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Pressure impact of autoclave treatment on water sorption and pectin composition of flax cellulosic-fibres

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ABSTRACT

The tensile properties of flax fibres might permit them to be used in composites as reinforcement in organic resin, as long as their mechanical properties are reproducible and their water sorption are reduced. In this study, to minimise the variability of mechanical properties, several samples of flax fibres were blended as a non-woven fabric. In order to reduce the water absorption of this non-woven technical fibres, an autoclave treatment was performed which was expected to remove the pectins and then to reduce the water sorption on their negative charges. The impact of autoclave pressure (0.5, 1 and 2 bars) on water sorption was investigated by using a gravimetric static equilibrium method. The Park model based on the three sorption modes: Langmuir, Henry's law and clustering, was successfully used to simulate the experimental sorption data. The lowest pressure treatments impacted only the Langmuir contribution while the 2 bar autoclave-treatment positively impacted the water resistance in the core of fibres by reducing Henry's absorption rate. This was shown to be related to the chemical modifications at the surface and in the core of fibres. A schematic model is presented relating the water sorption and the pectic composition of the fabric.

1. Introduction

Renewable resources are currently used in order to reduce the impact of petroleum material on the environment. In composite material, natural fibres such as flax, hemp, jute, sisal and ramie could be used to replace synthetic fibres (Baley, 2002; Wambua, Ivens, & Verpoest, 2003). The use of natural fibres in organic matrices is beneficial because the strength and toughness of resulting composites are greater than those of the unreinforced materials (Gindl, Zargar-Yaghubi, & Wimmer, 2003). Moreover, cellulosic fibres are usually strong (high modulus), light in weight (low density), abundant and renewable (Mohanty, Misra, & Hinrichsen, 2000). The ratio price to mechanical performance in combination with the low density and the environmentally friendly character is of importance for the acceptance of natural fibres in large volume engineering-markets, such as automotive (Ashori, 2008), aeronautic (Soutis, 2005) and building industries (Herrmann, Nickel, & Riedel, 1998). One difficulty that has prevented the use of natural fibres is the lack of reproducibility of the mechanical properties and the moderate adhesion with polymeric matrices. In particular, the great moisture sorption of natural fibres adversely affects adhesion with hydrophobic matrices leading to premature ageing by degradation and loss of strength (Stamboulis, Baillie, Garkhail, Van Melick, & Peijs, 2000). Interfacial adhesion and resistance to moisture absorption of natural-fibre composites can be improved by treating these fibres with different treatments (Bledzki & Gassan, 1999). Most of the treatments were shown to induce a division and a cleaning of the surface of the technical fibres. Among the chemical treatments, the most used were alkali ones (Van de Weyenberg, Chi Truong, Vangrimde, & Verpoest, 2006). Other approaches included physical ones such as corona-discharge treatment (Ragoubi et al., 2012), helium cold-plasma treatment (Marais et al., 2005), biological ones with enzymatic treatments (Akin et al., 2007; Alix et al., 2012; Bledzki, Mamun, Jaszkiewicz, & Erdmann, 2010; Ossala & Galante, 2004; Saleem, Rennebaum, Pudel, & Grimm, 2008; Stuart et al., 2006) or physico-chemical ones such as steam-explosion treatment (Deepa et al., 2011; Kessler, Becker, Kohler, & Goth, 1998; Thomsen et al., 2006) and autoclave treatment (Marais et al., 2005; Stamboulis, Baillie, & Peijs, 2001). Van de Weyenberg et al. (2006) have shown that a NaOH treatment on flax fibres decreased their mechanical properties but increased the mechanical properties of a flax/epoxy composite due to an improvement of the quality of

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the interface between fibres and matrix. Alkali treatment removed impurities and waxy substances from the fibre surface and created a rougher topography. Mechanical properties of the composite were increased because the chemical bonding between the fibres and the matrix was enhanced by more hydrogen bonds formed between the epoxy matrix and the hydroxyl groups of cellulose on the purified fibre surface. Ragoubi et al. (2012) have applied a corona discharge on miscanthus fibres and observed a chemical oxidation and a physical etching inducing an increase of mechanical properties of miscanthus/PLA and miscanthus/PP composites. Enzymatic treatments were shown to remove surface impurities of surface fibre and to improve the division of fibre bundles and increase the fineness as shown by Akin et al. (2007), Alix et al. (2012), Ossala and Galante (2004), Stuart et al. (2006) on flax, Bledzki et al. (2010) on abaca and Saleem et al. (2008) on hemp. Steam explosion (STEX) appeared to have similar effects than enzymatic treatments: scouring of fibres and division of fibre bundle, by temperature and pressure. Kessler et al. (1998) have applied a STEX treatment on flax fibre and observed degumming, defibrillation and partial cellulose decomposition. Similar results have been obtained by Thomsen et al. (2006) on hemp fibres and by Deepa et al. (2011) on banana fibres. On the other hand, Stamboulis et al. (2001) compared the water sorption properties and zeta potential of non-retted flax fibres and the commercially available autoclave-treated "Duralin" fibres. In this Duralin technical-fibres, a primary depolymerisation of hemicelluloses and lignins occurred after 30 min treatment at 160 °C; then, the aldehyde and phenolic functionalities were possibly linked by the post-curing at 150 °C. Such chemical remodelling was reported to explain the lower water-sorption of Duralin compared to green fibres.

In some previous studies of our laboratory (Gouanvé, Marais, & Bessadok, 2006; Gouanvé, Marais, Bessadok, Langevin, & Métayer, 2007, Marais et al., 2005), a 2 bar autoclave-treatment (during 30, 60 or 90 min) was performed, but instead of the post-curing at 150 °C, the treated fibres were abundantly washed in water in order to remove the polymer fragments. A significant decrease of the water sorption was observed and the hypothesis was raised that cell-wall structure of fibres might have been altered. It is known that the presence of pectins in the primary and secondary walls of fibres increased their cation exchange capacity and water sorption (Morvan, Abdul Hafez, Morvan, Jauneau, & Demarty, 1989). In the present work, we examined how the autoclave treatments have impacted the pectin composition of the flax fabric and subsequently affected the water sorption. A decrease of the technical-fibre diameter would impact the water sorption on two ways; Firstly, the Langmuir contribution would increase at low water activity, because the ratio between the surface area and the volume of fibres was increased so as higher water amount was adsorbed at the surface of the fibres. Secondly, the extraction/removal of pectins by the treatment would reduce the water aggregation at high water activity, and consequently decrease the total water sorption (Alix et al., 2012). The autoclave treatments were performed on the same flax non-woven technical fibres but using different pressures (0.5, 1 and 2 bars). Similarly, the fabrics were washed in water after the autoclave treatment before measuring the sorption properties. As a conclusion, a schematic representation of the impact of autoclave treatment in structure of fibres is proposed.

2. Material and methods

2.1. Non-woven flax fibres

The flax fibres used in this work were provided in tow form by the cooperative "Terre de lin" (Fontaine-le-dun, France). A non-woven fabric was prepared by "dry laying" at the Ecole Industrielle de Rouen (Rouen, France) as previously described (Marais et al., 2005).

2.2. Autoclave treatment

An autoclave treatment was carried out on the non-woven fabric as previously described, using wet fabric to prevent the carbonisation (Marais et al., 2005). The treatment was run during 30 min at three different pressures (0.5 bar at 112 °C; 1 bar at 120 °C; 2 bars at 134 °C).

2.3. Fibre morphology

The morphology of flax non-woven was analysed by scanning electron microscope (SEM). The shape and size of untreated and treated fibres were observed with a Hitachi Table top Microscope TM 3000. In order to observe the impact of autoclave treatment on the fibre surface, untreated and treated fibres was marked by calcofluor. When soaked in calcofluor White M2R (Sigma–Aldrich, 0.01%, w/v), a fluorescent probe which interacts with cellulose, the microscope was coupled with a Zeiss filter set (excitation filter, 350–410 nm wavelength; barrier filter, 470 nm wavelength).

2.4. Water-vapour sorption

A dynamic gravimetric vapour-sorption (DVS, Advantage 1 instrument; Surface Measurement Systems, London, United Kingdom) was used to gravimetrically measure the uptake of water, using a recording ultramicrobalance with a mass resolution of ±0.1 μg (Alix, Philippe, et al., 2009). The samples (≈5–20 mg) were exposed to the following RH profile: 0–5% RH in 2.5% RH increments, 5–20% RH in 5% RH increments, 20–90% RH in 10% increments and 95% RH. Mass equilibrium was reached at each humidity level by measuring the percent mass change with respect to time (i.e. slope or dm/dt). The values of water content at equilibrium were used to deduce the sorption isotherm using the relationship between water activity a_w (with $a_w = p/p_{sat}$, the ratio of pressure p to saturation vapor pressure p_{sat}) and the equilibrium moisture content M. M was defined by the ratio of the difference between wet and dry mass to dry matter mass:

$$M = \frac{M_{w(eq)} - M_d}{M_d} \quad (1)$$

where $M_{w(eq)}$ was the mass of the wet sample at equilibrium state and M_d the dry mass.

The Park model was used to correlate model parameters to physical characteristics (Park, 1986). This model is expressed by the relation 2:

$$M = \frac{A_L \cdot b_L \cdot a_W}{1 + b_L \cdot a_W} + k_H \cdot a_W + n \cdot k_H^n \cdot k_a \cdot a_W^n \quad (2)$$

with A_L the Langmuir capacity constant, b_L the Langmuir affinity constant, a_W the water activity, k_H the Henry's solubility coefficient, k_a equilibrium constant for the clustering reaction and n the mean number of water molecules per cluster.

To evaluate the goodness of the fit of each model, the mean relative percentage deviation modulus (E') was calculated by the following relation:

$$E' = \frac{100}{N} \cdot \sum_{i=1}^{N} \frac{|m_i - m_{pi}|}{m_i} \quad (3)$$

where m_i is the experimental value, m_{pi} is the computed value and N is the number of experimental points.

According to Lomauro, Bakshi, and Labuza (1985) a modulus value below 10% reveals a good fit.

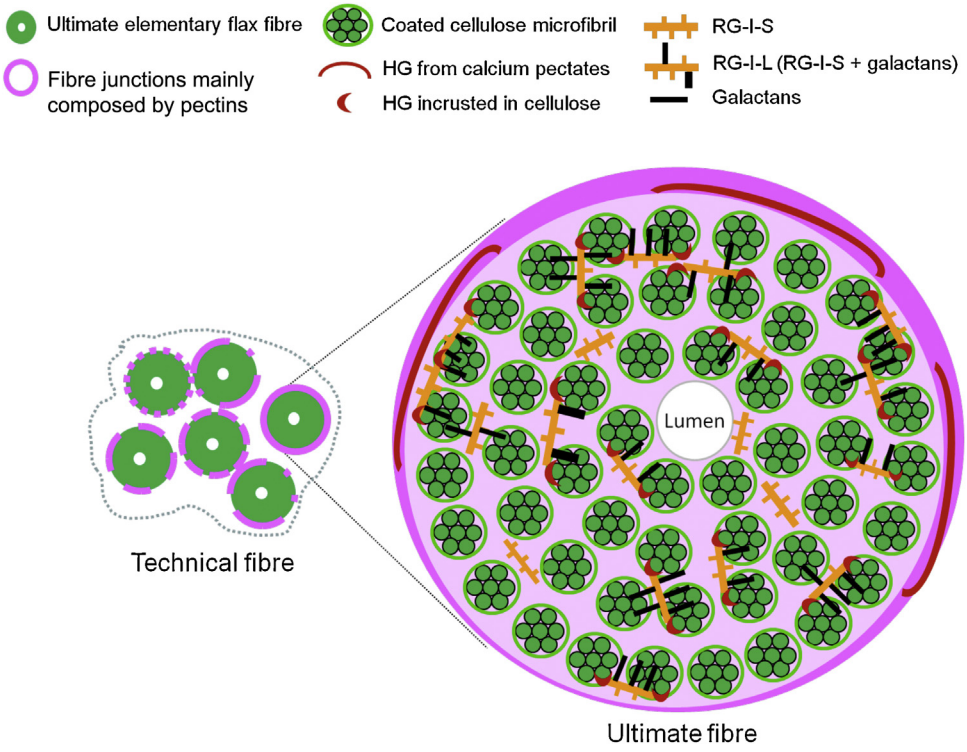

Fig. 1. Schematic representation of macrostructure of technical fibres and microstructure of elementary fibres of flax inspired by Alix et al. (2008).

2.5. Pectin composition of flax fibres

In the stem, flax fibres are located between the cortical parenchyma and the xylem. Organised in bundles within strands that overlap the length of the stem, elementary fibres are glued together by an interphase (the middle lamella) consisting mainly of pectins, a mixture of different branched (namely rhamnogalacturonan, RG) and linear (such as homogalacturonan, HG) polysaccharides (Fig. 1). Elementary fibres are single plant cells which consist at maturity of a so-called lumen made of residual cell-organites in the centre of the fibre, surrounded by two walls, a thin primary-wall and a thick secondary cell-wall. Both cell walls consisted of a composite-like material composed mainly of cellulose, hemicelluloses and pectins (Morvan et al., 2003). The cellulose crystallites in the secondary cell wall are laid down in oriented, highly crystalline microfibrils which are glued together by the amorphous hemicellulose/pectic matrix. The pectins from the most external cell-wall layers consisted of HG and RG-I with short side chains of galactose (designated as RG-I-S) while those located in the heart of the fibres consisted mainly of rhamnogalacturonan with longer side chains of galactose (Gorshkova & Morvan, 2006; Morvan et al., 2003). Depending on the variety the galactan polymerisation-degree was comprised between 5 and >10. The RG-I moieties were then designated as RG-I-L.

A schematic representation of macrostructure of technical fibres and microstructure of elementary fibres of flax are presented in Fig. 1. To determine the pectin composition of flax fibres, different extractions were successively run, as summarised in Table 1. After each extraction, two additional water washings/treatments were run. The two water solutions were collected and gathered with the corresponding extraction before characterisation of the liquor.

Water extraction at room temperature (EA) solubilised the components that were not linked anymore to fibres, as retting products and residues of degraded epidermis/cuticle. Boiling water (EB) extracts contained essentially pectins of residual cortical parenchyma. EDTA-Na_2(EC) extracts pectins from the surface of fibres, namely the middle lamella and partly from the primary cell-wall. In normally retted fibres, all these 3 extracts contained both HG and RG-S in various proportions (Goubet et al., 1995). The HCl extraction (EH) released the pectic matrix of the secondary wall, which encrusted the cellulose microfibrils (Charlet et al., 2007). The extract contained RG-L with a ratio Gal/Rha < 10. Depending on the variety, a certain proportion of RG-L remained associated to the cellulosic residue because a DP > 10 allowed hydrogen interactions with the cellulose microfibrils (Alix, Goimard, Morvan, & Baley, 2009).

Total sugars and galacturonic acids were colorimetrically assayed (Blumenkrantz & Asboe-Hansen, 1973; Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) and sugar composition determined after methanolysis and silylation and separation by gas chromatography as previously described (Goubet et al., 1995).

The following sugars (galactose (Gal), arabinose (Ara), rhamnose (Rha) and galacturonic acid (GalU)) were taken as representative of pectins. As reported above, two types of pectins were defined:

Table 1
Successive extractions for the determination of fibre pectin-composition.

Liquor code	Extraction	Concentration	Temperature	Time	Washing after extraction
EA	H_2O	–	25 °C	15 min	H_2O 2 × 15 min 25 °C
EB	H_2O	–	100 °C	1 h	H_2O 2 × 30 min 100 °C
EC	EDTA, Na_2	7.5×10^{-3} M	100 °C	1 h	H_2O 2 × 30 min 100 °C
EH	HCl	1.6×10^{-2} M	100 °C	1 h	H_2O 2 × 30 min 100 °C

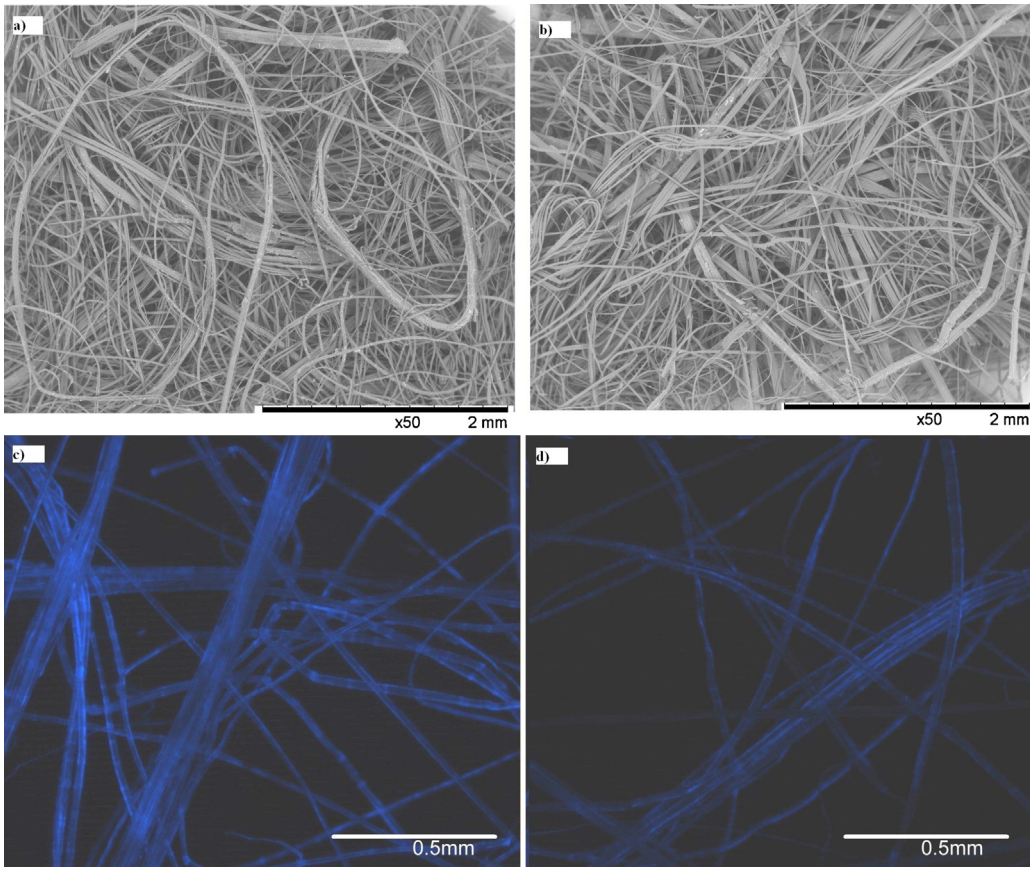

Fig. 2. Microscopic surface aspects of non-woven flax-fabrics. (a and c) Untreated samples, (b and d) 2-bar autoclave-treated samples. (a and b) Scanning electronic microscopy, (c and d) fluorescence microscopy after calcofluor staining of the samples.

rhamnogalacturonans and homogalacturonans. A rhamnogalacturonan of type I (RG-I) whose backbone consisted of the repetition of the dimer 2-Rha-1,4-GalU (calculated as 2 times the amount of Rha). RG-I comprised side chains (made of Gal and Ara) branched on Rha. The ratio between the amount of galactose (Gal) and rhamnose (Rha) represented the DP of the galactan side chain of RG-I. When the ratio was $\leq$3, the side chains were defined as short and the RG-I designated as RG-I-S (Girault et al., 1997). When the ratio was $\geq$3, side chains were considered long and the RG-I defined as RG-I-L (Zykwinska, Ralet, Garnier, & Thibault, 2005). The second type of pectin consisted of a homopolymer made of GalU and named homogalacturonan (HG) whose amount was estimated as GalU–Rha.

3. Results

3.1. Impact of treatments on fibre morphology

The fibre mats observed in scanning electronic microscopy did not show any major impact of 2-bar autoclave-treatment at the surface of the samples at least at the used scale (Fig. 2a and b). On the other hand, when the samples were observed in optical microscopy after staining with calcofluor that usually binds cellulose, the non treated sample seemed more contrasted than the A2 treated one (Fig. 2c and d). Interestingly, whatever the conditions, the highest in the particular zone designated as knees.

Besides, when the diameter of the elementary fibres was estimated, not much difference was found between the untreated (average diameter at 16.2 ± 5.2 μm) and the A2 samples (average diameter at 15.5 ± 5.5 μm) while after washing the smallest diameter fibres would be more frequent in A2 than in the non treated sample (Fig. 3).

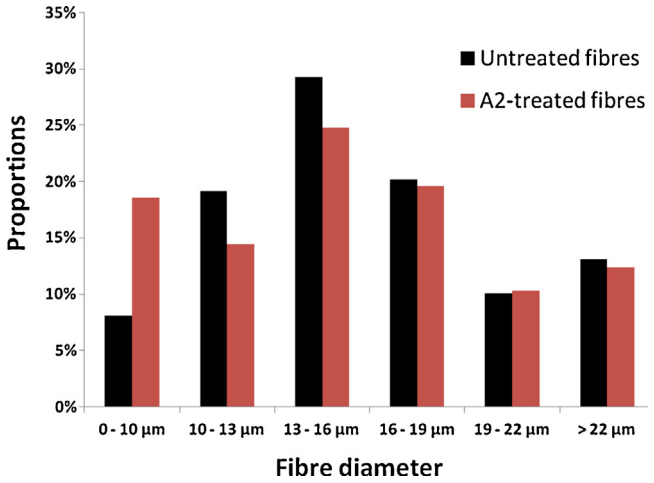

Fig. 3. Distribution of diameters of elementary fibres from untreated and A2-treated samples (100 diameters were measured from SEM micrographs for each untreated and A2-treated samples).

3.2. Water sorption isotherms

The water-sorption isotherm-curves were deduced from water sorption kinetics, and presented for untreated and autoclave-treated fibres in Fig. 4. As previously described for cellulosic fibres (Gocho, Shimizu, Tanioka, Chou, & Nakajima, 2000) including flax

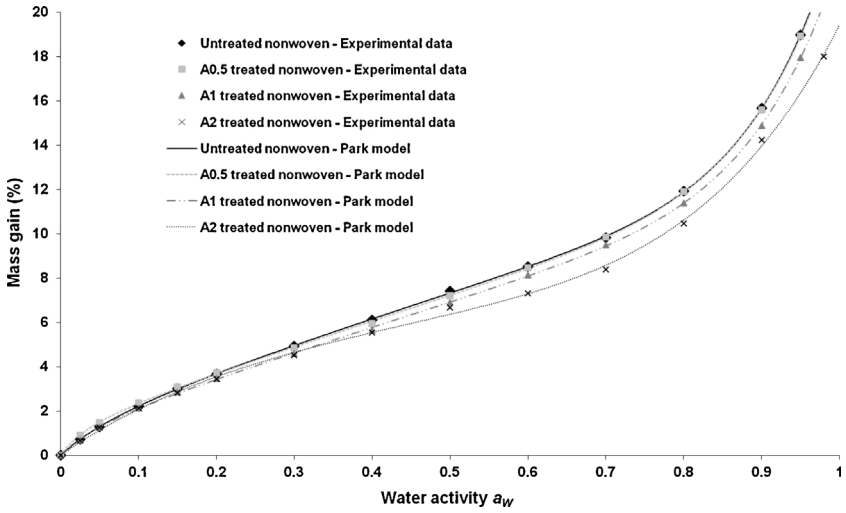

Fig. 4. Water sorption isotherm and Park model representation of untreated and treated flax fibre nonwoven.

Table 2
Sorption parameters of Park model determined from water sorption isotherm of untreated and treated flax fibres.

Park parameters						
Constants	A_L	b_L	k_H	k_a	n	E'
Untreated	2.3	10	10.8	5.2×10^{-11}	10.0	0.5
A0.5 treated	1.7	24	11.3	6.1×10^{-11}	9.8	1.1
A1 treated	1.6	17	10.9	8.9×10^{-11}	9.7	1.4
A2 treated	3.5	6	7.6	1.4×10^{-9}	10.2	2.5

(Gouanvé et al., 2006), all these curves had a sigmoid or S-shape profile and corresponded to type II of the classification of BET sorption. The moisture resistance was shown to increase with the pressure used during the autoclave treatment, especially at 1 and 2 bars.

In order to better understand the impact of each treatment, water sorption isotherms were fitted by the Park model and three series of parameters were characterising the water sorption of fibres in three water activity domains (Detallante et al., 2001). The low values (<10) of the deviation modulus, E', calculated between the theoretical and experimental points (Table 2), reveal the very good fitting of experimental data.

Langmuir's terms, A_L (Langmuir capacity constant) and b_L (Langmuir affinity constant) calculated at low water activity ($a_W < 0.2$), took into account the first layer of water molecules adsorbed at the fibre surface, on hydrophilic groups or within micro-cavities. Henry's solubility coefficient, k_H, defined the slope of the isotherm in zone $0.1 < a_W < 0.8$ and corresponded to random absorption (dissolution) and diffusion of the water molecules inside the secondary-wall of fibres. This absorption not only depended on the accessible hydroxyl functions of the polysaccharides but was also influenced by the pectic polyanions present in the matrix in which the cellulose microfibrils were embedded. The last values k_a (equilibrium constant for the clustering reaction) and n (mean number of water molecules per cluster) could be linked to the equilibrium state corresponding to the aggregate formation of water molecules at high water activity ($a_W > 0.8$).

The Langmuir-parameters variations appeared complex when the autoclave pressure increased. On the one hand, A_L, decreased and b_L, increased when the pressure was fixed either at 0.5 or 1 bar, compared to untreated sample. Although the sorption isotherms of the untreated and A0.5 sample were virtually identical (see Fig. 4), the Langmuir part of the isotherms were significantly different as expected from the values of A_L and b_L (see Fig. 5a). On the other hand, the A2 treatment had opposite effects showing highly different behaviour than the untreated-sample one (see Fig. 5b). Thus the various pressure treatments might differently impact the structure of the surface of fibres. At low autoclave pressures, some surface components of the non-treated fibres which had a relatively low affinity for water (e.g. the epidermis cuticle) were removed while the new surface structures (e.g. pectins) had higher affinity for water. Concerning the A2-treated fabric, the largest value of A_L might be mainly due to the division of the technical fibres while the lowest value of the affinity constant, b_L, indicated, at the surface of these fibres, the presence of neutral polysaccharides.

Low impacts of A0.5 and A1 treatments were observed at higher water activities, either in Henry or in aggregation domains. Nevertheless, as illustrated in Fig. 5a, a slight increase of k_H occured at 0.5 bar. Conversely there were significant impacts on fibre water-sorption at 2 bar pressure (Fig. 5b). The k_H constant was decreasing while k_a was observed to increase. Thus important structural modifications might occur in the secondary wall, which would reduce the number of absorption sites for water molecules in the fibre matrix, but would, at the highest values of water activity, slightly increase the number of water cluster associated to cellulose microfibrils. To approach how the structure and composition of fibres were altered, an analysis of the pectin composition was undertaken, since their negative charge might strongly impact the water sorption in cell walls.

To summarise at 0.5 bar pressure, Langmuir capacity decreased, Henry constant increased, the aggregation remained constant; the global isotherm appeared close to that of the untreated sample. At 1 bar pressure the Langmuir capacity also decreased but k_H was not affected while the water clustering decreased; the global isotherm was lower than that of the untreated sample. At 2 bar pressure, Langmuir capacity increased, but k_H greatly decreased while water clustering slightly increased; the global isotherm was much lower than that of the untreated sample.

3.3. Pectin composition of fibres

Flax fibres from the non-woven fabrics consisted of more or less divided bundles at the surface of which cortex debris remained more or less attached after the retting and scutching processes. The cell-wall of these cortical tissues were enriched in pectins including homogalacturonans (HG) and rhamnogalacturonans of type I (RG-I) with short side chains of galactose and arabinose (RG-I-S) (Davis, Derouet, du Penhoat, & Morvan, 1990; Gorshkova & Morvan, 2006;

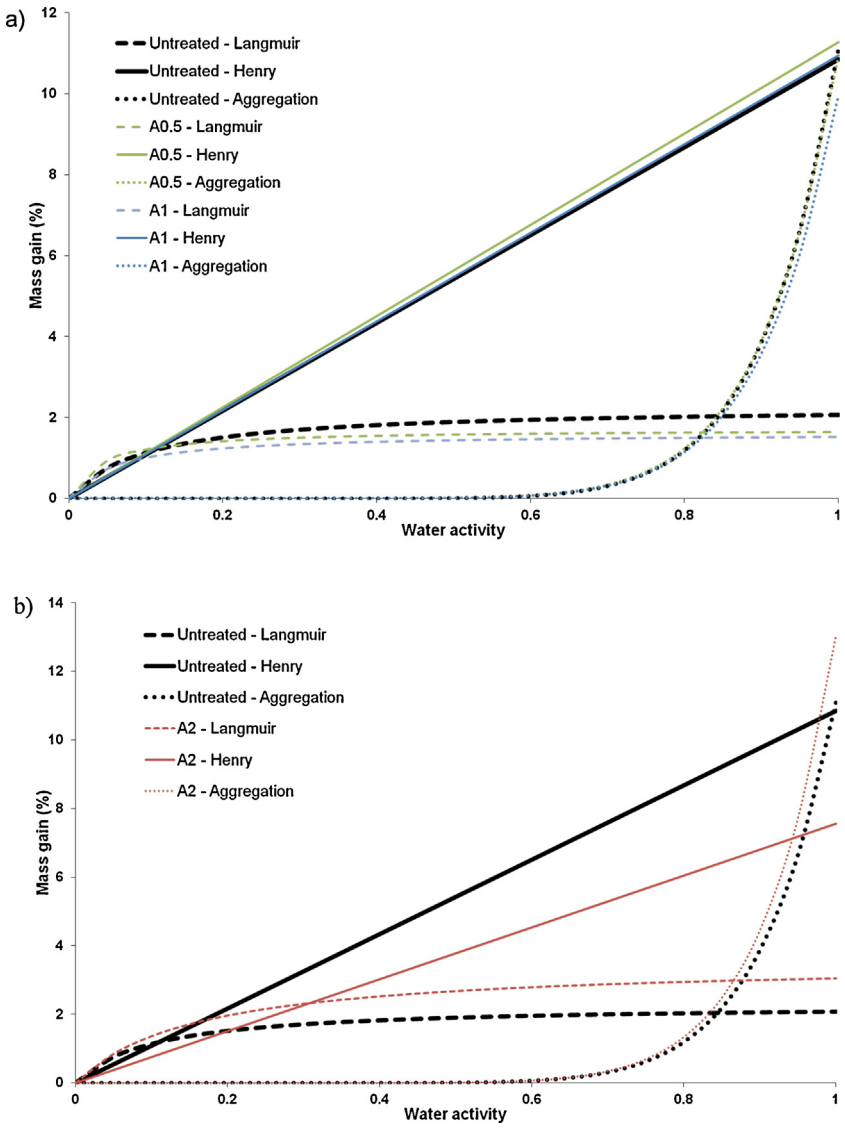

Fig. 5. Contributions (Langmuir, Henry and aggregation) of water sorption isotherm of (a) A0.5, A1 and (b) A2 treated flax-fibre non-woven compared to untreated one.

Morvan, Hafez, Jauneau, Thoiron, & Demarty, 1991). Loosely linked components remaining the surface of the so-called technical fibres were eliminated with water washings at room temperature (extract called EA). Pectin compositions of untreated and treated fibres are described in Fig. 6. Compared to non-treated samples, no significant impact of A0.5 and A1 treatments was observed on the pectic component release in EA. Conversely, the A2 treatment showed that no HG was present in EA anymore, while a large burst RG-I-S was released in this extract. Incidentally, these RG-I-S moieties might be responsible for the reduction of calcofluor signal observed after A2 treatment; due to the pressure they might cover the fibre surface and partly mask the cellulose microfibrils.

Pectins still attached to cortical tissues, either in the epidermis thick tangential-wall or in the middle-lamellae of cortical cells were reported to be extracted when using boiling water (extract designated as EB) (Morvan, Jauneau, Voreux, Morvan, & Demarty, 1990). They were not gelly pectins (giving no Langmuir isotherm) but were covalently linked to the cortical cell wall and might significantly participate to the building of the Langmuir layer. The amount of RG-I-S released in EB was not or slightly impacted whatever the autoclave treatment. On the other hand, the amount of HG decreased with A1 and more severely with A2 treatments.

The decrease of A_L and increase of b_L observed in A0.5 and A1 samples, compared to untreated sample, might be explained by the removal of the hydrophobic component of cortical tissues (e.g. the cuticule), the reduction of the surface tortuosity and by the appearance of surface covalent-pectins. In addition, the decrease of HG (known to present high affinity for hydrated cations) which was observed after A1 (in EB) and A2 (in EA and EB) would be responsible for the decrease of b_L Langmuir parameters in A1 (compared to A0.5) and much more in A2 treated fibres. Otherwise the increase of RG-I-S release in EA of A2 sample might explain part of the increase of A_L (the other part being due to the fibre-division impact).

After the removal of pectins from cortical tissues, the use of boiling EDTA (extract named EC) would allow to release the pectic components from the junctions especially of technical fibres. The gelly pectins of cell junction as the more internal pectins linked with the primary wall would contribute to the Henry part of the isotherm (but also to the aggregation of water molecules at higher water activity). In untreated samples, two thirds of the extract was composed of RG-I-S and one third of HG. No variation was observed in A0.5 fibres. The significant decrease of the pectin amounts in A1 and A2-treated fibres would be responsible for the decrease of water sorption observed when water activity became larger than

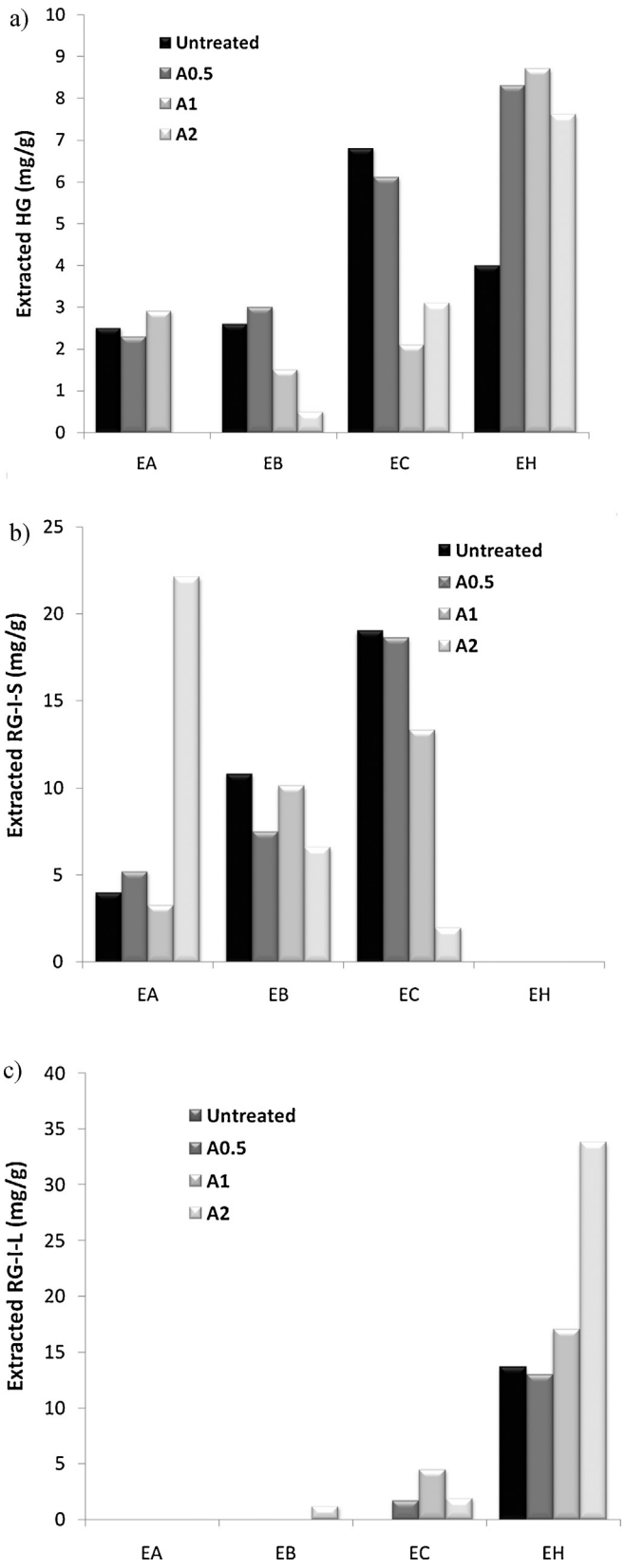

Fig. 6. Pectin composition of each extraction of untreated and treated flax fibres with (a) extracted HG, (b) extracted RG-I-S and (c) extracted RG-I-L. Homogalacturonan (HG) amount was estimated as GalU–Rha, rhamnogalacturonan of type I (RG-I) amount is calculated as 2 times the amount of Rha. RG-I-S is a RG-I with short chains of galactans (Gal/Rha < 3) and RG-I-L is a RG-I with long chains of galactans (Gal/Rha > 3).

0.3. In the case of A1 the impact dealt mainly with water clustering while the Henry contribution was the most affected in the case of A2. Worth to note the decrease of RG-I-S in A2-treated fibres (decrease also observed in EH) might be specifically related to the large decrease of k_H.

Besides, an acid extraction with HCl (extract EH) of untreated fabric would hydrolyse the matrix pectins that encrusted cellulose microfibrils within the secondary wall of flax fibres. In general, these pectins contained both HG and RG-I-L having moderately long chains of galactans ($3 < DP < 8$) depending on the variety (Alix, Goimard, Morvan, & Baley, 2008). It has been shown that β-1-4 galactan side-chains would interact with cellulose microfibrils as long as their DP was ≥10 (Zykwinska et al., 2005). Such RG-I with very long galactan side-chains would need a hot-alkali treatment to be released together with the hemicelluloses coating the cellulose microfibrils (Alix, Goimard, et al., 2009).

Increasing the autoclave temperature/pressure enhanced the amount of RG-I-L and most importantly caused a release of polymer fragments with longer side-chains of galactose into EH. The Gal/Rha ratio in EH increased from 6.5 in untreated and A0.5 treated samples to 9.1–9.5 in A1 and A2 treated samples, respectively (Table 3). The large amount of RG-I-L in the EH extract of A2 treated fibres indicated that the autoclave treatment affected the fine structure of the secondary wall by disrupting the hydrogen bounds between galactans and cellulose.

On the other hand, the three autoclave treatments led to a significant increase of HG moieties in EH, suggesting that some HG interacting with cellulose microfibrils (possibly as esters which would be extracted with alkali in untreated samples) were released into the matrix. Alternatively (or in addition) some HG in EH might originate from the autoclave-induced cross-linking of the moieties originally extracted in EA, EB and EC from non treated samples as suggested for Duralin fibres (Stamboulis et al., 2001). Opposite to A1 and A2, no decrease of HG was observed in EA, EB and EC of A0.5 sample, so as only the first hypothesis was retained for A0.5 sample. Thus, the increase of HG in the EH of A0.5 sample might explain the increase of water sorption in the bulk of their secondary wall and be responsible of the increase of k_H constant. Finally the increase of k_H, together with the decrease of A_L, explains why A0.5 isotherm remained very close to the untreated sample.

The decrease of HG and RG-I-S (having both high charge density) in EC and the presence of RG-I-L (low density of charges) in EH indicated a global reduction of the amount of negative charges in the secondary wall of A2 treated samples. Such event would contribute to the reduction of Henry k_H constant.

4. Discussion

It was previously shown that 2 bars (Gouanvé et al., 2006; Marais et al., 2005) or high temperature (Stamboulis et al., 2000, 2001) autoclave-treatments decreased the moisture sorption by flax fibres and their composites. The aim of the work was to cross data obtained on pectic composition of the non-woven flax-fabric to those on water-vapour sorption which led to a better understanding of the impact of autoclave treatments on the fibre structure (see Fig. 7 on schematic model).

As described by Stamboulis et al. (2001), a division of the technical fibres was induced by the autoclave treatments. In this study, we showed that the increase of division (2 bar treatment) led to an increase of the Langmuir layer while the significant solubilisation of the pectins from the surface of the fibres induced a decrease of the affinity of these water molecules for the fabric. The A0.5 and A1 treatments affected mainly the Langmuir's contribution. The increase of b_L could be attributed to the elimination of waxes by the autoclave treatments leading to an increase of the affinity of

Table 3
Pectin composition of each extraction of untreated and treated flax fibres. Homogalacturonan (HG) amount was estimated as GalU–Rha, rhamnogalacturonan of type I (RG-I) amount is calculated as 2 times the amount of Rha. RG-I-S is a RG-I with short chains of galactans (Gal/Rha < 3) and RG-I-L is a RG-I with long chains of galactans (Gal/Rha > 3).

Treatments	Untreated				A0.5 treated			
Extractions	EA	EB	EC	EH	EA	EB	EC	EH
HG (mg/g)	2.5 ± 0.2	2.6 ± 0.3	6.8 ± 0.6	4.0 ± 0.2	2.3 ± 0.1	3.0 ± 0.1	6.1 ± 0.4	8.3 ± 0.2
Gal/Rha	2.1	2.7	3.1	6.7	2.0	2.7	3.3	6.4
RG-I-S (mg/g)	4.0 ± 0.3	10.8 ± 0.2	19.0 ± 0.6		5.2 ± 0.2	7.5 ± 0.1	18.6 ± 0.4	
RG-I-L (mg/g)				13.7 ± 0.6			1.7 ± 0.2	13.0 ± 0.2
Treatments	A1 treated				A2 treated			
Extractions	EA	EB	EC	EH	EA	EB	EC	EH
HG (mg/g)	2.9 ± 0.3	1.5 ± 0.1	2.1 ± 0.5	8.7 ± 0.2	0.0 ± 0.0	0.5 ± 0.2	3.1 ± 0.1	7.6 ± 0.2
Gal/Rha	1.9	2.6	4.2	9.1	2.2	4.0	4.6	9.5
RG-I-S (mg/g)	3.3 ± 0.4	10.1 ± 0.1	13.3 ± 0.6		22.1 ± 0.7	6.6 ± 0.3	2.0 ± 0.2	
RG-I-L (mg/g)			4.5 ± 0.3	17.0 ± 0.4		1.2 ± 0.1	1.9 ± 0.2	33.8 ± 0.7

specific sites (charged sites). However, a decrease of A_L traduces a reduction of the number of accessible specific-sites at the surface or in microvoids in which water molecules could be sorbed. Such effects were easily related to the washing of the pectins constitutive of the cortical debris.

Besides, HG seemed to be subject to complex remodelling. On the one hand, and whatever the pressure, some HG release might occur from the cellulosic microfibril-coating into the matrix (e.g. increase of HG into EH extracts, whatever the pressure); If according to Alix, Goimard, et al. (2009), the hypothesis that some ester linkages can occur between HG and cellulose, then the release of HG in the matrix would increase the global number of negative charges. On the other hand, some HG cross-linking (via Maillard reaction, for example) might happen at 1 and 2 bars (e.g. HG decrease in EB and EC extracts) which would decrease the number of negative charges if the carboxylic group had been affected. The two antagonist effects might result in enlargement (A0.5) or decrease (A1 and A2) of the meso porosity, as defined by Mikhalovska et al. (2012).

Importantly, after a 2 bar treatment, the heart of the secondary wall was remodelled so as a large decrease of the Henry sorption happened. Comparing our process to Duralin one (as reported by Stamboulis et al. (2001)), it was interesting to observe that the washing of the autoclave-hydrolysed RG-I-S (and their elimination in EA extract) was the main factor of this water sorption reduction. As stated above it might be also responsible for the shift down of the calcofluor signal. Indeed, between 60% and 70% RH, the water sorption of A2 sample appeared less than the Duralin one. It was the opposite at higher RH, which can be explained, in the case of Duralin fabric, by the cross-linking of pectin and phenolics derived components due to the post-curing treatment. On the other hand, the A2 treatment would induce a RG-I-L de-associated from the microfibrils leading to a slight increase of the association of water cluster to those microfibrils. This might also explain the slight decrease of the tensile properties observed by Marais et al. (2005).

To some extent, the autoclave treatment could be compared to STEX treatment. According to Kessler et al. (1998), the impact of STEX treatment could be decomposed in four steps (with the increasing of activation energy, e.g. severity): opening, degumming, fibrillation of the fibre and cellulose decomposition. The autoclave treatment might be described by the two first terms in function of the pressure of the treatment (possibly three steps for A2), depending on the pressure.

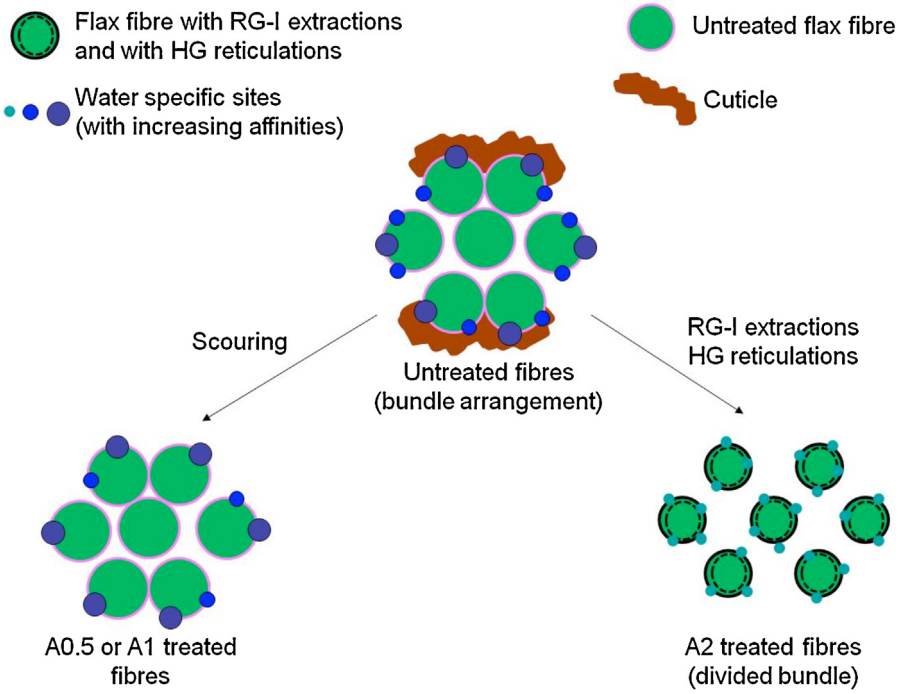

Fig. 7. Schematic effect of autoclave treatments on flax fibres.

In the future we might rather consider a treatment between A1 and A2 treatments over longer times with the aim of preparing/opening the fabric to coating/impregnation treatment before as a pre-step before the composite elaboration.

5. Conclusions

Gouanvé et al. (2006, 2007) have shown the impact of 2 bar autoclave-treatment on water sorption of flax fibres in function of treatment time and they obtained no influence of this time on fibre properties.

In this work, the same study has been done but with different treatment pressure (0.5, 1 and 2 bars). To understand the impact of each treatment on water sorption of fibre, the results were correlated with an analyse of the pectic composition of fibres.

By crossing results, lower autoclave treatments (0.5 and 1 bar) seem to only impact the fibre surface: affect the Langmuir sorption mode and slightly modification in pectin composition. However, the 2 bar autoclave-treatment induces modification on the fibres surface and in the internal part of the fibres. Extractions of RG-I-S and RG-I-L after A2 treatment could explain a bundle division correlated to sorption results. In addition, the Henry sorption mode is also affected (decreased) and could be correlated with RG-I extractions and a reticulation of HG phenomenon on single fibres.

To complete this study, mechanical properties characterisation of untreated and treated fibres is in progress to correlate with sorption and composition results.

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