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# Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites

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## A B S T R A C T

Mechanical and chemical processes used in the extraction of flax fibres for the production of technical flax fabrics and other flax products have a significant effect on their biochemical composition, structure and properties. In this work, we investigated the effect of different chemical extraction treatments on the biochemical composition and physical chemical properties of flax fabrics and their influence on the microstructure and mechanical properties of thermo-compressed flax fabrics reinforced epoxy composites. A unidirectional (UD) flax tow woven fabric with minimal processing was chosen in order to retain as much of the original flax cell wall structure as possible. The flax fabric was treated by various aqueous and organic solvents with increasing solvation capacity, so as to gradually extract cell wall components from the fibres. The treated flax fibre fabrics were characterised in terms of biochemical composition, wettability and dimensional characteristics. The influence of chemical extraction treatments and the role of cell wall components on the microstructural and mechanical properties of UD flax/epoxy biocomposites were investigated and discussed by means of Scanning Electron Microscopy (SEM), image analysis, Differential Scanning Calorimetry (DSC) and transverse tensile tests. Our results demonstrate that non-cellulosic cell wall components of flax fibres play a key role in the dispersion of flax yarns within the epoxy matrix, and in the mechanical behaviour of biocomposites.

### Keywords:

Biocomposites  
Epoxy  
Flax fibres  
Cell wall components  
Microstructure  
Mechanical behaviour

## 1. Introduction

Natural fibres are a promising alternative to synthetic fibres in technical textiles and composites applications due to their advantageous specific mechanical properties, their interesting viscoelastic and acoustic damping performances, as well as their lower environmental impact during their production and use phases, and their end of life (Dissanayake et al., 2009; Dufloy et al., 2014; Joshi et al., 2004; Le Duigou et al., 2011a,b). Mechanical performances of natural fibre based composites are strongly influenced by the intrinsic

mechanical properties of the fibres and matrices used and also by the fibre/matrix interfacial adhesion. Among all the natural fibres, flax fibres are nowadays the most advanced natural technical fibres (Holbery and Houston, 2006; Sliseris et al., 2016; Yan et al., 2014a,b, 2015). They indeed possess high modulus and tensile strength compared to other natural fibres (Baley, 2002; Faruk et al., 2012). They can be used as short fibres in thermoplastics for injection moulding applications, and can also be transformed in structured technical fabrics that are impregnated and processed with thermosets and thermoplastics intended to be used in structural applications.

In contrast to synthetic fibres, usually made of a mono-component in the bulk (glass, carbon, etc.), natural fibres such as flax fibres, present a complex hierarchical and layered structure made of several biopolymers constituting the core structure of the cell walls. As the main component, cellulose macromolecules crystallize in microfibrils which are reasonably oriented along the fibre axis with an angle of roughly 5 to 10° for flax fibres (Bledzki et al., 1996; Bledzki and Gassan, 1999; Dittenber and Gangarao, 2012; Mohanty et al., 2000), and embedded in a matrix of non-

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cellulosic components such as hemicellulose, lignin, pectins and proteins. In general, the cell walls in higher plants are made of an outer layer, the primary (P) wall and successively deposited concentric inner layers constituting the secondary (S1) and (S2) walls, in which the different biopolymers are distributed and organised, thus forming a multi-component and tri-dimensional fibrillar structure (Klemm et al., 2005, 1998; Krässig, 1993). These fibrillar cells, also called elementary fibres, are usually gathered in fibre bundles, also called technical fibres, within the stems of higher plants. A combined method using visible photomicrograph, associated with a 3-D mid-infrared transmission, allowed localizing the distribution of the different components across flax stem sections (Morvan et al., 2003). The authors observed that flax stem surfaces in the epidermal region are mainly composed of pectins and lipophilic components, such as waxes. Underneath the epidermis, the internal zone rich in bast fibres, where cellulose is predominant, showed substantial amounts of pectins and some acetylated non-cellulosic polysaccharides, whereas lignin and non-cellulosic polysaccharides are more concentrated in the inner core tissues of the stem. These observations showed that, in the case of flax fibres, cohesion of the bundles in bast fibres is not insured by lignin because it is present in very low amount. On the other hand, pectins are the major components accumulated in the primary cell wall and cell junctions, i.e. middle lamellae, and act as adhesives that ensure the cohesion of flax fibre bundles. Furthermore, the content and the nature of fibre surface components depend on the natural fibre considered. Marques et al. (2010) have analysed by gas chromatography the lipophilic extractives of four natural fibres (flax, hemp, sisal and abaca) and identified several components especially fatty alcohols and acids, aldehydes and ester waxes, in the case of flax fibres. Considering this complex multi-component microstructure, several kinds of interfaces should thus be considered when incorporating flax fibres in a polymer matrix: (i) the interface between the individualised elementary fibres and the polymer matrix, (ii) and the interface in between the elementary fibres within the fibre bundles whose cohesion is mainly ensured by pectic cements.

The production of flax fabrics from bast fibres in textile and composite applications requires several transformation steps involving mechanical processes, such as scutching and hackling, as well as chemical treatments such as desizing, scouring, alkali extraction, kiering or bleaching. Their main objectives are to remove shives, separate and refine fibre bundles and clean it by removing impurities such as waxes and proteins to obtain yarns that are further arranged to form woven or non-woven fabrics (Lacasse and Baumann, 2004; Müssig and Hughes, 2012). Coroller et al. (2013) investigated the microstructure and mechanical properties of unidirectional flax/epoxy composites. The authors used three varieties of flax fibres, i.e. Hermes, Andrea and Marylin, and found that the mechanical extraction process, especially the hackling step, has a strong influence on the fibre dispersion within the matrix. A significant improvement of the longitudinal tensile strength of the composite was obtained with hackled fibres due to their greater ability of individualization into elementary fibres that produces a more homogeneous composites microstructure. Bourmaud et al. (2010) investigated the effect of two "soft" water-washing treatments (72 h at 23 °C and 1 h at 100 °C) on technical flax fibres, and analysed sugar loss by thermogravimetric analysis (TGA) and the resulting separation and tensile properties of the fibres. They found that water-washing treatment removed non-cellulosic polysaccharides from the middle-lamellae and observed a much more drastic extraction of cell wall components at 100 °C during 1 h, because of the hydrolysis of pectin chains from the walls. The authors also noticed a decrease in fibre diameter scattering and a slight increase of average tensile properties for the treatment at 23 °C for 72 h. Stronger washings by alkali treatments were used by several authors to improve the mechanical properties of flax

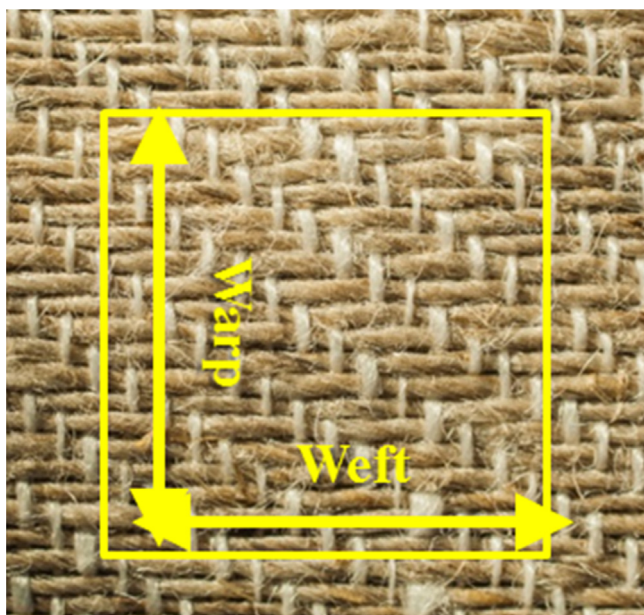
fibres reinforced epoxy composites. Van de Weyenberg et al. (2006) treated flax slivers with NaOH solutions at 1, 2 and 3% for 20 min at room temperature prior to their alignment, stacking with adhesive films of epoxy resin and autoclaving. The authors observed a slight increase in the longitudinal flexural strength and modulus of the composites with the increment of NaOH concentration. Transverse flexural strength and modulus were also improved by the treatments, especially with a NaOH solution at 1%. This was explained by the removal of impurities and waxes and the creation of a rougher fibre surface which should favour the mechanical interlocking and the chemical bonding at the fibre/matrix interface. Besides, a decrease of the fibre strength was reported after alikalisation, supporting the hypothesis that the increase in composites mechanical properties was mainly due to a significant improvement of interface quality. Yan et al. (2012) carried out an alkali treatment, with 5% w/w at 20 °C for 30 min, on flax, linen and bamboo woven fabrics to improve the mechanical properties of epoxy based composites manufactured by a vacuum bagging technique. The authors found a negative effect of the alkali treatment on the tensile strength and modulus of flax, linen and bamboo single-strand yarns extracted from the fabrics. On the other hand, an increase in longitudinal tensile and flexural properties was measured for all treated composites. These results supported that alkali treatments degrades the fibre properties but can significantly improve the fibre/matrix adhesion, and hence the composites mechanical performances. The different mechanical and chemical processes used for the extraction of flax fibres in the production of flax fabrics and other products thus have a significant effect on the biochemical composition, structure and properties of flax fibres, and hence should strongly influence the resulting microstructural and mechanical properties of biocomposites.

The aim of the present work is to investigate the effect of different chemical extraction treatments on the biochemical composition and physical chemical properties of flax fabrics and their influence on the microstructure and mechanical properties of flax fabrics reinforced epoxy composites. In order to keep as much as possible the original flax cell wall structure, a unidirectional (UD) flax tow woven fabrics that has undergone minimal processing, was selected. It was treated by various aqueous and organic solvents with increasing solvation capacity, so as to extract gradually cell wall components from the fibres. Untreated and treated flax fabrics were then processed by thermo-compression with a low viscosity epoxy resin to obtain UD flax/epoxy biocomposites. The treated flax fibre fabrics are characterised in terms of biochemical composition, wettability and dimensional characteristics. The influence of chemical extraction treatments and the role of cell wall components on the microstructural and transverse mechanical properties of UD flax/epoxy biocomposites are investigated and discussed.

## 2. Material and experimental methods

### 2.1. Flax fabrics, epoxy resin and chemicals

UD flax tow woven fabrics (FRD-UD41) with an areal density of 218 g/m<sup>2</sup> was provided by Fibre Recherche Développement (FRD, France). These flax woven fabrics (Fig. 1) are weaved in weft direction with flax tows, which are spinned from retted and hackled fibres. Flax tows were not washed, treated or oiled for the production of woven fabrics in order to minimise the chemical and mechanical degradation of fibre cell walls and/or the addition of chemical products. The dry linear density and insertion density of flax yarns within the untreated fabrics are 88.8 ± 5.8 tex and 19 picks/cm, and 25.2 ± 0.8 tex and 12.8 end/cm in the weft and warp direction, respectively. Accordingly, the relative amounts of flax yarns in the weft and warp direction for the untreated fabrics



**Fig. 1.** Micrographs of untreated unidirectional flax tow woven fabrics. Dry linear density and insertion density of flax yarns in weft direction:  $88.8 \pm 5.8$  tex and 19 picks/cm; in warp direction:  $25.2 \pm 0.8$  tex and 12.8 end/cm.

are 84 and 16 wt%, respectively. An infusion epoxy resin system, Resoltech® 1800, was purchased from Resoltech (France). It was mixed with a Resoltech® 1805 aliphatic amine hardener at a ratio 100/17 w/w. The resulting mixture presents a very low viscosity of 290 mPa.s at 23 °C.

Ethanol (96% purity) was supplied by Legallais (France). Etidronic acid (HEDP, 60% aqueous solution), polyethylene glycol (PEG,  $M_w$  200 g/mol) and dodecylbenzenesulfonic acid sodium salt (LAS), used for the surfactant treatment, were purchased from Analytic lab (France). Toluene (purity  $\geq 99.5\%$ ), used for the toluene/ethanol treatment and chemical composition analysis, and sodium hydroxide (purity  $\geq 98\%$ ), used for alkali and surfactant treatments and chemical composition analysis, were purchased from Sigma–Aldrich (France). Sodium chlorite (80%, pure, unstabilised), used for chemical composition analysis, was supplied by Acros Organics (France). Acetic acid (purity  $\geq 90.0\%$ ), used for chemical composition analysis, was purchased from Fisher Scientifics (France). Sulphuric acid (purity  $\geq 98\%$ ), used to extract lignin was supplied by Prolabo (France). Demineralised water was used for washing treatments.

## 2.2. Chemical extraction treatments on flax woven fabrics

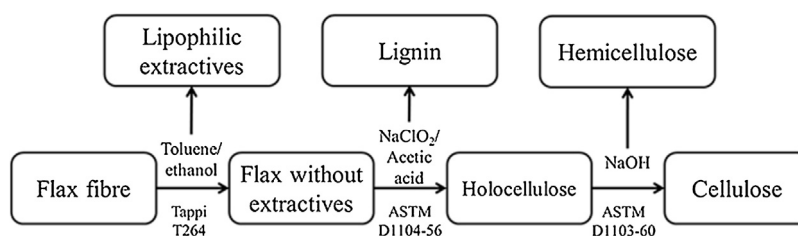
The extraction of flax cell wall components from flax fabrics was carried out by chemical treatments with increasing solvation capacity. Flax fabrics were immersed in the solutions in a 5 l round-bottomed flask for 1 h at boiling temperature. The six following treatment solutions were used: (a) demineralised water at 95 °C;

(b) ethanol at 75 °C; (c) toluene/ethanol at 75 °C; (d) industrial surfactants solution at 95 °C, composed of 1 g/Kg of flax of HEDP, 3 g/Kg of flax of non-ionic and anionic surfactants (70 wt% PEG, 30 wt% LAS), 2 g/Kg of flax of NaOH (Lacasse and Baumann, 2004); (e) and (f) an aqueous alkali solution at 1% NaOH, at 95 °C. A special device was designed to avoid damaging flax fabrics during treatments, i.e. flax fabrics were gently deposited on a grid positioned within the flask, and the stirring of the solutions was ensured by a magnetic stirrer below the grid to avoid any mechanical damages of the fabrics. Each treatment was followed by a first demineralised water washing at 50 °C for 10 min, except for the toluene/ethanol treatment for which the first washing was carried out with ethanol due to the insolubility of toluene in water. Finally, water rinsing at room temperature was carried out for each treated flax fabric.

## 2.3. Determination of the biochemical composition of flax fibre fabrics by solvent extraction

The biochemical composition of untreated and treated flax fabrics was quantified using a successive solvent extraction procedure of each non-cellulosic component based on TAPPI T264, ASTM D1104-56 and ASTM D1103-60 standards. The general procedure is detailed in Fig. 2. It should be noticed that variations in the biochemical composition may occur depending on the procedure used (Hatfield et al., 1994; Prosky et al., 1988; Selvendran and Verne, 1990; Van Soest et al., 1991).

In a first step, flax woven fabrics were cut so as to obtain a sheet sample of roughly 10 g (dry weight as determined with an infrared (IR) moisture balance Precisa XM66). The extraction of lipophilic extractives was carried out using a Soxhlet device with a solution of toluene/ethanol (2/1 w/w) for 24 h and then 6 h with only ethanol solution. The obtained solution was evaporated with a rotary evaporator then dried in a vacuum oven at 60 °C for 24 h and the dry weight of lipophilic extractives was measured with the IR balance (Precisa XM66) at 105 °C. Lignin extraction was carried out using 2.5 g of flax woven fabric (moisture free) from the first extraction step. The sample was introduced in a single neck glass boiling flask of 250 ml. 80 ml of hot demineralised water, 0.5 ml of acetic acid and 1 g of sodium chlorite was added and the mixture was heated at 70 °C and stirred during 3 h to achieve the delignification. Each hour, 0.5 ml of acetic acid and 1 g of sodium chlorite was added. After the last addition, the solution was stirred for 1 h and then filtered using a porcelain Buchner funnel. Demineralised water was used to clean the obtained holocellulose, i.e. cellulose plus hemicellulose, until the disappearance of the yellow colour. The resulting sample was then cleaned with ethanol and dried in a vacuum oven at 60 °C for 24 h. The dry weight of holocellulose was measured with the IR balance (Precisa XM66) at 105 °C. Finally, pure  $\alpha$ -cellulose was obtained by hemicellulose solubilization in sodium hydroxide solution and then acetic acid at 0.1 M. The holocellulose sample obtained from the previous extraction step was introduced in a 250 ml beaker immersed in water at  $20 \pm 0.1$  °C so as to maintain the solution cold and avoid modifying cellulose I in cellulose II. 10 ml of 17.5% NaOH solution was added to holocellulose for 2 min. 5 ml



**Fig. 2.** Schema of the successive solvent extraction procedure used to analyse the biochemical composition of non-treated and treated flax fabrics.

**Table 1**  
Density of flax fibre fabrics and epoxy as measured by gas pycnometer in helium atmosphere.

Samples	Measured density (g/cm <sup>3</sup> )	Density values from literature (g/cm <sup>3</sup> )	References
Flax fibre fabrics (untreated and treated)	1.5	1.4–1.5	Li et al. (2007); Van Den Oever et al. (2000); Vanleeuw et al. (2015)
Epoxy resin (System Resoltech 1800/1805)	1.2	1.1	(Resoltech® technical data sheet)

of 17.5 wt% NaOH solution was added each 5 min during 15 min. Then, the mixture was kept at 20 °C for 30 min. 33 ml of demineralised water was added to the mixture and was maintained for 1 h more. The resulting mixture was filtered and washed with 100 ml of 8.3% of NaOH solution and then with demineralised water in order to totally remove residual NaOH. Finally, 15 ml of acetic acid at 10% was added to fibres for 3 min so as neutralised cellulose. This was followed by washing and filtering with demineralised water. The obtained pure cellulose sample was dried and weighed using the IR balance (Precisa XM66) at 105 °C. Based on the measured weight, the biochemical composition as well as the total amount of extracts and the extraction yields for each non-cellulosic component were determined for untreated and treated flax woven fabrics. It should be noted that the procedure does not allow determining the pectin fraction, which is thus extracted and distributed within the hemicellulose and lignin fractions. Typical pectin content in flax fibre can vary from 1.8% to 4% (Bledzki et al., 1996; De Rosa et al., 2010; Mwaikambo and Ansell, 2002; Wang et al., 2010). As a consequence, the hemicellulose and lignin amounts were rather overestimated. Indeed, the lignin content determined for untreated flax fabrics was 6.2% (see Table 2). As reviewed by Gorshkova et al. (2000) lignin content may vary between 0.9% and 5% in literature, due to experimental difficulties in estimating cell wall phenolic components.

#### 2.4. Analysis of changes in the biochemical composition of flax fabrics by FTIR

A qualitative analysis of the changes in the biochemical composition of untreated and treated flax fabrics was performed by Fourier Transform Infrared (FTIR). FTIR spectra were recorded with a Bruker IFS66 spectrometer in attenuated total reflectance (ATR) mode, with a resolution of 2 cm<sup>-1</sup> and 32 scans in the range 4000–400 cm<sup>-1</sup>. All the spectra were normalised according to the band at 1202 cm<sup>-1</sup>, assigned to OH in plane bending of anhydroglucose units in cellulose chains (Klemm et al., 1998). This band was assumed to be unaffected by the treatments, the amount of cellulose within the flax fabrics remaining constant. FTIR analysis on pure lipophilic extractives, lignin, holocellulose and cellulose was carried out in order to identify the characteristic bands of each of the flax fabrics' components. Lipophilic extractives, holocellulose and cellulose were obtained from the solvent extraction procedure used for biochemical analysis (Section 2.3). Pure lignin was

**Table 2**  
Total extracts and biochemical composition of untreated and treated flax fibre fabrics as a function of the chemical extraction treatments used.

Treatment types	Total extracts (%)	Biochemical composition (%)				Extraction yield (%)		
		Cellulose	Hemicellulose	Lignin	Lipophilic extractives	Hemicellulose	Lignin	Lipophilic extractives
Untreated	–	81.3	11.1	6.2	1.5	–	–	–
Ethanol	1.1	82.2	11.0	6.1	0.7	1.8	2.7	50.5
Toluene/ethanol	3.8	84.7	9.0	6.0	0.3	19.7	4.6	77.1
Water	3.8	84.7	8.3	5.9	1.1	26.0	5.1	25.9
Surfactants	4.7	85.5	8.2	5.1	1.2	27.0	17.4	22.2
NaOH 1%	8.4	88.9	7.4	2.9	0.8	36.1	53.1	47.7

obtained by the immersion of flax fabrics free of extractives for 3 h in a solution of sulphuric acid 72%, which was then filtered and washed with demineralised water in order to remove cellulose and hemicellulose components.

#### 2.5. Dimension, linear and areal density of flax yarns and fabrics

The chemical extraction treatments applied on flax woven fabrics induce changes in their dimensions, caused by a shrinkage in the warp and weft direction, and also in their areal density, caused by the loss of components and the shrinkage. Flax woven fabric dimensions were measured by counting the number of ends per cm in the warp direction and the number of picks per cm in the weft direction over a width and length of 10 cm. The warp and weft shrinkages were determined from the ratio of the final number of ends and picks per cm to the initial number of ends and picks per cm, respectively. Linear density of yarns (g/km or tex) and areal density of fabrics (g/m<sup>2</sup>) were measured in the dried state using an IR-balance (Precisa XM66) at 105 °C. For these measurements, flax fabrics were cut in the form of discs of 25 mm diameter; 5 weft yarns and 30 warp yarns were cut to a length of 20 cm and 20 cm, respectively. Three measurements were performed for each flax fabric and flax yarn sample.

#### 2.6. Contact angle measurements on flax fabrics

The wettability of flax fabrics with water was determined with a Digidrop GBX goniometer apparatus equipped with a camera working at up to 50 images per second. Calibrated water droplets of 6 µl were deposited on untreated and treated flax fabrics and the static and dynamic water contact angle were measured in an air-conditioned room at 23 °C. A slight tilting angle of 3° was applied on flax fabrics to ease the determination of the edge of the droplets and contact angles. Measurements were achieved three times for each sample.

#### 2.7. Manufacturing of flax-epoxy composite plates

Untreated and treated UD flax woven fabrics were dried at 60 °C for 24 h in order to minimize the moisture content. 8 plies of UD flax woven fabric were alternately stacked (retaining a 0° orientation) and impregnated by 200 g of the mixture of Resoltech® 1800 epoxy resin and Resoltech® 1805 aliphatic amine hardener (100/17 w/w). The laminated UD flax/epoxy composites were hot-pressed using a

Daragon thermo-compression set up under a constant pressure of 50 bars and a constant temperature of 60 °C during 21 h (curing 6 h and post-curing 15 h). The final composites thickness was adjusted at  $3 \pm 0.2$  mm by the mean of shims. Under the effect of pressure and temperature, the excess resin flowed out of the edges of the laminates.

## 2.8. Determination of fibre volume fraction and porosity

Discs of 25 mm diameter were cut from each UD flax-epoxy composite plates with a holesaw. The areal density ( $\text{g}/\text{m}^2$ ) of the composites was measured in the dried state using an IR-balance (Precisa XM66). The fibre ( $\%_{mf}$ ) and matrix ( $\%_{mm}$ ) mass fraction of the composite plates were deduced from the respective areal densities of the composites and the 8 layers of UD flax woven fabric in the dried state. The bulk densities of flax fibre fabrics ( $\rho_f$ ), epoxy resin ( $\rho_m$ ) and composite plates ( $\rho_c$ ) were obtained on dried materials using a Gas pycnometer (Micromeritics AccuPyc 1330) in helium atmosphere. Untreated and treated flax fibre fabrics and epoxy resin densities are given in Table 1.

Based on these measurements, the fibre ( $\%_{vf}$ ), matrix ( $\%_{vm}$ ) and porosity ( $\%_{vp}$ ) volume fractions were calculated using Eqs. (1)–(3) (Gay, 1997):

$$\%_{vf} = \%_{mf} \times \frac{\rho_c}{\rho_f} \quad (1)$$

$$\%_{vm} = \%_{mm} \times \frac{\rho_c}{\rho_m} \quad (2)$$

$$\%_{vp} = 1 - (\%_{vf} + \%_{vm}) \quad (3)$$

## 2.9. Scanning Electron Microscopy (SEM) observations and image analysis

The effect of the extraction of flax cell walls components on the microstructure of UD flax/epoxy composites was investigated by SEM and image analysis. SEM observations were conducted on transverse sections of each composite plate perpendicular to fibre direction, with a Quanta 200 FEG (FEI Company) at an acceleration voltage of 15 KeV. The transverse sections were polished with sandpaper then diamond paste in dried conditions to avoid any fibre modifications. Finally, the resulting polished surfaces were sputter coated with carbon using a Carbon Evaporator Device CED030 (Balzers). SEM micrographs were used with the image analysis software Aphilion TM 3.2 (ADCIS) to determine flax fibre size distribution and analyse fibre dispersion. A multi scale analysis was performed: micrographs with a scale factor 85 (which cover the whole sample section) were used to evaluate fibre and yarns dispersion within the matrix by the signal analysis of the grey scale profiles. Micrographs with a scale factor 670 were used to evaluate elementary flax fibres and flax fibres bundles distributions. These micrographs were binarised and flax fibre elements were identified, filtered and numbered by their surface area values. For each composite several micrographs (around 20) were used to analyse a number of elements which are statistically representative of the overall microstructure (minimum 1500).

## 2.10. Differential Scanning Calorimetry (DSC)

Glass transition temperatures ( $T_g$ ) of neat epoxy resin and flax fabrics reinforced composites were measured by Differential Scanning Calorimetry (DSC) using a Pyris Diamond DSC thermal analysis system (Perkin Elmer) equipped with an Intracooler II. Samples of 15 mg were placed into aluminum pans. An empty aluminum pan was used as reference. Heating and cooling scans were performed at a rate of 10 °C/min from 25 °C to 150 °C, using  $\text{N}_2$  as purging

gas.  $T_g$  was determined from the cooling scan. Measurements were repeated twice for each sample.

## 2.11. Transverse tensile mechanical properties

Tensile mechanical properties were investigated in the transverse direction, i.e. perpendicular to fibre direction, so as to determine the effect of the chemical extraction of flax cell wall components on the mechanical behaviour of the UD flax/epoxy composites. Transverse tensile tests were carried out using a Zwick/Roell TH 010 machine equipped with a force sensor of 10 kN and an extensometer Zwick “clip-on” for the determination of the Young’s modulus. According to NF EN 2747 standard (AFNOR, 1998), composite plates were cut to obtain specimens of 3 mm × 10 mm × 163 mm with a reference length between tensile jaws of 50 mm. The crosshead speed was fixed at 1 mm/min and 2 mm/min for the determination of the Young’s modulus and the ultimate tensile strength and strain, respectively. As the ultimate properties of materials can be affected by point defects, an offset yield point was determined from stress/strain curves and set at 0.2% plastic strain. All the tests were performed at 27 °C and 54% relative humidity. Five samples were tested for each composite plate.

After transverse tensile tests, fracture surfaces of untreated and treated samples were sputter coated with carbon and observed by SEM at an acceleration voltage of (3.5 KeV) to investigate their modes of failure, i.e. adhesive or cohesive interfacial failure.

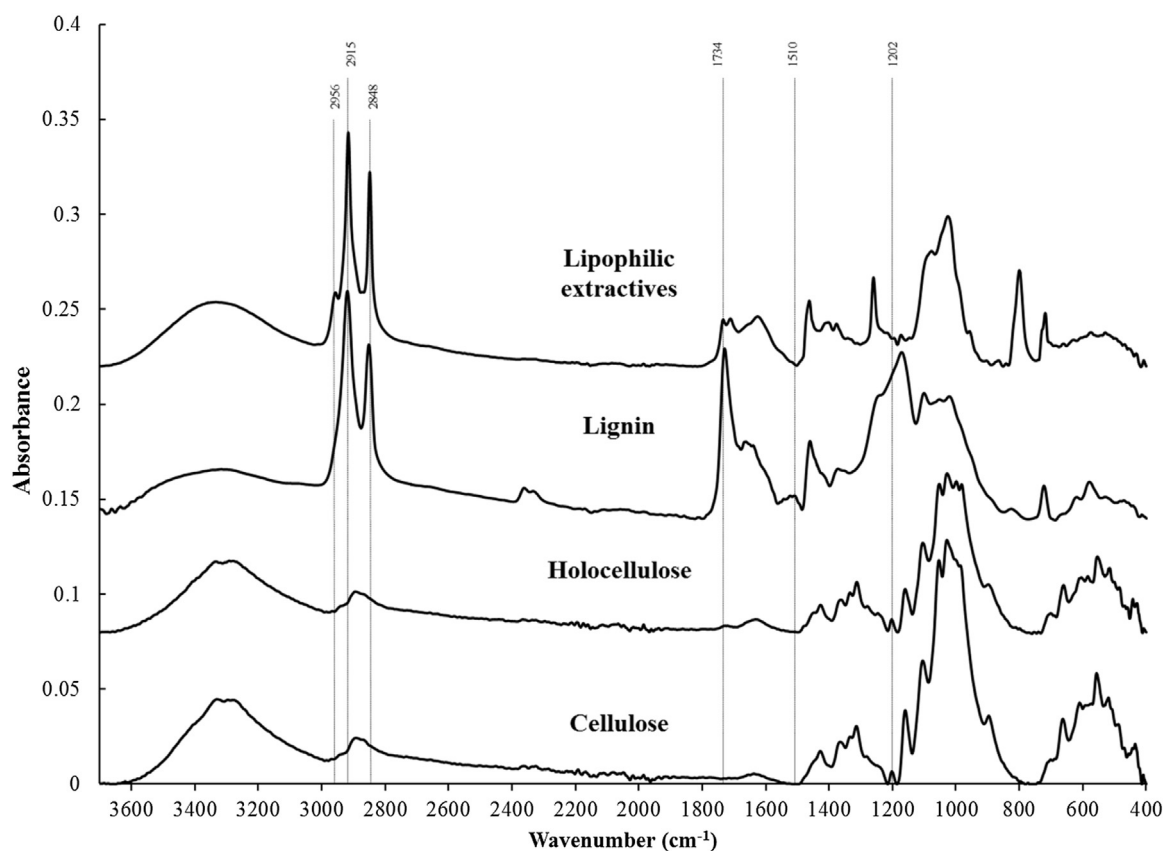
## 3. Results and discussions

### 3.1. Influence of chemical extraction treatments on flax fabrics properties

#### 3.1.1. Changes in the biochemical composition by chemical and FT-IR analysis

The biochemical composition of untreated and treated flax woven fabrics, as obtained by the solvent extraction procedure (Section 2.3), is given in Table 2. Generally speaking, solvation capacity of the chemical extraction treatments can be classified in three categories. The NaOH 1% alkaline solution was the most efficient extraction treatment with 8.4% of non-cellulosic components removed from the flax woven fabrics. On the other hand, the ethanol treatment led to the softest extraction with a removal of only 1.1% of non-cellulosic components. Toluene/ethanol, water and surfactants extraction treatments were moderate with 3.8%, 3.8% and 4.7% of non-cellulosic components removed. A gradual and significant increase of the cellulose amount was observed for all the treatments. Indeed, cellulose should not be affected by the chemical extraction treatments, and hence its relative amount increases when non-cellulosic components are extracted.

Regarding the hemicellulose extraction, it is clearly seen that the ethanol treatment has a very low extraction yield (1.8%). Toluene/ethanol, water and surfactants treatments have a moderate solvation capacity towards hemicellulose with extraction yields of 19.7%, 26% and 27%, respectively. Important amount of hemicellulose were removed by NaOH 1% treatment, with a high extraction yield of 36.1%. Similar conclusions can be drawn for the lignin extraction. NaOH 1% treatment exhibits a high solvation capacity towards lignin with extraction yield of 53.1%. Low extraction yields, not exceeding 5.1%, were observed for ethanol, toluene/ethanol and water treatments, attesting for their low solvation capacity towards lignin. A moderate extraction yield of 17.4% was obtained with the surfactants. Regarding the lipophilic extractives, high extraction yields of 50.5% and 77.1% were obtained with ethanol and toluene/ethanol treatments, respectively. Indeed, these organic solvents have very good physical chemical affinity for hydrophobic



**Fig. 3.** FT-IR spectra of lipophilic extractives, lignin, holocellulose and cellulose and characteristic vibration bands for lipophilic extractives and lignin.

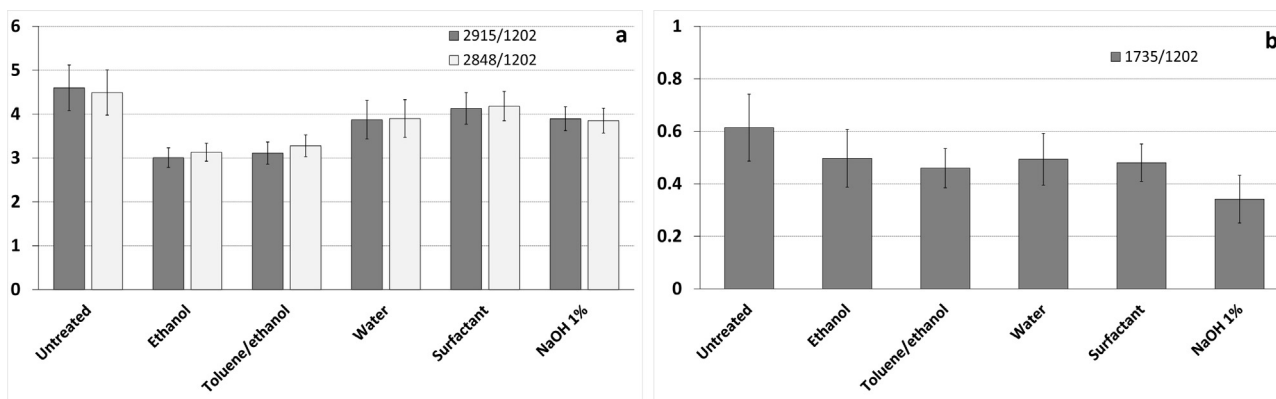
components. Besides, the toluene/ethanol mixture is classically used for the determination of the lipophilic extractives amounts (Tappi, 2007). Moderate extraction yields of 22.2 and 25.9% were obtained with water and surfactants treatments, respectively; the NaOH 1% treatment being more efficient to remove lipophilic extractives with an extraction yield of 47.7%. It should be pointed out that the quantity of lipophilic extractives in flax woven fabrics is much lower than other non-cellulosic components (roughly 1%), which makes more difficult the determination and analysis of mass losses.

In summary, the gradual increase of total extracts from 1.1% to 8.4% demonstrates that a gradient of solvation capacity of flax cell wall components has been obtained with the different chemical extraction treatments used. On one hand, high extraction yields of non-cellulosic components were obtained with NaOH 1% treatment. On the other hand, ethanol, toluene/ethanol and water treatments led to a softer extraction, mainly of lipophilic extractives and hemicellulose. These results are in accordance with literature. As studied by Theander (1991), ethanol extraction removes components non-covalently bonded to the cell walls. On the contrary, alkaline treatment leads as well to the extraction of covalently bonded compounds as lignin and hemicellulose, as discussed by Mwaikambo and Ansell (2002) and Li et al. (2007). The solvation capacity of the surfactants treatment was intermediate with higher amounts of lignin extracted. It should be pointed out that the selectivity of the chemical treatments towards individual non-cellulosic components of flax fabrics remained limited. As discussed by Morvan et al. (2003), this result shows that non-cellulosic components are intimately bound through hydrogen bonding and potential cross-linking within the primary and secondary cell walls, and hence are difficult to remove selectively by chemical extraction.

Nevertheless, high extraction selectivity towards lipophilic components was obtained with ethanol and toluene/ethanol treatments.

FT-IR spectra of each extracted residue from flax fabrics, i.e. lipophilic extractives, lignin, holocellulose and cellulose, were collected so as to determine their characteristic vibration bands and monitor the evolution of their intensity according to the chemical extraction treatments. As seen in Fig. 3, several vibration bands are common to each non-cellulosic component. However, the intense and narrow bands at 2915 and 2848  $\text{cm}^{-1}$ , characteristic of asymmetric and symmetric  $\text{CH}_2$  stretching vibrations (Lin-Vien et al., 1991), respectively, are mainly found in lipophilic extractives rich in aliphatic chains. The broad and intense vibration band around 1735  $\text{cm}^{-1}$ , related to saturated aliphatic and aromatic esters  $\text{C}=\text{O}$  stretching vibrations (Lin-Vien et al., 1991), is primarily found for lignin, although being also observed for lipophilic extractives due to the presence of ester waxes within flax fibres (Marques et al., 2010). Besides, the weak band at 1510  $\text{cm}^{-1}$ , corresponding to ester  $\text{C}=\text{O}$  in aromatic compounds (Lin-Vien et al., 1991), is only found for lignin. These four vibration bands, related to lipophilic extractives and lignin, were thus monitored for each chemical extraction treatments. No distinct bands were found for holocellulose and cellulose substrates, what did not allow detecting specifically the removal of hemicellulose components by FT-IR.

Fig. 4 shows the FT-IR intensity ratios of the bands 1735, 2848 and 2915  $\text{cm}^{-1}$  to the reference band 1202  $\text{cm}^{-1}$  for untreated and treated flax fibre woven fabrics. A significant reduction in the intensity ratios for peaks located at 2915 and 2848  $\text{cm}^{-1}$  (asymmetric and symmetric  $\text{CH}_2$  stretching) is observed for ethanol and toluene/ethanol treated flax fabrics, and in a lesser extent after NaOH 1% treatment. These results attest for a decreased amount of lipophilic extractives within the treated flax fabrics, and are in accordance with the biochemical composition analysis. Ethanol and



**Fig. 4.** FT-IR intensity ratios of (a) 2915  $\text{cm}^{-1}$  and 1202  $\text{cm}^{-1}$  bands and 2848  $\text{cm}^{-1}$  and 1202  $\text{cm}^{-1}$  bands (lipophilic extractives) and (b) 1735 and 1202  $\text{cm}^{-1}$  bands (lignin) as a function of the chemical treatments used.

toluene/ethanol extraction treatments were indeed found to be highly selective towards lipophilic extractives. The band located at 1735  $\text{cm}^{-1}$  and corresponding to ester C=O stretching, has almost disappeared after NaOH 1% treatment, giving a lower intensity ratio. This is also in agreement with the biochemical analysis, which revealed a significant removal of lignin components from flax fabrics with NaOH 1% treatment. Others treatments result in limited changes regarding the peak at 1735  $\text{cm}^{-1}$ , thus attesting that lower amounts of lignin were removed.

Concluding, FT-IR analysis and biochemical composition analysis are two complementary methods that were successfully used to characterize and compare the solvation efficiency of chemical extraction treatments. FT-IR analysis revealed to be an interesting method that allows quickly and efficiently identifying the extraction of lipophilic extractives and lignin components from flax substrates. Both approaches support that high extraction selectivity towards lipophilic components was obtained with ethanol and toluene/ethanol treatments, while NaOH treatment showed a high capacity to extract lignin but with limited selectivity, since large amounts of other non-cellulosic components were also removed. Besides, it should be noted that the respective solvation capacity of the solvents used could also be influenced by the treatment conditions. Longer treatment times or higher temperatures would result in higher extraction yields. Considering the above described cell wall structure of flax fibres, these results clearly evidenced that organic solvents such as ethanol or toluene were only able to extract low-molecular-weight and weakly bonded components present at the fibre surfaces. In contrast, chemical extraction with alkaline based solutions had a higher solvation capacity with an action in the bulk of the fibres by removing a large amount of matrix components, i.e. hemicellulose, pectin and lignin, from the middle lamellae but also from the cell walls. The significant changes in biochemical composition induced by the treatments should thus have an impact on the physical properties of the fibres as well as their behaviour when incorporated in epoxy based biocomposites.

### 3.1.2. Changes in wettability by contact angle measurements

Water contact angle measurements were performed on untreated and treated flax fibre fabrics so as to determine the changes in the hydrophilic/hydrophobic balance consecutive to the different chemical extraction treatments. Generally speaking, an increased hydrophobicity of flax fabrics should result in an increase of the initial contact angle and a decrease of the water absorption kinetics. As can be seen in Fig. 5, the initial water contact angle for untreated flax fibre fabrics is about 117.7°. The water droplet is stable until 10 s then its volume, and hence its contact angle, start to decrease gradually as it is absorbed by flax fibres. The initial water contact angles for untreated and treated flax fabrics were very

reproducible ( $\pm 2.4^\circ$ ) but larger deviations were observed during the absorption phase.

The selective extraction of lipophilic extractives by ethanol and toluene/ethanol treatments induced significant changes in the water contact angle kinetics. The initial contact angles were indeed close, even lower than for untreated flax fabrics. Moreover, the absorption kinetics was greatly increased, demonstrating that the selective removal of these hydrophobic components clearly enhances the hydrophilic character of flax fabrics. In contrast, water and surfactants treatments resulted in a slight increase of the initial contact angles and a decrease of the absorption kinetics, especially for water treatment. This can be explained by the limited removal of lipophilic extractives and the significant extraction of hydrophilic components contained in the hemicellulose fraction, which enhance in turns the hydrophobic character of flax fabrics. The substantial extraction of lignin in the case of surfactants treatment counter-balanced this phenomenon due to the more hydrophobic character of lignin. This explains the lower contact angles observed in the case of surfactants treatment as compared to water treatment. NaOH treated flax fabrics exhibit a more contrasted behaviour. As previously discussed, many components, hydrophilic as well as hydrophobic ones, were removed by these treatments (up to 8.4% of the total biomass, see Table 2). This leads to a hydrophilic/hydrophobic balance which goes in the sense of an increased hydrophilicity for NaOH 1% treated fabrics, i.e. lower contact angles over time.

Concluding, the removal of hemicellulose and lipophilic extractives fractions appears to play a key role in the hydrophilic/hydrophobic character of flax fibre fabrics. It was clearly evidenced that high extraction yield of lipophilic extractives resulted in an increased hydrophilicity of flax fabrics (case of ethanol and toluene/ethanol treatment), while extraction of hemicellulose resulted in an increased hydrophobicity of flax fibre fabrics (case of water and surfactants treatments). The role of lignin was more difficult to depict since it was removed by NaOH treatment, together with large amounts of hemicellulose and substantial amounts of lipophilic extractives. Besides, it has to be pointed out that extraction treatments may also have an effect on the surface texture and topography of flax fibre fabrics which, beyond purely physical chemical considerations, could have influenced the water contact angle measurements.

### 3.1.3. Changes in the dimensions and areal density of flax yarns and fabrics

The extraction treatments with hot solvents applied on flax fibre woven fabrics induced a significant loss of components (see Table 2), that is counterbalanced by a pronounced shrinkage effect, which modified their overall areal density. The dry linear density of



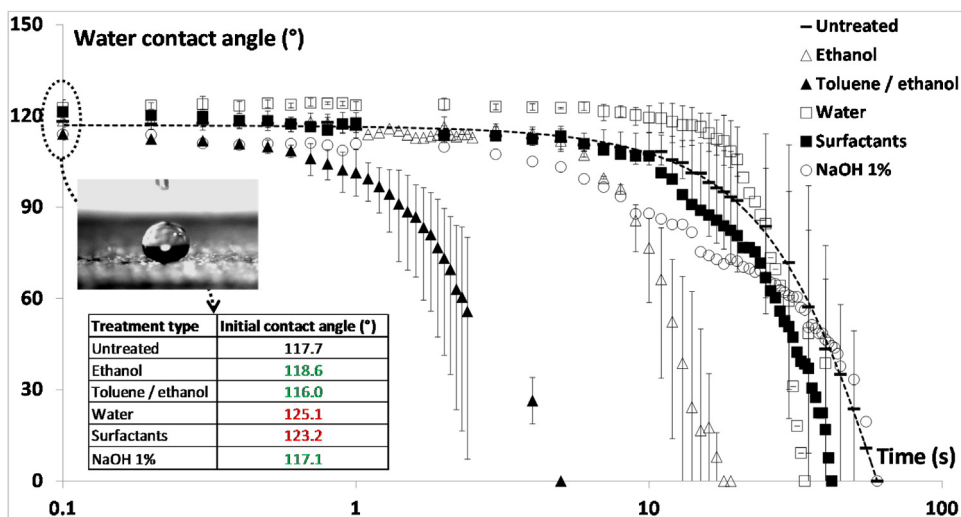


Fig. 5. Water contact angle kinetics for untreated (dashed line) and treated (open and closed symbols) flax fibre fabrics as a function of the chemical extraction treatments used.

Table 3 Dimensional and mass density of untreated and treated flax fibre yarns and fabrics as a function of the chemical extraction treatments used.

Treatment type	Dry linear density of flax yarns		Insertion density of flax yarns		Relative amount of flax yarns		Dry areal density of flax fabrics (g/m <sup>2</sup> )
	Warp (tex)	Weft (tex)	Warp (end/cm)	Weft (picks/cm)	Warp (wt%)	Weft (wt%)	
Untreated	25.2 ± 0.8	88.8 ± 5.8	12.8	19.0	16.0	84.0	217.6 ± 5.6
Ethanol	26.1 ± 1.0	86.1 ± 6.6	13.2	19.6	16.9	83.1	210.0 ± 4.0
Toluene/ethanol	26.8 ± 0.9	93.9 ± 0.4	14.0	21.0	16.0	84.0	246.1 ± 3.7
Water	28.1 ± 1.4	100.1 ± 1.4	13.4	20.0	15.8	84.2	233.6 ± 2.2
Surfactants	27.9 ± 0.6	84.0 ± 5.0	13.2	20.0	18.0	82.0	217.2 ± 2.9
NaOH 1%	25.5 ± 0.7	93.7 ± 0.7	13.5	20.1	15.5	84.5	216.8 ± 2.6

flax yarns, and the insertion (number of warp and weft) and areal densities of untreated and treated flax woven fabrics were determined and are given in Table 3. Shrinkage due to treatments is related to two cumulative effects: it increases the dry linear density of the yarns as well as their insertion number. These phenomena are partly due to a densification of the flax fibre network within the fabrics, through the formation of additional hydrogen bonds between flax fibres within the yarns, during the successive treatment and washing steps. This results in an increase of the overall areal density of flax fabrics.

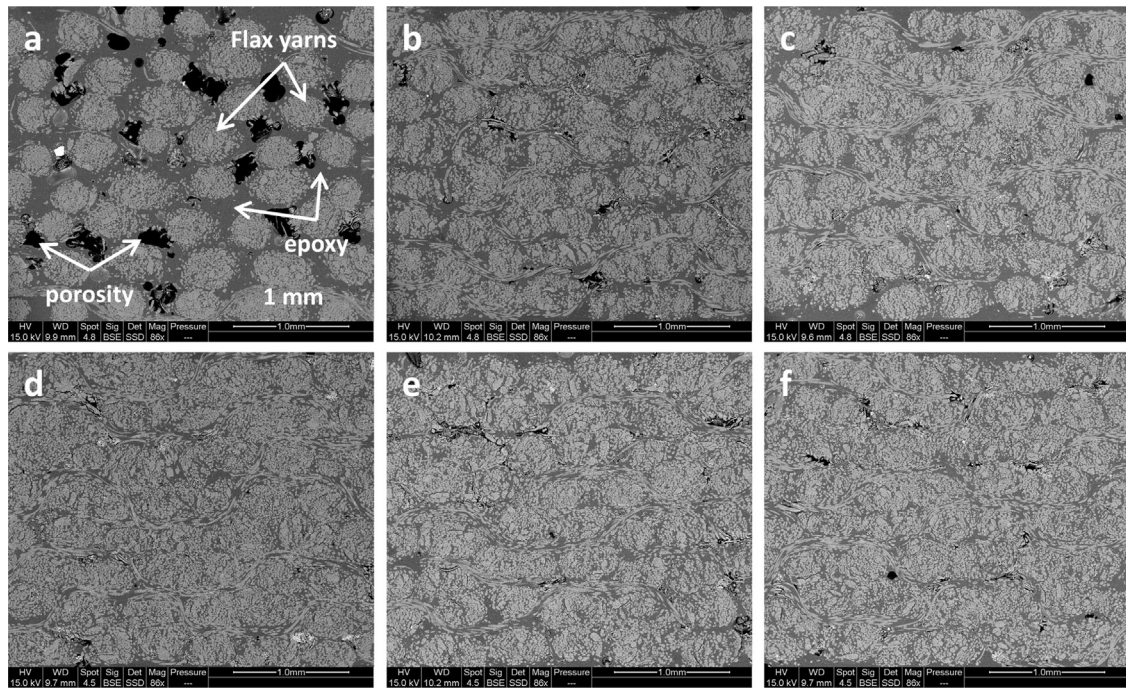
This increase in areal density was particularly significant for the toluene/ethanol treated fabrics (246.1 ± 3.7 g/m<sup>2</sup> versus 217.6 ± 5.6 g/m<sup>2</sup> for untreated fabrics), for which the extraction of non-cellulosic components was limited (3.8%), and mostly involved lipophilic extractives and weakly bounded hemicellulose. It seems that the removal of these components favoured the shrinkage of the fabrics, and possibly hydrogen bonding between flax fibres within the yarns. Linear and insertion densities for both warp and weft yarns were indeed significantly higher after toluene/ethanol treatment. Water treated fabrics had a similar behaviour with high shrinkage, illustrated by a significant increase of the weft yarn linear density (100.1 ± 1.4 tex versus 88.8 ± 5.8 tex for untreated fabrics) and the areal density (233.6 ± 2.2 g/m<sup>2</sup> versus 217 ± 5.6 g/m<sup>2</sup> for untreated fabrics). In the case of surfactants and NaOH 1% treatment, only the insertion density increased. The linear density of flax yarns was similar, even lower than untreated yarns, which suggests a lower cohesion of flax fibres within the yarns. This low shrinkage was also compensated by the large removal of non-cellulosic components (up to 8.4% for NaOH 1% treatment), which explains the very low variations in the areal densities for these treated fabrics. Finally, the highly selective extraction of lipophilic extractives obtained by ethanol treatment induced

almost no shrinkage, and only a slight decrease of the areal density was measured for this treated fabrics. So the removal of lipophilic extractives does not appear to favour the cohesion of flax fibres within the yarns.

The dimension and areal density of flax fabrics are thus substantially influenced by the treatments. However, the increase in areal density related to the shrinkage is partially compensated by the removal of non-cellulosic components. It is postulated that the moderate removal of lipophilic extractives and weakly bounded hemicellulose can favour the cohesion of flax fibres within the yarns, with regard to the significant increase in the linear density of the yarns and areal density of flax fabrics after toluene/ethanol and water treatments. On the other hand, higher extraction yield of non-cellulosic components could be responsible for decohesion of flax fibres within the yarns, considering the decrease of their linear density.

### 3.2. Influence of extraction treatments on the microstructure of UD flax fabrics reinforced composites

Fig. 6 presents transverse cross sections of non-treated and treated flax fabrics reinforced composites at low magnification (~85×). Flax yarns that are made of fibre bundles and elementary fibres, appear in light grey, epoxy matrix in dark grey and porosity in black (Fig. 6a). It is observed that for non-treated flax fabrics (Fig. 6a), yarns are easily identified and individualised with a relatively good cohesion. When observing treated flax fabrics reinforced composites, it is clearly seen that flax yarns are more and more dispersed within the epoxy matrix according to the extraction yield of the treatments. Ethanol and toluene/ethanol treated fabrics present a moderate dispersion of the yarns (Fig. 6b and c) in comparison with the high dispersion observed for surfac-

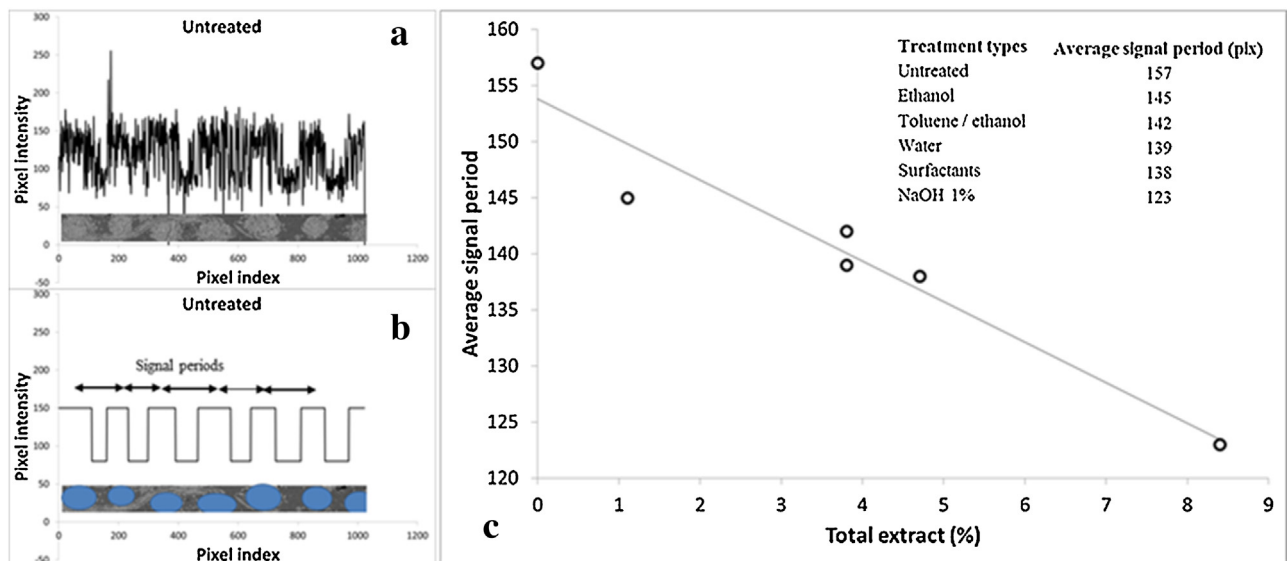


**Fig. 6.** SEM micrographs (85 $\times$ ) of transverse cross section of flax fabrics reinforced composites for the different treatments: (a) untreated, (b) ethanol, (c) toluene/ethanol, (d) water, (e) surfactants, (f) NaOH 1%.

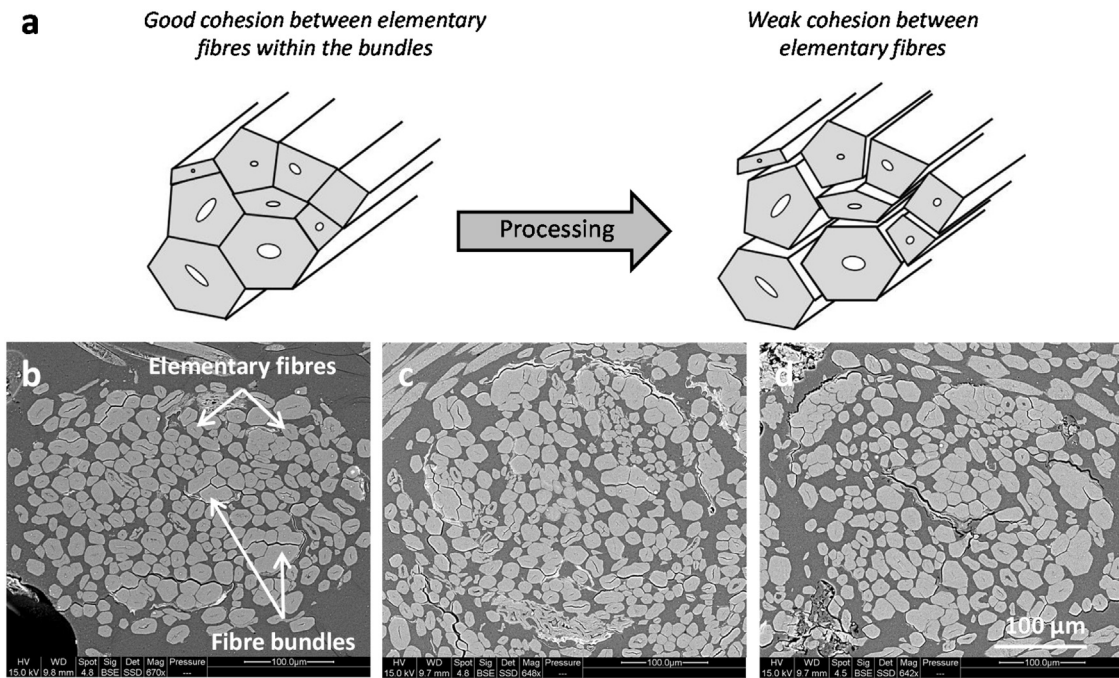
tants and NaOH 1% treated fabrics (Fig. 6e and f), water treated fabrics being an intermediate case (Fig. 6d). As postulated above, these results support a prior decohesion of the yarns subsequent to high extraction yield treatments. This decohesion appears to favour the dispersion of flax fibres and the diffusion of epoxy resin within the yarns between the elementary fibres during the thermo-compression process to such an extent that it is no longer possible to visualise individual yarns in the case of NaOH 1% treated fabric (Fig. 6f).

To corroborate these qualitative observations, image analysis was performed on SEM micrographs, and the grey scale profiles were plotted across the section. Fig. 7a clearly shows that non-treated flax fabrics reinforced composites exhibit a periodic profile

(average signal period 157 pixels, Fig. 7b) with large light and dark grey areas, corresponding to rich-flax fibres and rich-epoxy resin areas, respectively. This profile is characteristic of the cohesive and individualised yarns observed on SEM micrographs. With treated flax fabrics, the periodic greyscale variations are markedly increased, and hence light and dark grey areas are significantly smaller with reduced average signal periods (see results in Table of Fig. 7c). These results attest for the highest dispersion of flax yarns within the epoxy matrix. Furthermore, the periodic greyscale variations appear to be well correlated with the extraction yield of non-cellulosic components obtained with the various treatments: the higher the extraction yield, the lower is the signal period (Fig. 7c). This supports that the chemical extractions applied on



**Fig. 7.** Grey scale profile across the sections of flax fabrics reinforced composites for: (a) raw data, (b) normalised signal for untreated fabrics. Flax fibres correspond to pixel intensity of about 150 and epoxy resin corresponds to pixel intensity of about 80, (c) Average signal period versus total extract.



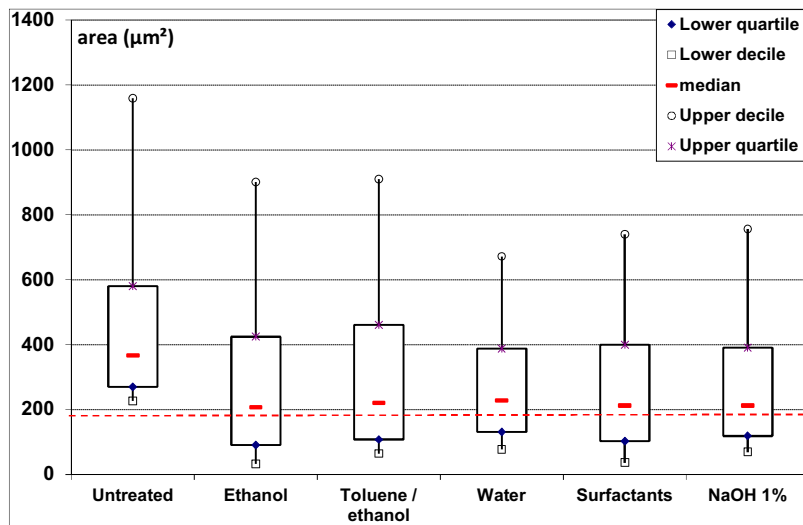
**Fig. 8.** (a) Illustration of the dispersion states of fibre bundles within the epoxy matrix before and after the chemical treatments and thermo-compression processes; and SEM micrographs (670 $\times$ ) of flax yarns in transverse cross sections of flax fabrics reinforced composites for: (b) untreated fabrics, (c) toluene/ethanol treated fabrics, (d) NaOH 1% treated fabrics.

flax fabrics are primarily responsible for the dispersion of the yarns and the individualization of the elementary fibres within the epoxy resin during the thermo-compression process. Higher extraction yields would result in a gradual loosening of the yarn periodic structure since elementary fibres will be more and more individualised and dispersed within the matrix.

At higher magnification ( $\sim 670\times$ ), it is clearly observed that the dispersion of flax yarns within the epoxy matrix has to be related to the decohesion at the micrometric scale, of flax fibres bundles in elementary flax fibres (Fig. 8a). As discussed previously, the chemical extraction treatments applied on flax fabrics indeed involved the removal of several non-cellulosic components such as hemicellulose and pectin cements, which are particularly concentrated in cell junctions and play a key role in the cohesion of elementary

fibres. In the case of non-treated flax tow fabrics, non-cellulosic components are present in large quantity ( $\sim 18\%$ ). This explains the presence of numerous bundles of elementary fibres within the yarns which are partially preserved even after the thermo-compression process (Fig. 8b). When treated in toluene/ethanol (Fig. 8c) and NaOH 1% (Fig. 8d), flax yarns exhibit a more dispersed microstructure with higher proportions of elementary fibres and higher fractions of epoxy resin within the yarns.

Image analysis was performed on these SEM micrographs to determine the area distribution number weighted of individual flax objects, i.e. elementary fibres and fibre bundles (Fig. 9). The median area of individual flax objects for untreated flax fabrics is about  $370\ \mu\text{m}^2$ . The different treatments induce a significant decrease of the median area which is  $214.5\ \mu\text{m}^2$  in average for



**Fig. 9.** Box plots of area distributions number weighted of flax objects within the yarns for untreated and treated flax fabrics reinforced composites. The dashed line stands for the typical section area of an elementary fibre.

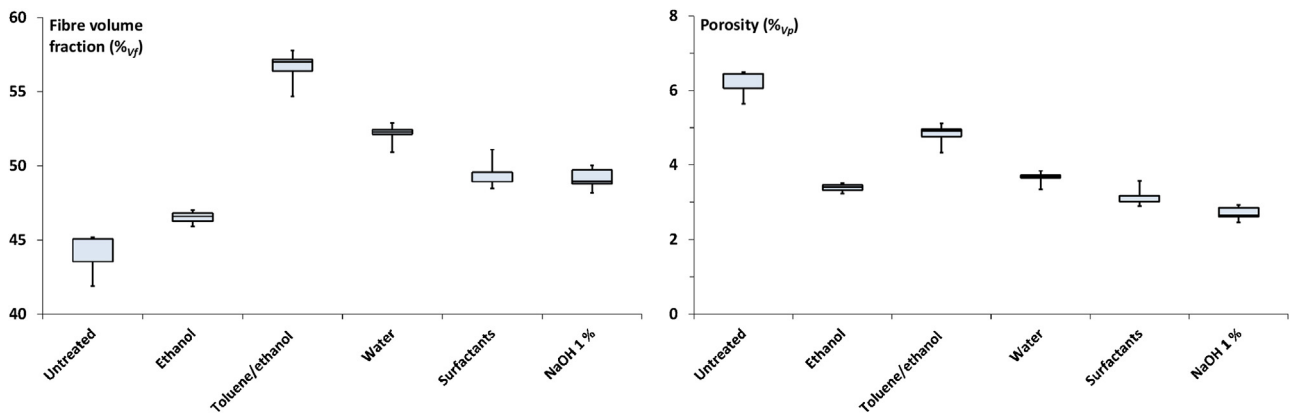


Fig. 10. Fibre volume fractions and porosity rates for untreated and treated flax fabrics reinforced composites as a function of the chemical extraction treatments used.

all the treatments. Moreover, the upper quartile and decile of the area distribution are strongly decreased for the treated fabrics reinforced composites. Assuming that the section area of an elementary flax fibre is about  $180 \mu\text{m}^2$  (corresponding to a fibre diameter of roughly  $15 \mu\text{m}$ ), the overall fraction of elementary flax fibres was determined for all the samples. This fraction is about 17% for the untreated sample and increases significantly with the different treatments: around 34% for ethanol, toluene/ethanol, water and NaOH 1% treatments, and 39% for the surfactants. Even if these treatments increased flax fibre dispersion, it should be pointed out that large fibre bundles can still be observed. Besides, a fraction of small flax objects having area below  $180 \mu\text{m}^2$  were also detected and attributed to cell wall fragments coming from elementary fibres.

In summary, the analysis of flax yarns dispersion show that the chemical extraction treatments induces an individualization of the fibre bundles in elementary fibres and favour the diffusion of epoxy resin within the yarns between the elementary fibres through pressure effects and capillary flow during the thermo-compression process. According to the solvation capacity of the treatments towards flax cell wall components, it results in a gradual disappearance of the yarns in favour of a more homogeneous microstructure in which elementary fibres and fibre bundles are better distributed within the epoxy matrix. Moreover, the numerous interfibrillar interactions existing within the bundles are partially degraded by the treatments and replaced by the formation of a greater interface between elementary fibres and epoxy matrix.

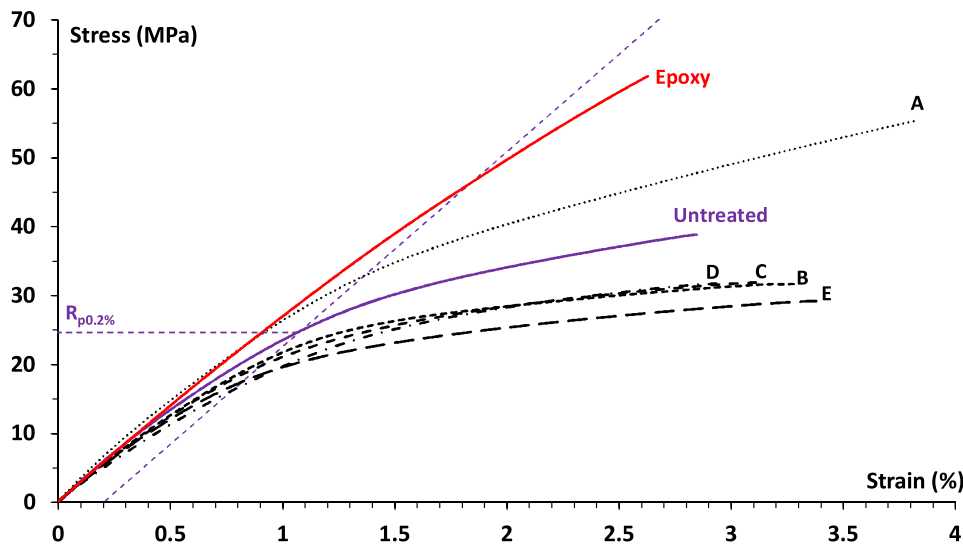
### 3.2.1. Fibre and porosity volume fraction

Fibre volume fraction is a key parameter that is related to the impregnation of the fibres with the matrix, and greatly influences the mechanical performances of composites. As observed in Figs. 6 and 8, impregnation of flax fabrics with epoxy resin is rather complex since it involves both macro and micro infusion around and within the yarns, fibre bundles and elementary fibres, respectively (Ziegmann and Elsabbagh, 2012). The quality of impregnation is governed by several parameters such as the processing protocol, the resin viscosity and the permeability of flax fabrics. The permeability itself is primarily conditioned by the structure of the fabrics, the wettability of flax fibres towards epoxy, as well as the intrinsic porosity of flax fibres. As seen in Fig. 10, the fibre volume fraction for untreated flax fabrics reinforced composite was around 45%, and increased fibre ratios were obtained with all the treated flax fabrics from 46% for ethanol treated fabrics up to 57% for toluene/ethanol treated fabrics. The extraction treatments thus significantly modify the permeability of flax fabrics. It was observed that more resin flowed out the edges of the laminates during the thermo-compression process for treated flax fabrics. Besides, SEM

micrographs in Fig. 8 clearly show that the micro infusion of the resin within the yarns and between the elementary fibres was enhanced by the treatments. The higher fibre volume fractions obtained with treated flax fabrics is thus partly explained by a better flow and diffusion of the epoxy resin within the yarns. Moreover, considering that the number of plies was constant for all the composites prepared, areal density of flax fabrics (Table 3) also had a strong influence on the final fibre volume fraction of the composites. Water and toluene/ethanol treated fabrics exhibited the highest areal density which resulted in the highest fibre volume fractions in the composite laminates.

As seen in Fig. 6, the cross section of untreated flax fabrics reinforced composite show several black areas corresponding to macro-porosity, mostly localised between the yarns in rich-epoxy zones. It is well known that porosity is a weak spot in composites that originates from poor impregnation of the resin within the fabrics during processing. Porosity found in natural fibres reinforced thermoset resins can be classified in four types from micro to macro-porosity (Madsen et al., 2007): (i) the fibre porosity that is found inside the unfilled cavities of elementary fibres, primarily in their lumen; (ii) the interface porosity that produces interstices in regions between fibres and matrix, and originates from a poor fibre/matrix interface; (iii) the impregnation porosity that is produced inside the yarns, between the elementary fibres and the fibre bundles, usually occurring with high viscosity resins, but also originating from a poor matrix impregnation of the fibre bundles due to lipophilic extractives and peptic cements; and (iv) the matrix porosity that produces macro-porosity in rich-matrix areas due to degassing and entrapped air bubbles. It is clearly observed in Fig. 6 that the number and size of the macro-porosities found in rich-epoxy zones for the untreated flax fabrics composite are significantly reduced with the treated flax fabrics. This is accompanied by a marked decrease of the overall porosity for treated flax fabrics composites, from 6.5% down to 2.7% for NaOH 1% treated flax fabrics as shown in Fig. 10.

These results suggest that the improved dispersion of the yarns and elementary flax fibres, as well as the physical chemical modifications of the fibres with chemical extraction treatments favoured the diffusion of epoxy resin during processing, and promote a better impregnation of epoxy resin within the yarns of flax fabrics, resulting in a more homogeneous and less porous microstructure. The selective removal of lipophilic extractives by ethanol and toluene/ethanol treatments, that increases the hydrophilic character of flax fabrics (Fig. 5) and exposes the surface hydroxyl groups, appears to be efficient enough to improve the matrix impregnation and enhance the fibre dispersion and fibre volume fraction, while significantly reducing the porosity. Improved fibres/matrix interactions through the esterification reaction between hydroxyl



**Fig. 11.** Median strain/stress curves of transverse tensile tests for untreated and treated flax fabrics reinforced composites: (A) ethanol; (B) toluene/ethanol; (C) water; (D) surfactants and (E) NaOH 1%.

and epoxide groups are also expected. In this respect, the highest extraction yields of non-cellulosic components from the cell walls obtained with the other treatments did not provide further improvement, and the fibre volume fraction and porosity remained similar. Besides, it should be pointed out that at higher magnification, micro-porosities originating from intrinsic fibre porosity and poor fibre/matrix interface are still observable on SEM micrographs in Fig. 8, whatever the treatment used.

### 3.3. Influence of extraction treatments on transverse mechanical behaviour of UD flax fabrics reinforced composites: effect of elementary fibres individualization

Coroller et al. (2013) investigated the effect of elementary fibres individualization on the longitudinal tensile properties of flax/epoxy composites. The authors prepared UD composites with three different varieties of flax fibres. Hermes flax fibres showed a high degree of dispersion within the epoxy matrix with numerous individualised elementary fibres (93%) whereas Marilyn and Andrea flax fibres showed higher amounts of fibre bundles with fraction of individualised elementary fibres of 69% and 74%, respectively. This was explained by the hacking step that greatly favoured the subsequent dispersion of the fibres during the composite processing. It should be noted that the flax tow fabrics used in the present study exhibited much lower dispersion with amounts of individualised elementary fibres not exceeding 40% for treated flax fabrics. This is explained by the high content of non-cellulosic components in flax tow fibres that favours the cohesion of the fibre bundles. Based on longitudinal tensile test, the authors showed that, beyond the intrinsic mechanical properties of the fibres, higher fibre dispersion can significantly enhance the ultimate strength of the composites due to a better stress transfer from the matrix to the fibres. It was also showed that flax/epoxy bond strength is rather good due to flax fibre roughness (Le Duigou et al., 2012) and their potential chemical interactions with epoxy.

#### 3.3.1. Transverse tensile behaviour

As demonstrated in the previous sections, the removal of non-cellulosic components by chemical extraction treatments resulted in a significant improvement of fibre dispersion, and hence of the interface relative area, whereas the cohesion within the fibre bundles and yarns was seriously degraded. To investigate the effect of

these phenomena on the mechanical properties of the composites, transverse tensile tests were conducted on untreated and treated flax fabrics reinforced composites so as to highlight interfacial effects, and to stress the interfaces between the individualised elementary fibres and epoxy matrix, and in between the elementary fibres within the fibre bundles. Benzarti et al. (2001) investigated the transverse mechanical properties of glass/epoxy composites with different glass fibre treatments so as to correlate their ultimate behaviour with interfacial properties. The authors found that reactive sizings promote higher interfacial strength and an increase in ultimate properties of laminates in transverse tension. This was attributed to the higher crosslink density of the polymer network in interfacial areas brought by the sizings.

Median stress-strain curves of transverse tensile tests are shown in Fig. 11 for epoxy resin, untreated and treated flax fabrics reinforced composites. Epoxy resin exhibits a brittle behaviour with a slightly marked plastic deformation. In contrast, a large non-linear domain with a yield plateau corresponding to plastic deformation is observed for all flax fabrics reinforced composites. Except for the ethanol treatment which greatly enhances modulus and stress and strain at break of the composite, other treatments significantly lowered the modulus, offset yield point ( $R_{p0.2\%}$ ) and stress at break of the composites, the stress at break being slightly increased.

Transverse mechanical properties of untreated and treated flax fabrics reinforced composites are given in Table 4. In overall, Young moduli and ultimate strengths were decreased by the chemical treatments, from about 4.6 GPa to 3.8 GPa, and from  $38.8 \pm 2.7$  MPa to  $22.7 \pm 1.7$  MPa, respectively. In contrast, the ethanol treatment induces a great increase of Young's modulus and ultimate strength, up to around 5 GPa and  $54.8 \pm 1.8$  MPa, respectively. Several parameters are expected to have an influence on the mechanical behaviour of the composites. Fibre volume fraction is obviously a key parameter. As detailed in Table 4, fibre volume fraction in the longitudinal direction (weft direction) and transverse direction (warp direction) are between 37.1% and 47.6%, and 7.1% and 9.1%, respectively, depending of the flax fabrics treatments. As discussed above, porosity within the composites was significantly decreased by the chemical treatments applied on flax fabrics, and this should also greatly influence the mechanical properties. Besides, it has been shown that fibre dispersion was enhanced by the treatments, hence increasing the relative interface area. Intrinsic mechanical properties of the fibres may have been affected by

**Table 4**

Transverse mechanical properties of untreated and treated flax fabrics reinforced epoxy composites.

Type of fibre treatment	Fibre volume fraction (Vol.%)	Warp volume fraction (Vol.%)	Weft volume fraction (Vol.%)	Porosity rate (Vol.%)	$T_g$ (°C)	Transverse Young modulus (MPa)	Offset yield point $R_{p0.2\%}$ (MPa)	Ultimate stress (MPa)	Ultimate strain (%)
Epoxy	–	–	–	–	91.7 ± 3.4	3135 ± 58	–	64.2 ± 4.0	2.7 ± 0.3
Untreated	44.2 ± 1.4	7.1	37.1	6.2 ± 0.3	86.6 ± 1.4	4642 ± 96	24.7 ± 0.8	38.8 ± 2.7	2.9 ± 0.2
Ethanol	46.5 ± 0.5	7.4	39.1	3.4 ± 0.1	94.8 ± 0.5	5037 ± 303	29.9 ± 0.6	54.8 ± 1.8	3.8 ± 0.2
Toluene/ethanol	56.6 ± 1.0	9.1	47.6	4.8 ± 0.3	85.3 ± 1.8	4027 ± 92	22 ± 0.3	31.0 ± 1.4	3.3 ± 0.2
Water	52.1 ± 0.6	8.3	43.9	3.7 ± 0.2	83.6 ± 3.1	4309 ± 39	20.9 ± 0.5	31.3 ± 1.4	3.0 ± 0.4
Surfactants	49.5 ± 0.9	8.9	40.6	3.2 ± 0.2	98.5 ± 4.1	3810 ± 225	20.6 ± 0.9	31.2 ± 0.7	3.0 ± 0.6
NaOH 1%	49.1 ± 0.6	7.6	41.5	2.7 ± 0.2	82.7 ± 1.4	3973 ± 90	19.3 ± 0.9	28.8 ± 0.9	3.2 ± 0.2

the chemical treatments. Indeed, Yan et al. (2012) showed that alkali treatments applied on flax fabrics can induce a decrease of the tensile strength and modulus of flax yarns. Finally, the glass transition temperature ( $T_g$ ) was measured for each sample from cooling scans (Table 4), and the results showed that reinforcing epoxy matrix with flax fabrics can induce a decrease of the  $T_g$ , which suggests that crosslinking of epoxy was impeded by the presence of natural fibres. This should have decreased the tensile modulus and ultimate strength of epoxy within the composites as compared to the neat epoxy matrix. Possible reasons for this lowering of  $T_g$  in presence of natural fibres are the migration of some non-cellulosic compounds from the fibres to the matrix upon curing that can react with epoxy functions and/or amine functions of the hardener, and should hinder the crosslinking of epoxy. The diffusion and absorption of the hardener by the fibres which would decrease the local concentration of hardener at the fibre/matrix interface could also hinder the crosslinking of epoxy in the interfacial zone.

As many parameters involved in the composite microstructure are varying (porosity, reinforcement rate, epoxy curing, fibre dispersion and intrinsic properties), an analytical model based on thin Laminate Plate Theory (LPT) (Reddy, 2003) was used to analyse the effect of chemical treatments on transverse mechanical properties at equivalent reinforcement and porosity rates. Thereby, the variations in mechanical properties of the composites can be directly attributed to modifications in the intrinsic properties of the fibres and matrix, and/or interfacial properties related to fibre/matrix interactions and fibre dispersion. The model assumes the laminates to be an array of individual flax fabrics layers which are perfectly bounded among plies. The number of layers is  $N=8$ . In each layer, the orientation (warp, weft) and fibre volume fraction are known (Table 4). Flax fibres were assumed to have transverse isotropic elastic properties (longitudinal and transverse elastic moduli  $E_l$ ,  $E_t$ , respectively; in-plane Poisson's ratio  $\nu_{lt}$ , shear modulus  $G_{lt}$ ) and the epoxy matrix was assumed to have isotropic elastic properties: elastic modulus  $E=3135$  MPa, Poisson's ratio  $\nu=0.35$  (Joudon et al., 2014). Perfect bonding between fibres and matrix is assumed in this modelling. The values of composites Young's modulus are, for all the treatments, higher than the one of the matrix. The load transfer between fibres and matrix is therefore achieved (perfectly or partially). As the porosity volume fraction is also known for all composites, epoxy elastic properties was modified via Mori-Tanaka micro mechanical model (Mori and Tanaka, 1973), assuming spher-

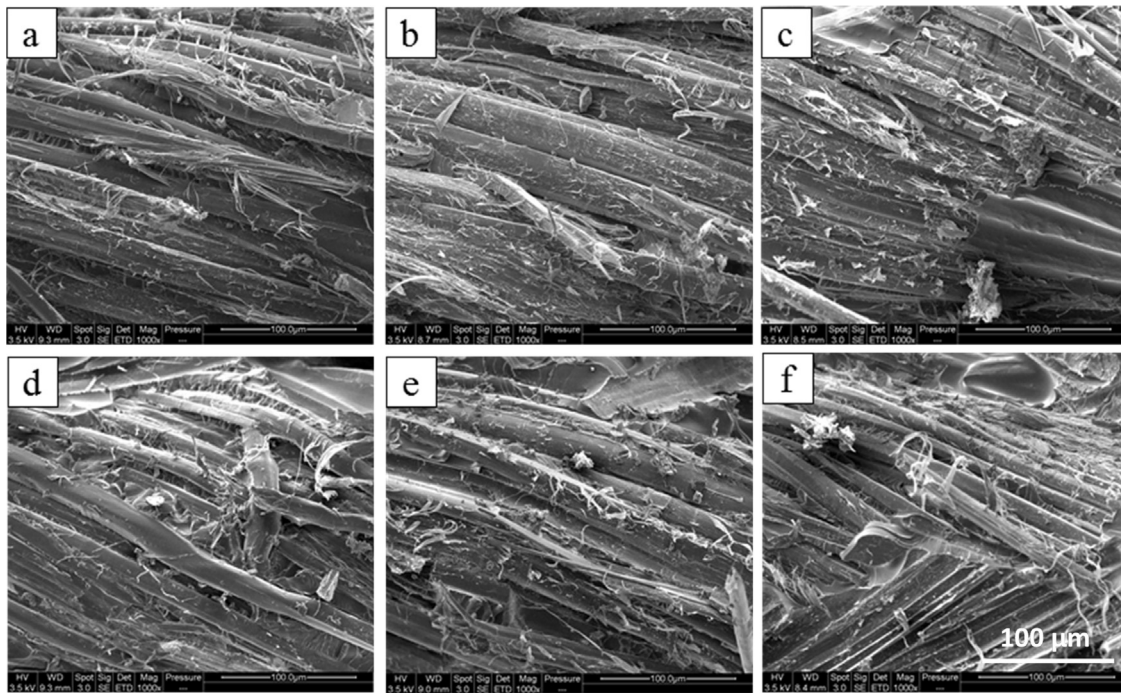
ical shape macro-porosities only localised within the matrix. Based on these assumptions, thin laminate plate theory (Reddy, 2003) was used to identify the fibre longitudinal and transverse elastic properties. For sake of simplicity the fibre transverse Young modulus is deduced from the longitudinal one:  $E_l/E_t=7$  (Baley et al., 2006). The resulting elastic longitudinal properties are summarised in Table 5 as a function of flax fabrics treatments. The estimated longitudinal modulus of flax fibres for untreated fabrics was  $49.7 \pm 2.1$  GPa, which is close to values found in literature for elementary flax tow fibres (Martin et al., 2013). The results clearly show that chemical treatments deteriorate fibres elastic properties, with longitudinal and transverse Young moduli decreasing up to  $26.3 \pm 3.3$  GPa and  $3.7 \pm 0.5$  GPa, respectively, for surfactants treatment. In contrast, the ethanol treatment did not affect the longitudinal and transverse Young moduli, being  $52.9 \pm 6.4$  GPa and  $7.5 \pm 0.9$  GPa, respectively.

These results can be understood as follows. On one hand, the removal of non-cellulosic components from the cell walls with high extraction yield treatments degrade the macromolecular assemblies of biopolymers within the cell walls, which explains their lower elastic properties. Some of these components should indeed be involved in the fibre/matrix load transfer and the transverse elastic response of elementary fibres and fibre bundles. For instance, Lefevre et al. (2015) showed that tensile strength and stiffness gradually decrease when flax cell wall components are removed of the fibres by successive and selective chemical extractions. The authors suggested that matrix pectins are primarily involved in the load transfer whereas structuring polysaccharides (hemicelluloses and structuring pectins) contribute to the cohesion of cellulose microfibrils and the stiffness of flax fibres. On the other hand, the low extraction yield (1.1%) achieved with ethanol treatment does not impact the elastic properties of flax fibres. The removal of lipophilic extractives mostly present at the fibre surface should not induce significant changes in the fibre microstructure. Considering that Young's modulus for ethanol treated flax fibres should not be higher than for untreated flax fibres, the highest Young modulus obtained with the LPT theory can be explained by a modification of the fibre/matrix interface. Indeed, an improvement of the interface quality is expected through the combined effects of enhanced fibre dispersion and fibre/matrix interactions when lipophilic extractives are removed from the fibre surface. This is also supported by the great increase in ultimate stress, up to  $54.8 \pm 1.8$  MPa, for the ethanol treated flax fabrics reinforced composite, while other treat-

**Table 5**

Flax fibres elastic moduli deduced from LPT theory.

Type of fibre treatment	Longitudinal fibre modulus $E_l$ (GPa)	Transverse fibre modulus $E_t$ (GPa)
Untreated	49.7 ± 2.1	7.1 ± 0.3
Ethanol	52.9 ± 6.4	7.5 ± 0.9
Toluene/ethanol	30.8 ± 1.3	4.4 ± 0.2
Water	36.0 ± 0.6	5.1 ± 0.1
Surfactants	26.3 ± 3.3	3.7 ± 0.5
NaOH 1%	31.1 ± 1.5	4.4 ± 0.2



**Fig. 12.** SEM transverse fracture surfaces for flax fabrics reinforced composites according to the chemical treatments used: (a) untreated, (b) ethanol, (c) toluene/ethanol, (d) water, (e) surfactants, and (f) NaOH 1%.

ments induce a large decrease of the stress at break as compared to the untreated flax fabrics reinforced composite.

These results suggest that removing waxes by ethanol treatment can improve the transverse mechanical strength of the composite by improving the fibre/matrix interfacial adhesion, while a large removal of non-cellulosic components induces a degradation of the fibres and bundle cohesion, and strongly affects the transverse mechanical response of composites. Besides, it should be pointed out that the variations of a few degrees of the glass transition temperature of the matrix, indicating possible variations in its mechanical response, were not taken into account in the modelling. A more precise determination of the fibre elastic properties and their variations would thus be achieved by implementing the real mechanical properties of the matrix from in-situ mechanical measurements within the composites.

### 3.3.2. Fracture surface

Fig. 12 shows transverse fracture surfaces observed by SEM of untreated and treated flax fabrics reinforced composites. Due to high fibre volume fractions, fracture surfaces are not easily interpretable. In general, untreated and treated flax fabrics reinforced composites present an adhesive interfacial failure. SEM micrographs clearly show that matrix did not stay bonded to fibres upon failure, and some printed of fibres appear in the matrix, suggesting fibre/matrix debonding. This is in accordance with the transverse mechanical response of the composites. The ultimate stress of the composites was always lower than the one of the neat matrix, even for ethanol treated flax fabrics (i.e.  $64.2 \pm 4.0$  MPa versus  $54.8 \pm 1.8$  MPa, respectively). A cohesive interfacial failure would have required that the ultimate stress of the composites reached the one of the neat matrix. Moreover, strong treatments, as surfactants and NaOH 1%, seemed to produce a more pronounced decohesion of the elementary fibres within the yarns (Fig. 12f), which is related to the removal of interfibrillar components (pectic cements) and the weakening of the elementary fibres cohesion within the fibre bundles.

## 4. Conclusions

In this study, we analysed the role of flax cell wall components on the biochemical composition and physical chemical properties of flax fabrics, and on the microstructure and transverse mechanical properties of flax fabrics reinforced epoxy biocomposites.

A gradient of solvation capacity of flax cell wall components has been obtained with different chemical extraction treatments. High extraction yields of non-cellulosic components were obtained with NaOH treatment. Ethanol, toluene/ethanol and water treatments led to a softer extraction, mainly of lipophilic extractives. The solvation capacity of the surfactants treatment was intermediate with higher amounts of extracted lignin. Biochemical composition results were confirmed by FT-IR analysis. The study of the water contact angle kinetics clearly gave evidence that high extraction yield of lipophilic extractives results in an increased hydrophilicity of flax fabrics, as is the case for ethanol and toluene/ethanol treatments. In contrast, water and surfactants treatments resulted in a slight increase of the initial contact angles and a decrease of the absorption kinetics, explained by the limited removal of lipophilic extractives and the significant extraction of hydrophilic components contained in the hemicellulose fraction, enhancing in turn the hydrophobic character of flax fabrics. As concerns NaOH treatment, large quantities of hydrophilic and hydrophobic components were removed leading to an increased hydrophilicity of flax fabrics. The dimension and areal density of flax fabrics were also substantially influenced by the treatments. It was shown that the increase in areal density related to the shrinkage was partially compensated by the removal of non-cellulosic components. The moderate removal of lipophilic extractives and weakly bounded hemicellulose can favour the cohesion of flax fibres within the yarns, with regard to the significant increase in the linear density of the yarns for toluene/ethanol and water treatments. Finally, higher extraction yield of non-cellulosic components could be responsible for decohesion of flax fibres within the yarns, considering the significant decrease of their linear density.

The analysis of untreated and treated flax yarns dispersion within the composites showed that the chemical extraction of cell wall components induced a pronounced individualization of the fibre bundles in elementary fibres and favoured the diffusion of epoxy resin within the yarns between the elementary fibres during the thermo-compression process. Moreover, the numerous interfibrillar interactions existing within the fibre bundles were partially degraded by the treatments and replaced by the formation of a greater interface between elementary fibres and epoxy matrix. Finally, the number and size of the macro-porosities found in rich-epoxy zones for the untreated flax fabrics composite were significantly reduced for treated flax fabrics reinforced composites. Investigations on the transverse mechanical response of the composites and modelling of the resulting fibre properties show that the selective removal of lipophilic extractives by ethanol treatment does not affect their elastic properties, and significantly improves the transverse mechanical strength of the composite, due to an enhanced fibre/matrix interfacial adhesion. On the other hand, a large removal of non-cellulosic components induces a degradation of the fibres and strongly affects the transverse mechanical properties of composites.

Our results demonstrate that non-cellulosic cell wall components of flax fibres play a key role in the microstructure, interfacial and mechanical properties of biocomposites. This highlights the need for the development of selective and non-degrading treatments so as to better control the final performances of natural fibres reinforced biocomposites.

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