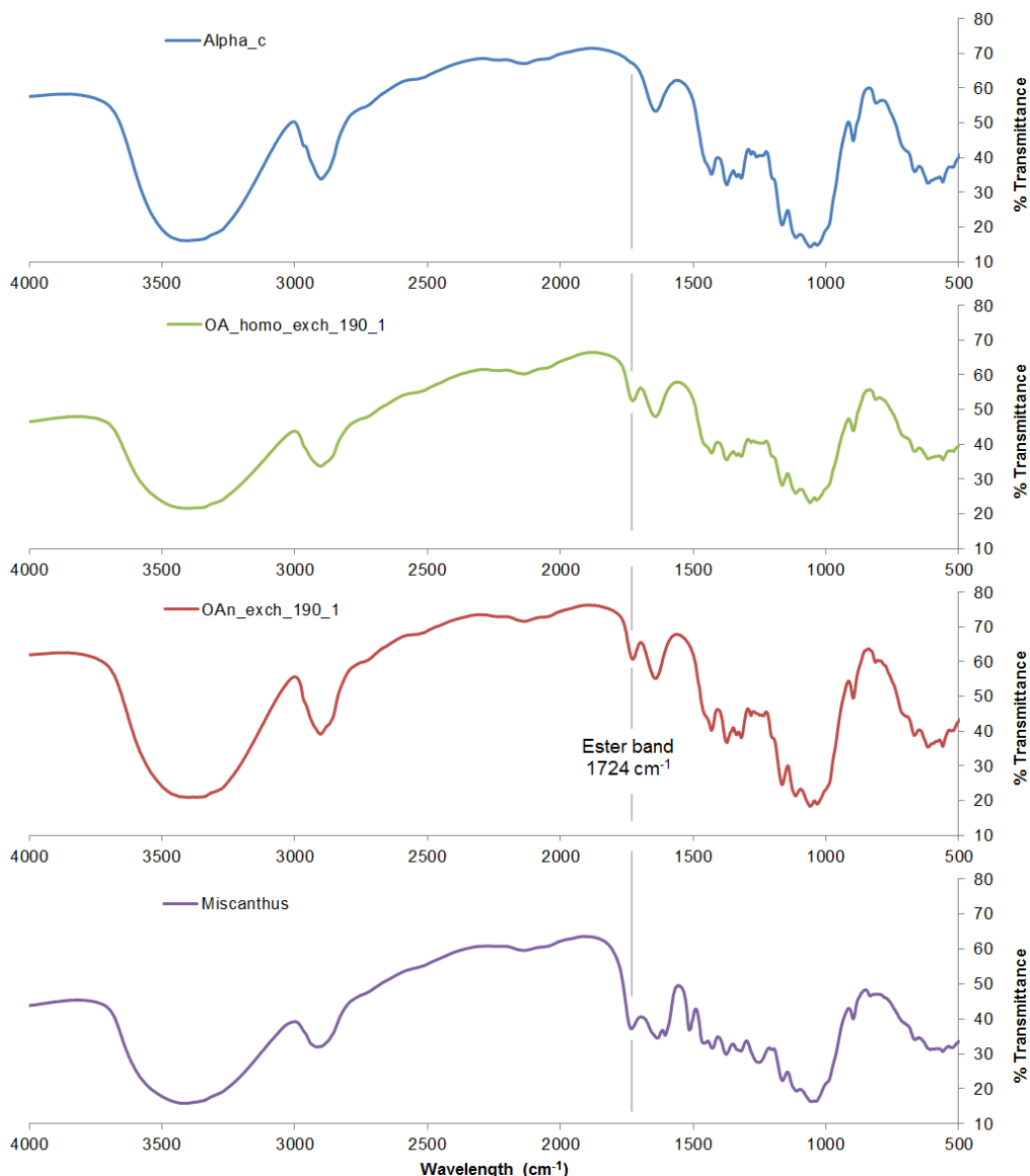
Fig. 2. FTIR spectra of washed powders with ester band appearing at 1724 cm^{-1}

Drop angle determination method

An R&D Digidrop apparatus from GBX (Bourg de Péage, France) was used to perform the drop angle measurements with distilled water. To avoid surface effects due to

high-pressure molding and to account for the fact that homogeneity in the compressed material could not be guaranteed, the measurements were made using washed and ground powder recompressed in a standard IR tablet press. The analysis was kinetically measured; thus, initial water drop angle (θ_0) and penetration time (t_{final}) data were collected from the experiments and reported here.

Degree of substitution (cellulose) and grafting rate measurements

This method was derived from Peydecastaing *et al.* (2009). The methyl ester transesterification was performed on a precisely weighted quantity (30 to 40 mg) of solid material (cellulose or miscanthus) by trimethylsulfonium (TMSH) in tertbutylmethylether (TBME). The reaction was carried out at 75 °C for 1 h, 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 chromatograph from Agilent Technologies (Santa Clara, USA). The separation was performed using a fused silica capillary column CP7419 model (50 m, 0.25 µm internal diameter, 0.25 µm film thickness) from Agilent Varian (Santa Clara, USA) specially designed for FAME (fatty acid methyl esters). Helium was used as a carrier gas at a flow rate of 1.2 mL min^{-1}. Injector and detector temperatures were set to 260 °C. The oven temperature was set to 110 °C and remained stable for 4 min before it was increased at a rate of 15 °C min^{-1} to 230 °C, where it was left to plateau for 7 min. Detector gases had flow rates of 25, 30, and 300 mL min^{-1} for helium, hydrogen, and air respectively. 1 µL of supernatant sample was injected. The grafting yield (GR) was calculated, using Eq. 1, as the number of millimoles of OA divided by the mass of the tested grafted material (cellulose or miscanthus) in kg. For cellulose samples, the degree of substitution (DS) was calculated using Eq. 2,

$$GR = \frac{10^6 \times C \times V}{m - C \times V \times (M - 18.02)} \quad \text{(mEq}_{OA}\text{ kg}^{-1}) \tag{1}$$

$$DS = \frac{162.14 \times C \times V}{m - C \times V \times (M - 18.02)} \quad \text{(no dimension)} \tag{2}$$

where C is the concentration of octanoïc acid methyl ester (OAME) in mol L^{-1} after transesterification (determined by the GC peak integration), V is the internal standard volume added to the sample in L (500 µL were injected into each vial), m is the solid test specimen mass in g, M is the molar mass of OA in g mol^{-1}, 18.02 is the molar mass of H$_2$O in g mol^{-1} lost during transesterification reaction, and 162.14 is the molar mass of cellulose monomer in g mol^{-1}.

Duplicate vials were prepared from the same sample, and two injections were performed for each vial. The mean of four obtained values was determined, and the standard deviation was calculated to evaluate reproducibility.

Mechanical properties

Bending strength and moduli were measured on hot-pressed specimens in an H5KT universal testing machine from Tinius Olsen (Surrey, England). The mechanical properties were measured on three specimens, and the mean and standard deviation were then calculated.

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RESULTS AND DISCUSSION

List of Experiments

Eleven different experimental conditions were tested to evaluate the possibility of grafting OA and 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."

RESULTS

Table 1 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.

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Table 1. Summary of Results

Experiment code	Material	Pretreatment	Graft	Temp (°C)	Time (h)	Drop angle θ_0 (°)	Absorb. time t_{final} (s)	IR peak 1724 cm^{-1}	GR Mean (mEq$_{OA}$ kg^{-1})	GR St. dev.	DS Mean	Modulus Mean (MPa)	Modulus St. dev.	Strength Mean	Strength St. dev.
Alpha_c	α Cellulose	none	none	none		N/A		-	0.03	0.05	5.3E-06	N/A			
				165	2	49	7	-	0.02	0.02	2.7E-06	4387	539	35.3	3.8
				190	1	49	5	-	0.03	0.04	5.1E-06	4757	1484	33.1	11.3
Emul	α Cellulose	OA-water emulsion	OA	none		N/A		-	2.7	0.2	4.3E-04	N/A			
				165	2	57	12	-	5.1	0.4	8.3E-04	1489	320	6.7	1.2
				190	1	52	79	-	12.3	0.7	2.0E-03	677	436	3.1	1.6
OA_exch	α Cellulose	Solvent exchange	OA	none		N/A		-	4.2	0.1	6.8E-04	N/A			
				165	2	50	16	+	48	3	7.8E-03	3742	600	17.6	0.4
				190	1	50	18	+	34	2	5.5E-03	3033	605	11.7	0.5
OA_exch_pH	α Cellulose	Solvent exchange at pH2 (water step)	OA	none		N/A		-	5.0	0.3	8.1E-04	N/A			
				165	2	54	74	+	125	36	2.0E-02	3025	112	19.8	4.1
				190	1	48	5	+	78	3	1.3E-02	3448	86	22.7	1.0
OA_exch_pH_6	α Cellulose	Solvent exchange at pH2 (water) + 6h in OA	OA	none		N/A		-	3.0	0.2	4.9E-04	N/A			
				165	2	64	12	+	170	10	2.8E-02	2707	854	19.2	2.3
				190	1	67	39	+	171	13	2.8E-02	2781	863	21.5	6.3
OAn_exch	α Cellulose	Solvent exchange	OAn	none		N/A		+	274	11	4.4E-02	N/A			
				165	2	77	208	+	266	5	4.3E-02	2724	118	16.7	1.7
				190	1	77	492	+	297	26	4.8E-02	1918	100	11.5	1.4
OA_homo	α Cellulose	HP-Homogeneizer (in OA)	OA	none		N/A		-	1.0	0.5	1.6E-04	N/A			
				165	2	58	65	-	16.0	0.4	2.6E-03	3510	1182	22.2	4.0
				190	1	41	17	-	12.8	0.7	2.1E-03	3108	395	20.5	6.2
OA_homo_exch	α Cellulose	HP-Homogen. (in water) + Solvent exchange	OA	none		N/A		-	7.2	0.2	1.2E-03	N/A			
				165	2	63	102	+	207	10	3.4E-02	2622	255	12.5	1.2
				190	1	73	88	+	241	13	3.9E-02	2259	519	10.8	2.8
Mis	Miscanthus	none	none	none		N/A		+	3.9	0.4	N/A	N/A			
				165	2	81	5	ND	2.18	0.03	N/A	4287	449	28.6	1.8
				190	1	78	17	ND	4.41	0.07	N/A	3537	370	26.1	2.6
Mis_OA_homo	Miscanthus	HP-Homogen. (in OA)	OA	none		N/A		ND	1.6	0.1	N/A	N/A			
				165	2	70	11	ND	16	6	N/A	4678	493	27.5	5.0
				190	1	72	2	ND	24	3	N/A	4516	385	29.0	6.0
Mis_OAn_homo	Miscanthus	HP-Homogen. (in OA) + OAn suspension	OAn	none		N/A		ND	21.9	0.3	N/A	N/A			
				165	2	83	153	ND	31.6	0.6	N/A	3736	339	20.4	2.5
				190	1	81	106	ND	39	3	N/A	3978	1106	15.0	1.5

(N/A: not applicable, ND: not determined)

The detection limit of the IR setup was between GR values of 16 and 34 mEq kg^{-1} (*i.e., a* DS value between $2.6 * 10^{-3}$ and $5.5 * 10^{-3}$), as can be 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 1 h 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 hours 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_c). 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.

DISCUSSION

Reports concerning heterogeneous modification of cellulose fibers in conditions comparable with the present study (soft chemicals and without solvents) either use heavy physical treatments (*e.g.* plasma, Cabrales and Abidi 2012) or did not bring significant proof of chemical modification (Dankovich and Hsieh 2007; Dong *et al.* 2013). In the present study, the maximum DS using a fatty anhydride was measured as being around $5 * 10^{-2}$, which is far lower than what can be obtained in optimal conditions for reaction with the nonanoic anhydride (presence of a catalyst, solvent, optimized reactor conditions : reactant excess – 4 Eq of reactant per anhydroglucose unit, 13 h, 160 °C), wherein a DS of 1.35 can be obtained (Heinze and Liebert 2001). Concerning fatty acids, few results have

been published with raw fatty acids, in most cases, the acid chloride path is used wherein the DS can reach values between 1 and 3 (Freire *et al.* 2006). However, the direct use of the fatty acid, which is a lot more eco-friendly has a limited reactivity, maximum DS of 0.23 is obtained (reactant excess – 2 Eq of reactant per anhydroglucose unit, 3 h, 195 °C, Peydecastaing *et al.* 2005).

In our study, even with the low GR and unusual conditions, 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 Fig. 3. The extrapolation of the linear regression indicated that hydrophobicity (evidenced by an angle > 90°) would have been obtained at a GR value of 370 mEq kg^{-1} (DS value of $6 * 10^{-2}$).
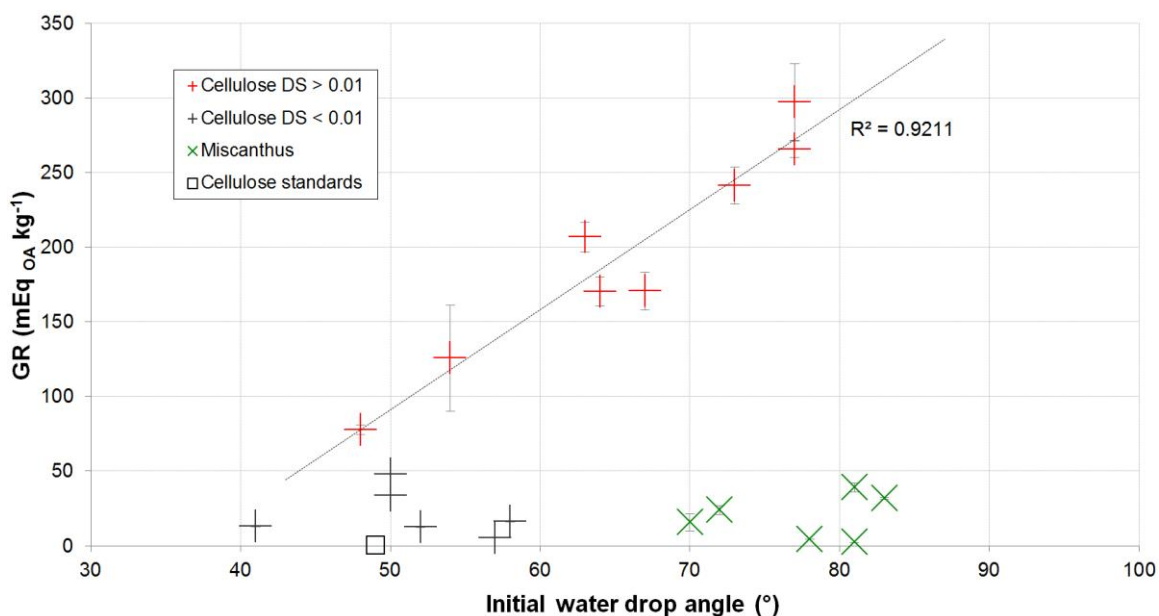

Fig. 3. Correlation between GR value and initial water drop angle of recompressed specimens.

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 $5 * 10^{-3}$ (C18 basis) was sufficient to induce an hydrophobic character. 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 the hemicellulose and lignin before their fractions that would have been grafted with OA/OAn 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 Fig 4, confirming that higher GR values were correlated with a longer absorption time.
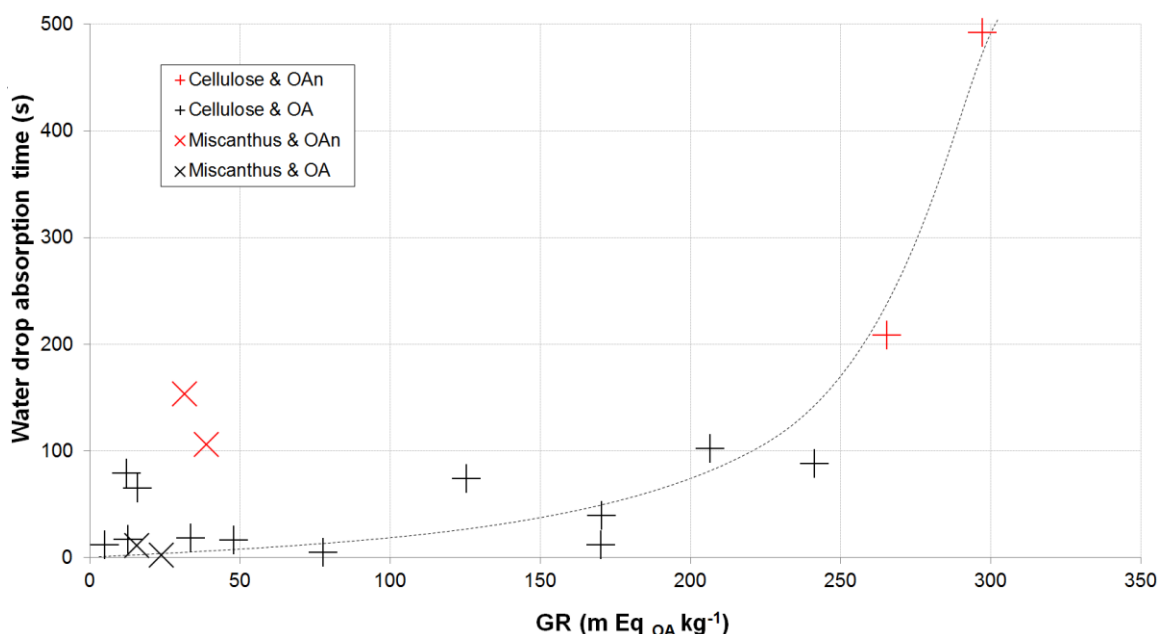
Fig. 4. Starting material, grafted material, and comparison of the water drop absorption time on recompressed specimens

However, there was no correlation between the initial drop angle and absorption time (Table 1), 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 Fig. 4) produced longer absorption times than any other OA experiment.

From extrapolation of the data in Fig. 4, 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 Fig. 3 (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 Fig. 5 (correlation between the bending modulus and the GR value).

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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 1); 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.
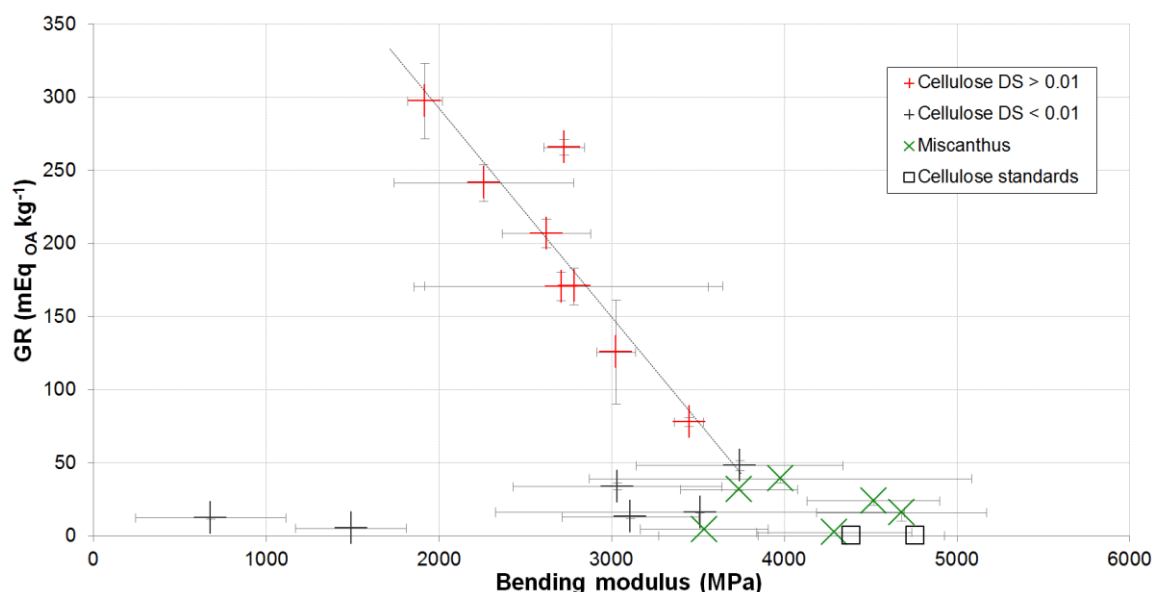

Fig. 5. The correlation between DS value and the bending modulus of compressed specimens

CONCLUSIONS

1. High-pressure compression molding was successfully used to perform the esterification of octanoïc 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 octanoïc anhydride instead of octanoïc 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 octanoïc anhydride, which should provide higher grafting yields.

3. Water properties were measured on ground and recompressed specimens. The water resistance of the specimens should be tested directly on the recompressed 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.

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