



HAL
open science

Modification of flax fibres for the development of epoxy-based biocomposites: Role of cell wall components and surface treatments on the microstructure and mechanical properties

J. Acera Fernandez

► To cite this version:

J. Acera Fernandez. Modification of flax fibres for the development of epoxy-based biocomposites: Role of cell wall components and surface treatments on the microstructure and mechanical properties. Chemical and Process Engineering. Université de Montpellier, 2015. English. NNT : . tel-03245945

HAL Id: tel-03245945

<https://hal.science/tel-03245945v1>

Submitted on 2 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THÈSE

Pour obtenir le grade de
Docteur

Délivré par l'**Université de Montpellier**
Faculté des Sciences

Préparée au sein de l'école doctorale GAIA
(Biodiversité, Agriculture, Alimentation, Environnement,
Terre, Eau)

Et de l'unité de recherche C2MA – Ecole des Mines d'Alès

Spécialité : **Génie des Procédés**

Présentée par **José ACERA FERNÁNDEZ**

**Modification of flax fibres for the development of
epoxy-based biocomposites**

Role of cell wall components and surface treatments
on the microstructure and mechanical properties

Soutenue le 15 Décembre 2015 devant le jury composé de

Confidentiel jusqu'au 31 Octobre 2018

Remerciements

Cette thèse est née d'un intérêt industriel, écologique et scientifique pour la valorisation des fibres végétales dans l'élaboration des matériaux composites. Pour cette raison et tout d'abord, je voudrais remercier la société Fibre Recherche Développement (FRD), l'Agence de l'Environnement et la Maitrise de l'Energie (ADEME) et le Centre des Matériaux des Mines d'Alès, d'avoir rendu possible la réalisation de ce projet.

Ensuite, je voudrais exprimer ma plus profonde gratitude à ma directrice de thèse Anne Bergeret et à mon encadrant de thèse Nicolas Le Moigne pour leur soutien, leur sympathie et leur temps consacré à ma formation.

Je tiens aussi à remercier mes rapporteurs de thèse, Mme. Usha Massika Behary, Maître de conférences à l'ENSAIT-Roubaix et M. Julien Bras, Maître de conférences au PAGORA-Grenoble, pour avoir participé à mon jury de thèse et examiné mon travail. Merci également à M. Jean Jacques ROBIN, Professeur à l'ICGM-Montpellier et à M. Jean François CHAILAN, Professeur au SEATECH-Toulon, pour avoir participé à mon jury en tant qu'examineurs. Mes remerciements vont aussi à M. Jean-Paul Gourlot HDR au CIRAD-Montpellier et à M. Vincent Lapinte, Maître de conférences à l'ICGM-Montpellier pour avoir accepté de faire part de mon comité de thèse.

Je remercie l'équipe de FRD, Pierre, Marie, Anne, Arnaud, Clément, Alexis, Sarah et Nicolas de m'avoir accueilli dans leur laboratoire et de m'avoir aidé tout le long de la thèse.

Je remercie également Roland El Hage, Anne Sophie Caro-Brettelle, Marc Longerey et Jean Marie Taulemesse de leur collaboration très importante dans le développement de cette thèse, sans oublier Alain Diaz, Robert Lorquet et Jean Claude Roux pour leur aide.

Pendant la réalisation de cette thèse, j'ai eu l'opportunité d'encadrer un groupe d'étudiants de l'Ecole des Mines d'Alès et de collaborer avec des étudiants de l'Ecole d'Ingénieurs SeaTech (Université de Toulon et du Var). Merci à Pierre Hennequin, Guillaume Giraud et Antoine Guenet de l'Ecole des Mines d'Alès et à Thaïs Armagnat et Léa Distaso, ainsi qu'à leur encadrante Mme. Lenaïk Belec de l'Ecole d'Ingénieurs SeaTech, pour leur collaboration et leur aide dans le déroulement des travaux réalisés.

Je ne peux pas oublier dans mes remerciements mes collègues et amis, Angélique, Remi, Lata, Florian, Violette, Laurent, Aicha, Charlotte, Guilherme, Morgan, Pierre Batiste, Marie, Benjamin et Kevin pour avoir rempli de bons moments ces dernières années. Aussi je tiens à remercier Claire Longuet et Belckacem Otazaghine pour leurs conseils toujours bien appréciés. J'ai certainement oublié des personnes donc je remercie le personnel du C2MA et de l'Ecole des mines d'Alès qui m'ont aidé directement ou indirectement pendant ces 3 dernières années.

Et pour finir, mon remerciement le plus important je l'adresse à mes parents, mes sœurs et mes grands-parents pour avoir cru en moi tout le long de ma vie et m'avoir donné l'énergie, la confiance et le support nécessaires pour aborder et réussir les différents défis que j'ai pu rencontrer. En même temps, je voudrais remercier la personne qui a été à mes côtés ces dernières années pour m'aider, m'encourager et m'exiger chaque jour plus, pour que je puisse réussir dans mes projets. Merci Nibal, car tu sais que sans toi, ça n'aurait pas été possible.

Index

Résumé **1**

De la filasse au fil : propriétés chimiques et mécaniques à travers les différentes étapes de transformation de la fibre de lin.....	2
Rôle des composants des parois cellulaires des fibres de lin sur la microstructure et les propriétés mécaniques de bio-composites lin/époxy.....	4
Modification chimique de la surface de la fibre de lin pour l'amélioration de l'adhésion interfaciale fibre/matrice dans les bio-composites lin/époxy.....	7
Conclusions et perspectives.....	10
Références.....	12

General introduction **15**

Chapter I: Plant fibres, thermoset agro-composites and their interface modification **19**

1.1. Introduction.....	20
1.2. Plant fibres.....	21
1.2.1. Structure and chemical composition.....	21
1.3. Flax fibres.....	29
1.3.1. Flax structure.....	29
1.3.2. From the stem to the final product: Flax fibre transformation steps..	31
1.3.3. Flax fibre properties.....	34
1.4. Thermoset agro-composites.....	36
1.4.1. Textile structures for composites reinforcement.....	36
1.4.2. Main processes for thermoset composites production.....	44
1.4.1. Physical and mechanical properties of thermoset agro-composites..	47
1.5. Interface modification on plant fibres – epoxy composites.....	48
1.6. Conclusions.....	61
1.7. References.....	62

Chapter II: From sliver to yarns: chemical and mechanical properties through the different transformation steps of flax fibres

73

2.1.	Description of the successive transformation steps from flax silver to flax yarns	74
2.2.	Materials and experimental methods	75
2.2.1.	Materials	75
2.2.2.	Visual aspect of flax fibres	75
2.2.3.	Determination of biochemical composition of flax fibres by Van Soest method	75
2.2.4.	Determination of lipophilic component of flax fibres by FT-IR	78
2.2.5.	Moisture content of flax fibres	78
2.2.6.	Linear density of flax fibres	78
2.2.7.	Tensile test of flax fibres	78
2.3.	Influence of the different transformation steps on the visual aspect of flax fibres	79
2.4.	Evolution of the biochemical composition measured by Van Soest method through the process transformation steps	79
2.5.	Evolution of the lipophilic content measured by FT-IR through the process transformation steps	82
2.5.1.	Methodology	82
2.5.2.	Reference FT-IR spectra of lipophilic extractives, lignin, holocellulose and cellulose	83
2.5.3.	Evaluation of the lipophilic content according to the process transformation step	84
2.6.	Evolution of the flax fibre moisture content through the transformation steps	86
2.7.	Mechanical properties of flax fibres through	87
2.8.	Conclusion	91
2.9.	References	91

Chapter III: Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites **95**

3.1.	Introduction.....	96
3.2.	Material and experimental methods.....	99
3.2.1.	Flax fabrics, epoxy resin and chemicals.....	99
3.2.2.	Chemical extraction treatments on flax woven fabrics.....	100
3.2.3.	Determination of the biochemical composition of flax fibre fabrics by solvent extraction.....	100
3.2.4.	Analysis of changes in the biochemical composition of flax fabrics by FTIR.....	102
3.2.5.	Dimension and density of flax yarns and fabrics.....	103
3.2.6.	Contact angle measurements on flax fabrics.....	103
3.2.7.	Manufacturing of flax-epoxy composite plates.....	103
3.2.8.	Determination of fibre reinforcing rate and porosity.....	104
3.2.9.	Scanning Electron Microscopy (SEM) observations and image analysis.....	104
3.2.10.	Differential scanning calorimetry (DSC).....	105
3.2.11.	Transverse tensile mechanical properties.....	105
3.3.	Results and discussions.....	106
3.3.1.	Influence of chemical extraction treatments on flax fabrics properties.....	106
3.3.2.	Influence of extraction treatments on the microstructure of UD flax fabrics reinforced composites.....	114
3.3.3.	Influence of extraction treatments on transverse mechanical behaviour of UD flax fabrics reinforced composites: effect of elementary fibres individualization.....	121
3.4.	Conclusions.....	128
3.5.	References.....	129

Chapter IV: Chemical surface modification of flax fibres to improve the fibre/matrix interface in flax/epoxy composites 135

4.1.	Introduction.....	136
4.2.	State of the art on the molecules used for the chemical modification of flax fibres.....	137
4.2.1.	Organosilanes.....	138
4.2.2.	GABA.....	138
4.2.3.	Chitosan.....	141
4.3.	Materials and experimental methods.....	143
4.3.1.	Materials.....	143
4.3.2.	Preparation of functionalization solutions.....	144
4.3.3.	Chemical modification of flax woven fabrics.....	145
4.3.4.	Manufacturing of flax-epoxy composite plates.....	148
4.3.5.	Determination of physicochemical properties of flax yarns and fabrics and of composites.....	148
4.3.6.	Microstructure analysis.....	150
4.3.7.	Mechanical characterizations.....	151
4.4.	Evaluation of the molecules grafting efficiency onto flax fibre fabrics.....	152
4.4.1.	Characterization of the grafting of organosilanes (APS, GPS) onto flax fibres.....	152
4.4.2.	Characterization of the grafting of biopolymers (GABA, chitosan) onto flax fibres.....	156
4.4.3.	Comparison between organosilane and biopolymer graftings onto flax fabrics.....	163
4.5.	Changes in the dimension and areal density of flax yarns and fabrics after chemical surface modification.....	164
4.5.1.	Organosilane (APS, GPS) treatments.....	164
4.5.2.	Biopolymers (GABA, chitosan) treatments.....	166
4.6.	Influence of chemical surface modification on flax fabrics/epoxy composite microstructure.....	168
4.6.1.	SEM observations.....	168
4.6.2.	AFM observations.....	172

4.7.	Influence of chemical surface modification on the interfacial properties in flax fabrics/epoxy composite.....	178
4.7.1.	Dynamic tensile properties.....	179
4.7.2.	Static mechanical properties.....	186
4.8.	Conclusions.....	194
4.9.	References.....	196

Conclusions **201**

	Perspectives.....	205
--	-------------------	-----

Résumé

Ces dernières années, la sensibilisation écologique a pris une grande importance dans la société. En ce sens, le secteur industriel a fait un effort afin de s'adapter à de nouveaux procédés et de nouveaux produits qui respectent mieux l'environnement. Concrètement, dans le secteur des matériaux composites, on recherche la réduction des émissions de CO₂, à travers la réduction de la consommation énergétique des procédés et l'allègement des structures, ou encore l'utilisation de matériaux bio-sourcés en substitution aux matériaux d'origine fossile. Des réflexions sur la fin de vie des matériaux composites sont également en cours.[1–5]

Actuellement, les matériaux les plus utilisés dans la fabrication de renforts pour les composites sont d'origine synthétique (fibre de verre, fibre de carbone, fibre aramide, etc.). Les fibres d'origine végétale connaissent quant à elles un fort engouement, du fait de leur caractère bio-sourcé et renouvelable, de leur faible densité et de leur bonnes propriétés mécaniques spécifiques, et dans certains cas (en utilisation avec des matrices biodégradables) leur biodégradabilité. [1–5]

Ce projet de recherche est né des besoins du marché et du désir de la société FRD (Fibres Recherche Développement, Troyes), de l'ADEME (Angers) et du Centre des Matériaux des Mines d'Alès (C2MA, Alès) de remplacer les matériaux composites synthétiques par des biocomposites à base de fibres végétales plus respectueux de l'environnement tout en favorisant le développement de produits hautes performances. La performance de ces nouveaux composites est en effet l'un des verrous majeurs à leur développement. Dans ce cadre, l'objectif principal de ce projet de recherche est d'optimiser l'adhésion fibre-matrice dans ces composites en **développant des prétraitements et des traitements de fonctionnalisation de surface des fibres végétales ainsi que les procédés associés**. On cherchera notamment à obtenir un **degré de comptabilisation fibre/matrice optimal transposable à l'échelle industrielle** permettant à terme de développer de nouveaux produits et même de substituer les matériaux composites d'origine fossile.

La fonctionnalisation des fibres végétales est conditionnée en partie par la composition chimique globale des fibres, ainsi que les groupes fonctionnels localisés en surface des fibres. Pour cette raison, un deuxième objectif important de ces travaux est d'étudier d'une part,

l'évolution de la composition et de la chimie de surface des fibres végétales que ce soit lors des différentes étapes de transformation mécanique et chimique qu'elles subissent depuis l'état de tige à l'état de fibre technique, ou lors des procédés de traitement de leur surface et d'autre part, l'effet de ces évolutions sur la microstructure et les propriétés mécaniques du biocomposite.

Afin de traiter les différents objectifs de ce projet, trois études ont été réalisées correspondant aux chapitres 2, 3 et 4:

- Etude sur l'évolution de la composition chimique et des propriétés mécaniques des fibres végétales à travers différentes étapes de transformation allant de la filasse jusqu'au fil technique (chapitre 2).
- Etude du rôle des composants de la paroi cellulaire de la fibre végétale sur la microstructure et les propriétés mécaniques des biocomposites (chapitre 3).
- Etude sur la modification chimique de la surface de la fibre végétale pour l'amélioration de l'interface fibre/matrice dans les bio-composites (chapitre 4).

La fibre utilisée dans le cadre de cette étude a été la fibre de lin. Cette fibre a la particularité d'être la fibre longue de hautes performances la plus produite dans l'Union Européen et en France. Les résines thermodurcissables, en particulier polyesters insaturés, vinylester et époxy, représente 75% de l'industrie des composites. Dans le cadre de cette étude, une résine époxy a été choisie, du fait de ces hautes performances.

De la filasse au fil : propriétés chimiques et mécaniques à travers les différentes étapes de transformation de la fibre de lin

Les propriétés de la fibre de lin et, par conséquent des matériaux composites renforcés par des fibres de lin, dépendent de son génotype, du lieu de production, des conditions pédoclimatiques lors de sa croissance, de sa maturité et des transformations effectuées à travers les procédés d'extraction et de conditionnement. En effet, à partir de la plante de lin, en utilisant différentes transformations mécaniques et chimiques, divers produits et sous-produits utilisés dans la fabrication de matériaux composites, sont obtenus. Afin de maintenir les propriétés constantes entre les différents lots et au fil des années, les producteurs réalisent des mélanges de fibres de

lin de différents génotypes, années de production, etc. La sélection des différents lots de lin, utilisés dans chaque mélange, n'est pas basée sur une analyse scientifique précise, mais plutôt suivant le savoir-faire, les critères et l'expertise des producteurs de lin. Pour cette raison, dans cette première étude, une analyse scientifique de l'évolution de la composition chimique et des propriétés mécaniques de différents lots de lin mélangés par les producteurs, est effectuée aux différents stades de leur transformation.

Pour cette étude, le lin a été obtenu par teillage et peignage à partir de la tige de lin rouie. Deux lots de filasse ont été obtenus à partir d'un mélange de 12 filasses différentes pour chaque lot. Ces filasses ont ensuite été transformées en mèche, en mèche lavée et en fils par des procédés d'étirage et de torsion comme illustré sur la Fig. 1, le premier lot aboutissant à un fil à faible torsion et le second à un fil torsadé. L'évolution de la composition biochimique au cours des différentes étapes de transformation a été déterminée par une analyse par extractions successives selon la méthode de Van Soest, ainsi que par une analyse par spectroscopie infrarouge (FTIR). Des analyses complémentaires ont permis également d'évaluer l'évolution de l'humidité, de la densité et de la résistance mécanique à la traction linéaire à chaque étape de transformation.

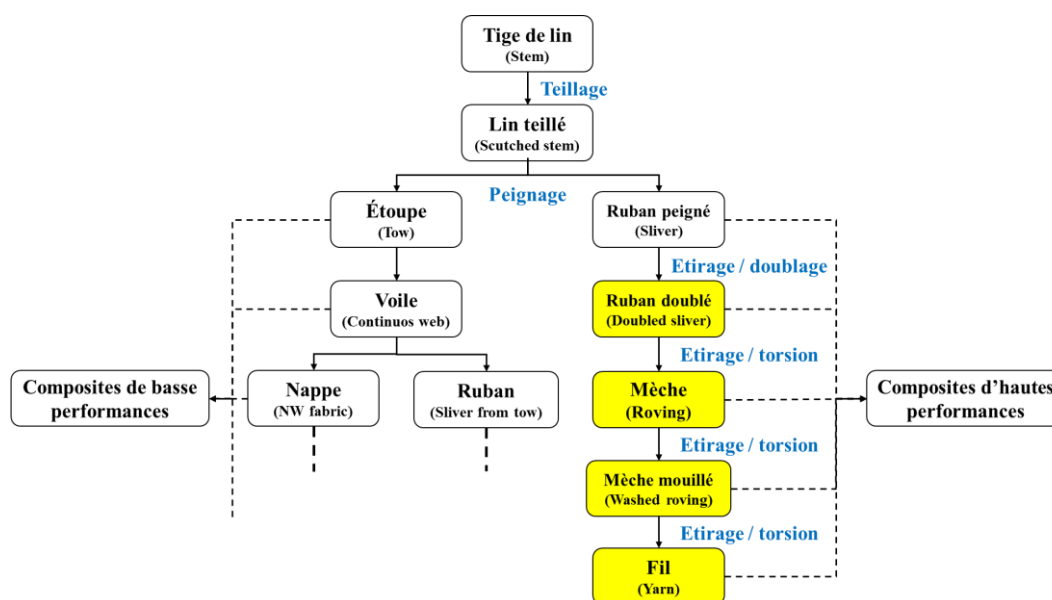


Fig. 1 Schéma avec les différentes étapes de transformation de la fibre de lin (les étapes analysées en jaune)

Après l'étape de lavage, une extraction importante des contenus de la paroi cellulaire (essentiellement la pectine) et de l'hémicellulose a été observée. Une composition biochimique proche entre les deux lots de fils produits a été observée lors de la dernière étape du procédé de transformation de la fibre. Ceci confirme que les étapes de transformation mécaniques et chimiques peuvent homogénéiser des lots différents de lin avec des compositions biochimiques initiales différents.

Tout au long des différentes étapes de transformation, la densité linéaire a diminué de 5000 tex pour la filasse à 100 tex pour le fil avec une augmentation de la résistance à la rupture de 0,2-0,3 mN / tex dans le cas de la filasse, jusqu'à 200 et 450 mN / tex pour les fils à faible torsion et torsadé, respectivement. Cette augmentation peut être d'une part liée à une augmentation de la friction entre les fibres, particulièrement importante après l'étape de lavage des fibres, et d'autre part, à l'augmentation de la torsion. La formation de fibres agglomérées par l'incrément significatif de l'adhérence entre fibres après l'étape de lavage, peut être due à la phase de gélification de la pectine formant des liaisons entre les différentes fibres.

Rôle des composants des parois cellulaires des fibres de lin sur la microstructure et les propriétés mécaniques de bio-composites lin/époxy

Les fibres végétales telles que les fibres de lin sont des fibres ligno-cellulosiques composées essentiellement de cellulose, d'hémicellulose, de lignine, de pectine et d'extractibles lipophiliques répartis dans les différentes parois cellulaires. Afin de déterminer le rôle exercé par chacun de ces composants dans les propriétés des fibres de lin et son implication dans les propriétés mécaniques de biocomposites lin/époxy, une extraction chimique sélective des composants par différentes solutions de traitement a été réalisée dans cette étude. Afin de bien identifier le rôle des composants non-cellulosiques, un tissu unidirectionnel fabriqué à partir de mèches non traitées d'étoupes (environ 84% de mèches sens trame et 16% sens chaîne), qui possèdent une quantité importante de ces composants a été utilisé.

Six différentes solutions de traitements en base aqueuse ou solvants organiques ont été appliquées sur les tissus : a) un traitement à l'éthanol à 96% pendant 1h à 75°C, b) un traitement à l'aide d'une solution de toluène/éthanol (2/ 1 en volume) pendant 1h à 75°C, c) un traitement

avec de l'eau déminéralisée pendant 1h à 95°C, d) un traitement avec une solution industrielle de tensioactifs constituée de 1g d'acide étidronique (HEDP) et de 3g de tensioactifs non ioniques et anioniques (70% en volume de polyéthylène glycol (PEG) et 30% en volume d'acide dodecylbenzenesulfonique/sel de sodium (LAS) pour 1kg de tissu pendant 1h à 95°C, e) deux traitements avec une solution de soude NaOH à 1% et à 5% pendant 1h à 95°C.

La composition biochimique de chaque tissu traité, ainsi que du tissu initial, a été quantifiée en utilisant un protocole d'extractions successives suivant les normes TAPPI T264, ASTM D1103-60 ASTM D1104-56. Les résultats ont été corroborés par analyse FTIR.

Les analyses ont montré que selon la nature des composants extraits, les traitements peuvent être classés en 3 groupes:

- Extraction légère, produite par les traitements à l'éthanol et au toluène/éthanol. Ces traitements extraient respectivement 1,1% et 3,8% en masse des composants non-cellulosiques de la fibre (principalement les extractibles lipophiliques).
- Extraction modérée, produite par les traitements à l'eau et avec la solution de tensioactifs. Dans ce cas, l'extraction de composants non-cellulosiques est de 3,8% et 4,7% en masse respectivement, extrayant modérément les hémicelluloses et des extractibles lipophiliques dans le cas du traitement à l'eau et les différents composants non-cellulosiques dans le cas du traitement avec la solution tensioactive.
- Extraction sévère, produite par les traitements à la soude: une extraction totale de 8,4% et 10,4% en masse s'est produite pour les concentrations à 1% et 5% respectivement, où tous les composants non-cellulosiques (principalement la lignine et les hémicelluloses) ont été affectés.

Une étude de l'effet de l'extraction de ces composants sur les propriétés de surface des tissus a été menée par la mesure de l'angle de contact d'une goutte d'eau sur le tissu et de sa cinétique d'absorption. Une augmentation de la cinétique d'absorption a été observée pour les traitements avec l'éthanol et le mélange toluène/éthanol. Cette augmentation est liée à l'extraction sélective des extractibles lipophiles qui sont hydrophobes. Dans le cas de traitements plus sévères tels

que la soude, l'extraction simultanée des composants hydrophiles et hydrophobes produit un effet compensatoire ; en conséquence, l'effet sur la cinétique d'absorption a été moins marqué.

Pour l'élaboration des composites, tous les tissus ont été séchés à 60°C pendant 24h. Ensuite, 8 couches orientées à 0° et imprégnées d'une résine époxy RESOLTECH 1800/1805 ont été thermo-compressées pendant 21h à 60°C.

La microstructure des composites obtenus a été étudiée par analyse d'images MEB des sections transverses polies. La dispersion des fibres, à l'échelle du faisceau ainsi qu'à celle de la fibre technique, a été observée et évaluée qualitativement et quantitativement. Une diminution significative de la macroporosité et une augmentation de l'état de dispersion des mèches de fibres aux différentes échelles a été obtenues après les traitements, due à l'élimination des ciments présents dans la lamelle mitoyenne, en particulier les pectines, responsables de la cohésion des fibres élémentaires au sein des faisceaux de fibres (fibres techniques) constitutifs des mèches. Ceci facilite la pénétration de la résine au sein des mèches entre les fibres élémentaires et ainsi leur dispersion.

Pour étudier l'effet des traitements d'extraction sur l'interface fibre-matrice au sein des composites, ceux-ci ont été soumis à un essai de traction dans le sens transversal. Une amélioration de la contrainte maximale à rupture a été observée uniquement avec le traitement éthanol contrairement aux autres traitements pour lesquels une diminution très significative a été notée. En raison des nombreux paramètres impliqués qui font varier la microstructure du composite (porosité, taux de renfort, taux de réticulation de la résine et dispersion des fibres dans la résine), la théorie des composites stratifiés («Thin Laminate Plate Theory» ou LPT) a été utilisée pour analyser les résultats à taux de renfort et porosité équivalente. En utilisant cette théorie, le module de Young des fibres de lin dans les sens longitudinal et transversal a été évalué (Tableau 1). Comme pour la contrainte maximale à rupture des composites, seule une amélioration des modules dans le cas du traitement l'éthanol a été observée. La réduction des propriétés mécaniques pour les autres traitements est induite par une dégradation importante de la microstructure des fibres en raison de l'extraction sévère des composants non-cellulosiques.

Tableau 1 Module de Young de la fibre déduit par la théorie des composites stratifiés

Traitement	Module longitudinal E_l (GPa)	Module transverse E_t (GPa)
Non traitée	49.7±2.1	7.1±0.3
Éthanol	52.9±6.4	7.5±0.9
Toluène / éthanol	30.8±1.3	4.4±0.2
Eau	36.0±0.6	5.1±0.1
Tensioactifs	26.3±3.3	3.7±0.5
NaOH 1 %	31.1±1.5	4.4±0.2
NaOH 5 %	28.6±2.0	4.1±0.3

Les résultats obtenus ont montré un rôle clefs des composants non-cellulosiques sur la microstructure et les propriétés mécaniques transverses des composites lin/époxy, associés notamment aux transferts de charge aux interfaces fibres / fibres et fibres / matrice. La maîtrise des traitements de lavage des fibres végétales, afin d'éviter la dégradation des fibres tout en favorisant leur dispersion, constitue donc facteur primordiale sur les performances finales des biocomposites à renfort végétal.

Modification chimique de la surface de la fibre de lin pour l'amélioration de l'adhésion interfaciale fibre/matrice dans les bio-composites lin/époxy

Les propriétés mécaniques des matériaux composites dépendent des propriétés intrinsèques de la matrice, de la fibre et de l'interface. En outre, la qualité de l'interface est régie par l'accrochage mécanique (lié à la topographie et au mouillage) et le couplage physico-chimique (lié aux énergies de surface et aux interactions) existants entre les fibres et la matrice. L'amélioration des propriétés mécaniques des composites lin/époxy peut donc être réalisée en améliorant l'adhésion interfaciale entre la fibre et la matrice, notamment en utilisant des agents de couplage [6].

Les organosilanes ont déjà été utilisés pour la fonctionnalisation des fibres végétales pour améliorer les propriétés mécaniques des composites à matrice époxy [7–9]. Dans ce projet, deux types d'organosilanes ont été étudiées : le 3-amino-propyltriéthoxysilane (APS) et le 3-glycidoxypropyltriméthoxysilane (GPS).

Toutefois, l'un des intérêts majeurs de la substitution des fibres synthétiques par des fibres végétales, est la réduction de l'impact environnemental lors de la fabrication et de l'utilisation de ces fibres renouvelables ; cet intérêt peut se trouver diminué suivant la nature des traitements utilisés. En ce sens, l'une des exigences spécifiées par l'ADEME, est la valorisation de la fibre de lin par le développement de traitements propres, d'où le choix d'utiliser dans ce projet de recherche des molécules de fonctionnalisation bio-sourcées et de procédés associant des solutions aqueuses. Dans le but d'améliorer l'interface fibre/matrice, le choix de ces molécules de fonctionnalisation s'est basé sur la présence de groupes fonctionnels compatibles avec les fibres (en majorité alcool) et avec la matrice (amine ou époxyde). A cet égard, deux molécules ont été choisies pour cette étude: un acide aminé (γ -aminobutyrique ou GABA) et un polysaccharide (chitosane). Un schéma de réaction entre les différents groupes réactionnels portés par la matrice, les fibres et les molécules de fonctionnalisation sélectionnées est représenté sur la Fig. 2.

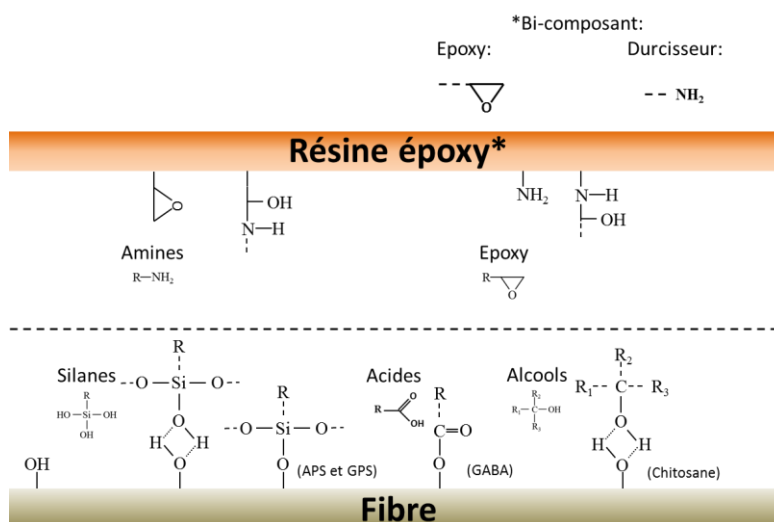


Fig. 2 Schéma représentant les différents groupes réactionnels lors de fonctionnalisation fibre végétale/matrice époxyde

Pour cette étude, un tissu réalisé à partir de la filasse a été utilisé. Ce tissu a été choisi pour sa faible teneur en extractibles lipophiles et ses hautes performances mécaniques. L'application des molécules de fonctionnalisation a été effectuée par un procédé de foulardage durant lequel les tissus ont été imprégnés avec les molécules en solution à 1% et 5% en concentration pour

les organosilanes (APS et GPS), 1, 5 et 10% pour le GABA et 0,5, 1, 2 et 5% pour le chitosane. La masse réelle de molécules sur le tissu était beaucoup plus importante que la masse de molécules théoriquement appliquée (par exemple, pour le APS 1% le pourcentage de molécule sur le tissu était de 2,3%, pour le GABA 1% était de 6,3% et pour le chitosane 1% de 6,4%) Les tissus ont ensuite été séchés à 60°C pendant 24h afin de fixer par condensation ou par l'intermédiaire de ponts hydrogène, les molécules sur le tissu tout en réduisant le taux d'humidité. Ensuite, les composites ont été obtenus par thermocompression pendant 21hs à 60°C en utilisant 8 couches de tissu orientées à 0° et imprégnées avec une résine époxy RESOLTECH 1800/1805.

La présence des molécules de fonctionnalisation à la surface des tissus a été confirmée dans le cas des traitements avec l'APS, le GABA et le chitosane, en observant par FTIR des bandes N-H (1564 cm^{-1}) correspondant aux groupes amine portés par ces molécules. Cette présence n'a pas pu être confirmée par cette technique dans le cas du GPS, du fait de la superposition des bandes époxy avec des bandes de H₂O. En utilisant des autres techniques comme l'analyse gravimétrique ou l'analyse ICP, la présence des molécules GPS sur la fibre de lin a été vérifiée.

La microstructure des composites époxy / lin et l'interface fibre / matrice ont été analysées par différentes techniques (MEB, AFM, DTMA). Une décohésion interfaciale entre la fibre de lin non traitée et la matrice époxy a été observée par analyse AFM. Cette mauvaise adhésion interfaciale a été surmontée d'une manière satisfaisante par la fonctionnalisation des tissus avec les différentes molécules appliquées. Ainsi, une bonne cohésion a été observée au niveau de l'interface fibre/matrice avec les différents traitements, attestant d'une amélioration du couplage mécanique et des interactions physico-chimiques entre les fibres et la matrice époxy (formation de ponts hydrogène ou de ponts covalents avec la fibre, et formation de ponts covalents avec la matrice).

Finalement, l'efficacité des traitements a été confirmée par des essais de traction des composites dans les sens transversal et longitudinal. Une augmentation du module de Young dans la direction transversale a été observée pour les composites avec des tissus fonctionnalisés, à l'exception du traitement avec du chitosane à 5% : en effet, la viscosité de ce traitement produit un revêtement polymérique autour de la fibre, modifiant ainsi les propriétés du composite et

provoquant une diminution du module de Young. Des facteurs d'efficacité du transfert de charge pour le module de Young (k_E) et la contrainte maximale (k_σ) ont été évalués à partir des résultats de traction longitudinale, en utilisant une loi des mélanges applicables aux composites à renforts continus unidirectionnels. Le Tableau 2 montre les différents résultats obtenus : une efficacité du transfert de charge plus importante pour les traitements APS, GPS et GABA à 1% à la fois sur le module de Young (env. 1) et sur la contrainte maximale (jusqu'à 0,6) a été notée. Ceci semble donc indiquer qu'une meilleure adhésion interfaciale fibre / matrice a été obtenue dans ces conditions de traitements avec ces molécules de fonctionnalisation.

Tableau 2 Facteur d'efficacité du module de Young et de la contrainte maximale

	Facteur d'efficacité k_E	Facteur d'efficacité k_σ
UD 19	0,65	0,52
APS 1%	1,01	0,55
APS 5%	0,72	0,51
GPS 1%	0,96	0,60
GPS 5%	0,71	0,49
GABA 1%	1,05	0,53
GABA 5%	0,67	0,49
GABA 10%	0,71	0,41
Chitosane 0,5%	0,75	0,47
Chitosane 1%	0,69	0,48
Chitosane 2%	0,70	0,46
Chitosane 5%	0,65	0,49

Conclusions et perspectives

D'un point de vue environnemental, ce travail fournit de nouvelles solutions dans la mise en œuvre de matériaux composites à base de fibres végétales.

Un des problèmes fondamentaux des fibres végétales, et en particulier la fibre de lin, est leur hétérogénéité en fonction de leur origine, le génotype, l'année de récolte, les conditions de croissance ou le lieu de production. Après leur récolte, les tiges sont transformées par plusieurs étapes mécanique et chimique afin d'obtenir une série de produits et de sous-produits avec des compositions et des propriétés différentes.

Dans ces travaux, une étude préliminaire sur l'évolution de la composition chimique des fibres de lin a été réalisée au cours des étapes de transformation subies depuis la filasse au fil. Elle a

montré une homogénéisation de la composition chimique des fibres à l'étape du fil, et que l'une des étapes clés pour l'homogénéisation de la composition des fibres est le lavage. Dans cette étape, un grand nombre de composants non-cellulosiques ont été éliminés.

Dans le cas des composites fabriqués à partir de fibres végétales, on constate souvent des performances mécaniques limitées. Les performances mécaniques des composites dépendent des propriétés intrinsèques de la fibre, de la matrice et de l'interface. Comme constaté dans le cadre de ce projet, une décohésion entre les fibres végétales et la matrice époxy a lieu si la fibre n'est pas traitée. Afin d'améliorer l'adhésion interfaciale, une première étude pour évaluer le rôle des composants non-cellulosiques sur les propriétés des composites a été menée, en utilisant différents prétraitements des tissus de lin (éthanol, éthanol/toluène, eau, soude, tensioactifs). Selon le traitement, une extraction faible (éthanol, toluène/éthanol), modérée (eau, tensioactifs) ou sévère (soude) des composants non-cellulosiques a été obtenue. Au niveau de la microstructure, un des résultats majeur est la diminution de la macroporosité dans les composites et une individualisation des fibres, plus marquée dans le cas des traitements sévères. En conséquence, pour la majorité des traitements de lavage, une individualisation des fibres a été observée et ainsi une augmentation de la quantité d'interface fibre/matrice. Contrairement à ce qui est espéré, cette augmentation de la quantité d'interface a diminué les performances mécaniques des composites (à exception du traitement avec l'éthanol), du fait d'une dégradation des fibres par l'extraction des composants non-cellulosiques qui participent aux transferts de charge fibre / fibre et fibre / matrice dans les composites.

Enfin, différentes molécules de fonctionnalisation ont été choisies afin d'augmenter l'adhésion interfaciale entre la fibre et la matrice : deux molécules de type organosilane (APS et GPS) porteuse de fonctions amine et époxy, une molécule biosourcée, un acide aminé GABA porteur de fonctions amine, et un polysaccharide, le chitosane porteur de fonctions amines. Les tissus de fibres de lin ont été traités avec ces molécules de fonctionnalisation à différentes concentrations. Une amélioration des propriétés mécaniques des composites a été remarquée, particulièrement dans le cas de la fonctionnalisation avec l'APS, le GPS et le GABA à 1%.

L'étude de la microstructure des composites réalisé tout au long de ces travaux de recherche, nous a permis d'observer, dans un premier temps, que l'extraction des composants non-

cellulosiques de la fibre de lin produisent une individualisation des fibres unitaires, en augmentant ainsi la quantité d'interface fibre / matrice, et, dans un deuxième temps, qu'une optimisation de l'adhésion interfaciale peut être obtenue par un choix judicieux des molécules de fonctionnalisation appliquées sur les tissus de lin. En perspective, la combinaison des traitements d'extraction (prétraitements) avec des traitements de fonctionnalisation pourrait permettre d'améliorer à la fois la quantité d'interface et l'adhésion interfaciale fibre / matrice. Nos résultats ont également montré que les composants non-cellulosiques semblent jouer un rôle important dans les mécanismes de transfert de charge fibre / fibre et fibre / matrice au sein des composites. En ce sens, une étude plus approfondie doit être menée afin de mieux comprendre comment les assemblages supramoléculaires rencontrés dans les fibres végétales contribuent aux propriétés mécaniques des biocomposites, et ainsi de mieux maîtriser les étapes de traitements en limitant au maximum les processus de dégradation associées.

Ces travaux de recherche ouvrent donc des perspectives très intéressantes sur la fonctionnalisation de surface des fibres végétales en vue de leur intégration dans des matériaux composites structuraux, et démontrent la nécessité de développer des traitements ciblés et adaptés à leurs caractéristiques microstructurales et à leurs physico-chimie de surface.

Références

- [1] M. John, R. Anandjiwala, Recent developments in chemical modification and characterization of natural fiber reinforced composites, *Polym. Compos.* 29 (2008) 187–207. doi:10.1002/pc.20461.
- [2] M.M. Kabir, H. Wang, K.T. Lau, F. Cardona, Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview, *Compos. Part B Eng.* 43 (2012) 2883–2892. doi:10.1016/j.compositesb.2012.04.053.
- [3] S. Kalia, B.S. Kaith, I. Kaur, Pretreatments of Natural Fibers and their Application as Reinforcing Material in Polymer Composites — A Review, *Polym. Eng. Sci.* (2009). doi:10.1002/pen.
- [4] O. Faruk, A.K. Bledzki, H.-P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000–2010, *Prog. Polym. Sci.* 37 (2012) 1552–1596. doi:10.1016/j.progpolymsci.2012.04.003.

- [5] Y. Xie, C. a. S. Hill, Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review, *Compos. Part A Appl. Sci. Manuf.* 41 (2010) 806–819. doi:10.1016/j.compositesa.2010.03.005.
- [6] G. Cooper, A. Kelly, Role of the interface in the fracture of fiber-composite materials, *Interfaces Compos.* (1969) 90 – 106.
- [7] I. Van de Weyenberg, J. Ivens, A. De Coster, B. Kino, E. Baetens, I. Verpoest, Influence of processing and chemical treatment of flax fibres on their composites, *Compos. Sci. Technol.* 63 (2003) 1241–1246. doi:10.1016/S0266-3538(03)00093-9.
- [8] T.-T.-L. Doan, H. Brodowsky, E. Mäder, Jute fibre/epoxy composites: Surface properties and interfacial adhesion, *Compos. Sci. Technol.* 72 (2012) 1160–1166. doi:10.1016/j.compscitech.2012.03.025.
- [9] E. Bisanda, M. Ansell, The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites, *Compos. Sci. Technol.* 41 (1991) 165–178. <http://www.sciencedirect.com/science/article/pii/026635389190026L>.

General introduction

Over the last few years, society and industries became increasingly concerned by environmental issues, related to greenhouse gas emissions and climate change. As far as composite industry is concerned, several attempts are conducted to reduce CO₂ emissions by lightening structures and substituting synthetic materials, such as glass fibres, by bio-based materials, such as natural fibres. The use of natural fibres in composite materials can help to reduce CO₂ emissions due to their neutral carbon cycle and lower energy consumption during production. Moreover, their low density could possibly reduce the weight of composite structures, and hence allow significant energy savings in transports.

In this context, *Fibre Recherche Développement (FRD)* Company in collaboration with the *Centre des Matériaux des mines d'Alès (C2MA)* and the *French Environment and Energy Management Agency (ADEME)*, launched a research program focused on the improvement of mechanical properties of natural fibres/epoxy composites in order to replace synthetic fibres for the development of high performance biocomposites intended to be used in structural applications.

The main important parameters that define the mechanical behaviour of a composite are: i) the intrinsic mechanical properties of the reinforcement, ii) the intrinsic mechanical properties of the matrix and iii) the stress transfer between reinforcement and matrix, depending on the interface(s) behaviour. Besides, the composites mechanical behaviour depends on many different parameters, such as the reinforcing dimensions, rate, and dispersion; the porosity, the curing rate or degree of crystallinity of the matrix, etc., which are greatly influence by composite processing methods. In this regard, synthetic fibres reinforced composites and natural fibres reinforced ones present great differences.

Compared to synthetic fibres commonly used in the composite manufacturing, which usually possess a homogeneous chemical composition and bulk structure, natural fibres have a complex cell wall structure and biochemical composition that could vary significantly depending on different factors, such as the fibre type, the specie, the year and the processes of harvesting, the maturity degree or the growing conditions. Concerning the fibre / matrix interface, a considerable difference appears between synthetic and natural fibres reinforced composites. While in synthetic based composites, such as glass fibre composites, a unique interface between the fibres and the matrix is observed; for natural fibres based composites, multiple interfaces

coexist, (i) between the different components, layers and walls within the elementary fibre microstructure, (ii) between the elementary fibres within the fibre bundles (middle lamella zone), (iii) as well as between the fibres or bundles and the matrix. Besides, the surface topography and the diversity of cell wall components present at the fibre surfaces makes the control and improvement of the interfacial adhesion with the matrix more difficult.

Among several strategies, the development of functionalizing treatments applied to natural fibres is promising to improve chemical interactions and mechanical interlocking at the fibre / matrix interface. However, each fibre cell wall component presents different functional groups and reactivity with other molecules and secondary reactions can be produced with the functionalizing treatments. Some of these components can also be weakly bonded at the fibre surface. These aspects must thus be considered for an efficient chemical functionalization or sizing of natural fibres. In this context, the main objective of this research work is the improvement of mechanical performances of flax fibres reinforced epoxy composites by the development of mastered and targeted surface treatments of flax fibres using environment-friendly processes. Accordingly, this dissertation deals with the study and modification of interfacial properties in flax fibres/epoxy composites and is divided in four main chapters.

The first chapter is focused on a general review of literature about the biochemical composition, the structure, the transformation steps to obtain the products and sub-products and the physical properties of natural fibres, especially flax fibres. Moreover, composite manufacturing methods, general composite properties and the different strategies developed to improve the interfacial adhesion in natural fibre/thermoset composites, focused on epoxy based ones, are reviewed.

In a second chapter, an analysis of the evolution in biochemical composition and mechanical properties of flax fibres through their different transformation steps (from slivers to yarns), is investigated. Indeed, flax fibres used for this project were previously mixed with different species, years of collection, and degree of maturity, etc. by the yarn manufacturer in order to homogenize the physical and chemical properties of the different batches. This blending technique is usually used by manufacturers in order to obtain similar quality and properties over the years.

The chapter three is focused on the effect of variations in biochemical composition of natural fibres on the microstructure and mechanical behaviour of natural fibres reinforced composites. Extraction treatments with increasing solvation capacities towards cell wall components are applied on unidirectional flax tow fabrics. The resulting treated flax fabrics are characterized 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 flax fabrics reinforced epoxy biocomposites are investigated and discussed.

Finally, the fourth chapter deals with the modification and improvement of the interfacial adhesion between flax fibres and epoxy matrix. Different functionalizing molecules are applied to high performance flax woven fabrics so as to enhance chemical interactions between the fibres and the epoxy matrix, and improve the stress transfer at the fibre/matrix interface. Two types of molecules bearing amino or epoxy groups are used: non bio-based molecules (organosilanes) and bio-based molecules (polysaccharide and amino-acids); and pilot-scale treatment processes based on eco-friendly aqueous solutions are developed. The influence of developed functionalizing treatments on the microstructural, viscoelastic and mechanical properties of flax fabrics reinforced epoxy biocomposites are analysed.

Chapter I:
Plant fibres, thermoset agro-composites
and their interface modification

1.1.Introduction

Composites are heterogeneous materials that are composed of a reinforcing material and a matrix. Currently, composites are produced using non-renewable reinforcing materials, such as glass fibres, carbon fibres or aramid fibres. But nowadays, ecological awareness has taken a huge importance in the society so that plant fibres are more and more used in the industry. The agro-composites production involves lower CO₂ emissions than conventional fossil derived composites. At the same time, the growth of the plant fibres may reduce the CO₂ emitted in the air during photosynthesis. Moreover, plant fibres reduce significantly the density of composites in comparison with, for example, glass fibre based composites [1–5].

In this part, a detailed state of the art on plant fibres will be exposed with a focus on flax fibres. Afterwards, specificities on agro-composites and mainly on thermoset ones will be presented. Whatever the type of composite materials, their mechanical properties depend on the intrinsic properties of the matrix and the fibres, but also on the quality of the interface in between for allowing a good stress transfer under solicitation. The control of the interfacial adhesion is currently a scientific challenge and the subject of numerous studies as concerns agro-composites. Therefore the last part of this chapter will be dedicated to the different strategies developed to modify the plant fibre surface with a focus on epoxy based agro-composites.

1.2.Plant fibres

Plant fibres are a kind of natural fibres obtained from the stem, the seed, the fruit or the leaf of higher plants some plants, grass or wood. In 2009, the Food and Agriculture Organization (FAO) of the United Nations estimated the global production volume of the main plant fibres (cotton, kapok, jute, kenaf, flax, hemp, ramie, abaca, sisal, henequen and coir) equal to 29.61 million tons per year without taking into consideration wood fibres. Natural fibres end-markets are principally textile fabrics for wear, home furnishing, construction, geotextiles, cellulose and paper and composites [6].

1.2.1. Structure and chemical composition

The main component of plant fibres is cellulose. Its amount varies as a function of plant type, but also growing (maturity) and harvesting (retting) conditions. Many other components are found in plant fibres such as lignin, hemicellulose, pectin, proteins and lipophilic extractives, as for example, waxes. Natural fibres can be considered as a composite material (Fig. I - 1a) with cellulose microfibrils as reinforcing element embedded in a matrix of hemicellulose, pectin, protein and lignin [7]. Each elementary fibre is composed of two main walls, i.e. the external wall called the primary wall and the internal walls called the secondary walls (Fig. I - 1c). The thin primary wall is the first layer formed during the cell growth of the fibre, and it is rich in non-cellulosic components. The secondary wall, rich in cellulose, is composed of three layers (S1, S2, S3). Mechanical properties are partly determined by the thick middle layer S2. In this layer, cellulose microfibrils are helically oriented along the fibre axis. The microfibrillar angle varies from one fibre to another, and strongly influences the stiffness and the ultimate properties of natural fibres [8].

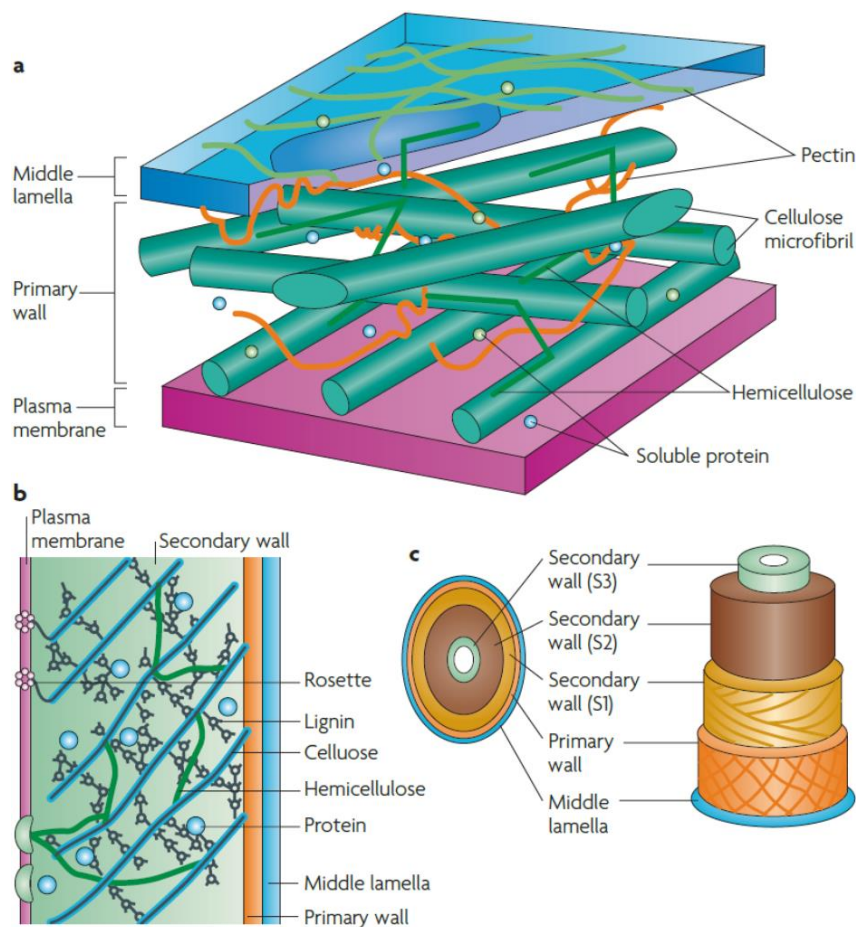


Fig. I - 1 Plant plasma membrane and cell-wall structure: a) First step of the biosynthesis with the primary cell wall containing cellulose microfibrils embedded in a matrix of hemicellulose, pectin, lignin and soluble proteins. b) Cellulose synthase enzymes are in the form of rosette complexes, which float in the plasma membrane. c) Elementary fibre microstructure with the external primary wall and the internal wall secondary walls : lignification occurs in the S1, S2 and S3 layers of the cell wall (taken from [9])

In the next sections, the main individual chemical components of plant fibres will be described.

1.2.1.1. Cellulose

Cellulose is the main polysaccharide and the major reservoir of organic carbon on earth, with an annual production of about 180 billions tons [10]. It is produced mainly by higher plants and some algae but also by sea squirts and tunicates, the only animals that can produce cellulose [11].

Chemical structure of plant cellulose consists in linear macromolecules of about 1,000-30,000 anhydroglucose units (AGU) depending of sources, which are linked together by β -1,4 linkages (Fig. I - 2). The three hydroxyl groups and the oxygen atoms of the AGU rings can interact with each other to form a dense intra- and inter-molecular hydrogen bonds network. This gives rise to the formation of highly ordered and crystalline cellulose microfibrils of 3 to 30 nm in diameter that are composed of several tens of cellulose macromolecules [12,13]. In the secondary cell wall of plants, cellulose microfibrils are aligned parallel to each other along the fibre axis. Typically, cellulose composes 15 to 30% of dry mass of primary cell wall and more than 40% of dry mass of secondary cell wall in higher plants [9].

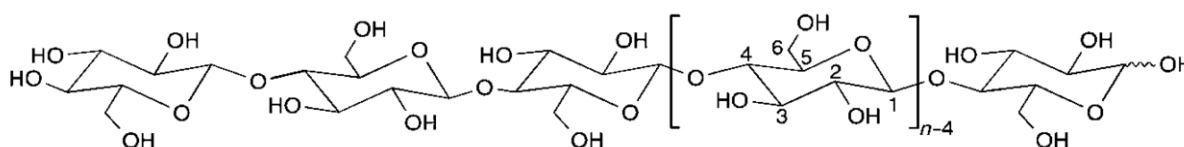


Fig. I - 2 Molecular structure of cellulose (taken from [12])

1.2.1.2. Hemicellulose

Hemicellulose is a group of polysaccharides that represents around 20 – 35% of lignocellulosic biomass in nature [14]. Chemical composition of hemicelluloses, as well their amount and localization in primary and secondary walls, depend on the type of plant considered. As a combination of several repeating disaccharide units (Fig. I - 3), the main types of hemicelluloses are: xyloglucan, glucuronoxylan, glucuronoarabinoxylan, (gluco)mannan, galactoglucomannan and β -(1 \rightarrow 3, 1 \rightarrow 4)-glucan. Scheller et al. suggested [15] that hemicelluloses should only be considered as glycans with equatorial configuration at C1 and C4 and hence that the backbones have significant structural similarities. The principal differences between cellulose and hemicelluloses are (i) the composition as cellulose contains only 1,4- β -D-glucopyranose units; (ii) the crystallinity as hemicellulose is amorphous unlike cellulose that is semi-crystalline; and (iii) the degree of polymerisation that is around 10 to 100 times higher for cellulose than for hemicellulose. Moreover hemicellulose is a very hydrophilic component. It is soluble in alkali and easily hydrolysed in acids [8].

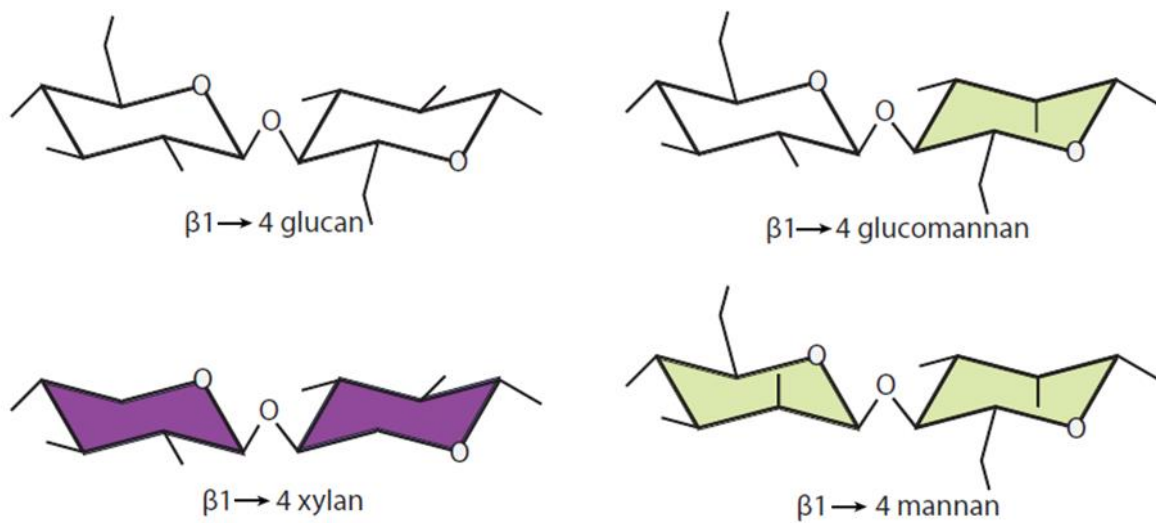


Fig. I - 3 Molecular structure of the main repeating disaccharideunits in hemicelluloses (taken from [15])

1.2.1.3. Lignin

Lignin is a complex hetero-biopolymer that represents 30% of the organic carbon on earth, just after cellulose that is the most abundant terrestrial biopolymer. It is mainly composed of three phenolic building blocks: p-hydroxyphenyl, guaiacyl and syringyl (Fig. I - 4). This forms a complex three-dimensional cross-linked network [16]. The main functions of lignin in plants are: (i) to preserve the structure of the cell walls, (ii) to bring stiffness and strength to the stems because of its covalent bonds with hemicelluloses [17]; (iii) to allow the transport of water and solutes by waterproofing cell walls; and (iv) to protect the plant against pathogens [16].

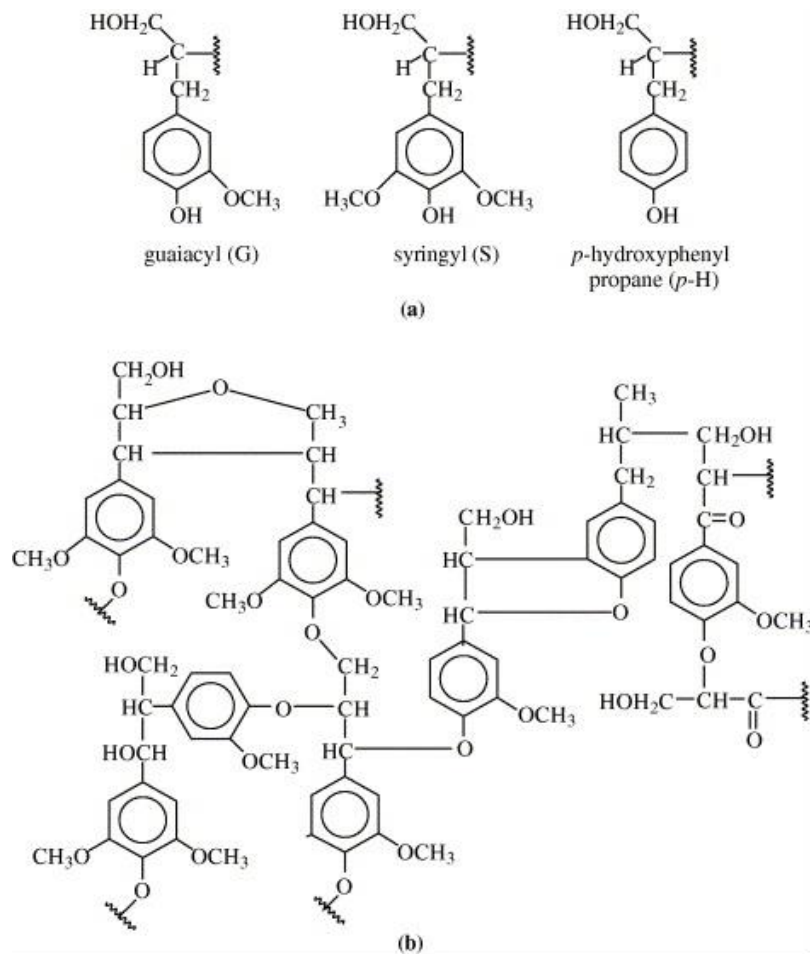


Fig. I - 4 (a) Schematic representation of the structural units of lignin, and (b) lignin structure proposed by Adler (1977) (taken from [18,19])

1.2.1.4. Pectin

The pectin is a structural hetero-polysaccharide found principally in the primary wall of non-wood plant fibres, being the main component of the primary wall in land plants. Pectin is also abundant in the middle lamellae between elementary cell fibres, where it regulates the intercellular adhesion. In the second cell wall, pectin is present in low amounts or absent. Pectin is constituted by a group of polysaccharides rich in galacturonic acid (GalA) residues, in which varying proportions of the acid groups are present as methoxyl esters, while a certain amount of neutral sugars might be present as side chains[20]. Pectins species are formed by different polysaccharides, eg. homogalacturonan (HGA), xylogalacturonan (XGA), rhamnogalacturonan-I (RG-I) and rhamnogalacturonan-II (RG-II), arabinan (ARA),

arabinogalactan I (AGI) and arabinogalactan II (AGII) [20,21]. Different cross links of pectins are shown in Fig. I - 5.

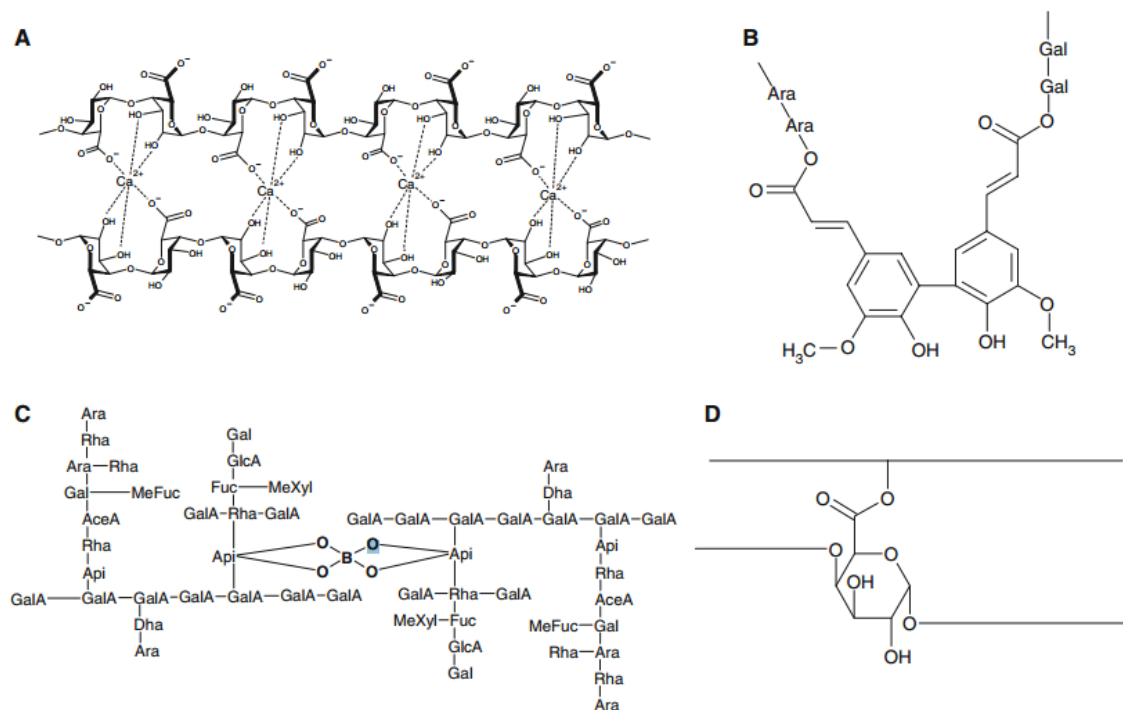


Fig. I - 5 Pectin cross links as described in literature. A) Calcium-pectin crosslink as egg box model, B) 5-5-diferulic esterified with neutral sugar side chains of pectin, C) Rhamnogalacturonan II diester, D) uronyl ester of pectin with a hydroxyl group of another polysaccharide chain (taken from [20])

1.2.1.5. Lipophilic extractives

The lipophilic extractives are a combination of many different components with low molecular mass, as fatty acids, and high molecular mass, as waxes, sterol esters and tri-glycerides [22]. The main chemical structures of lipophilic extractives are shown in Fig. I - 6.

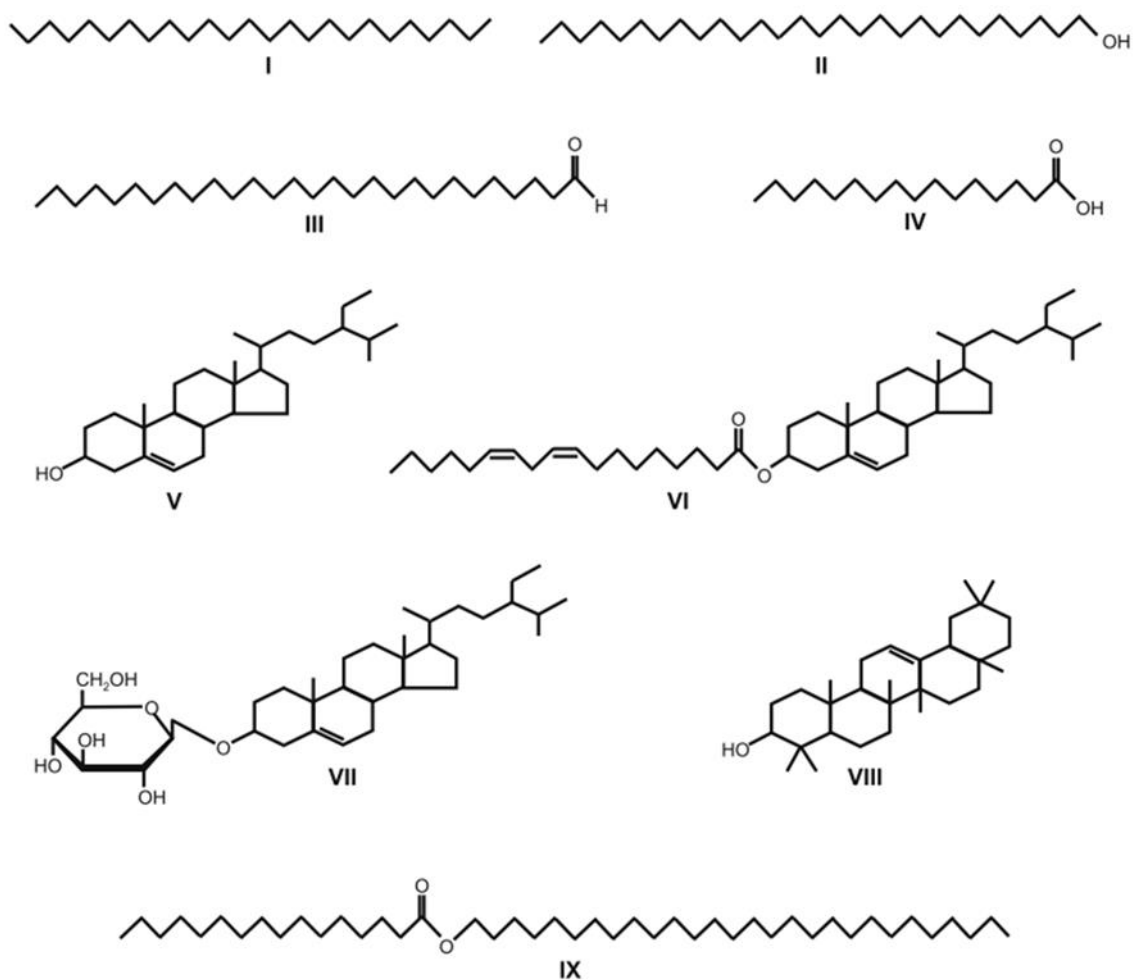


Fig. I - 6 Chemical structures of compounds representing the main classes of lipophilic extractives found in lignocellulosic fibres: (I) pentacosane; (II) octacosanol; (III) octacosanal; (IV) palmitic acid; (V) sitosterol; (VI) sitosteryl linoleate; (VII) sitosteryl 3b-D-glucopyranoside; (VIII) b-amyrin; and (IX) octacosyl hexadecanoate (taken from [23])

In Table I - 1, the diversity in terms of biochemical composition is presented for different types of plant fibres. Considering this wide diversity, one can expect very different physical properties and behaviours when comparing different types of natural fibres.

Table I - 1 Biochemical composition of different plant fibres

Source	Type of fibre	Cellulose wt. %	Hemicellulose wt. %	Lignin wt. %	Pectin wt. %	Wax wt. %	References
Fruit	Coir	32 - 43	0.15 - 0.3	40 - 45	3 - 4	–	[24–33]
	Kapok	63.5 - 64	23	13 - 19	23	–	[34,35]
	Oil Palm	65	–	19 - 29	–	–	[32,36]
	Sponge gourd	63	19.4	11.2	–	3	[32]
Grass	Alfa	45.4	38.5	14.9	–	2	[32]
	Bagasse	32 - 55.2	16.8 - 24	23 - 32	–	–	[32,33]
	Bamboo	26 - 73.83	12.49 - 30	10.15 - 32.2	0.37	–	[29,32,37]
	Sea grass	57	38	5	10	–	[30]
	Switchgrass	30 - 50	10 - 40	5 - 20	–	–	[38]
Leaf	Abaca	56 - 70	14.9 - 22	5 - 14	0.8	1.4	[39–41]
	Agave Americana	59 - 68.42	15.67 - 38.4	2.5 - 4.85	–	0.26	[42–44]
	Banana	60 - 83	6 - 19	5 - 10	–	–	[26,28–33,45]
	Coconut tree leaf sheath	27	14	27.7	–	–	[30]
	Corn stover	32 - 40	21 - 33	6 - 21	0 - 1	0 - 3	[28,33,46]
	Curuaua	85 - 90	5.7	–	–	0.6	[32]
	Henequen	60 - 77.6	4 - 28	8 - 13.1	–	0.5 - 3.6	[24,30–32,47,48]
	Piassava	28.6	25.8	45	–	–	[30,32]
	Pineapple	67.12 - 82	7.1 - 19	4.4 - 15.4	1.1 - 3	3.2 - 4.2	[24,26,28,31– 33,45,49,50]
	Phormium tenax	45.1 - 72	30.1	11.2	0.7	0.7	[30,31]
	Sisal	65 - 78	8 - 14.2	8 - 14	0.8 - 10	2	[24–27,29–32,41,45]
Seed	Cotton	82.7 - 93	3 - 6	–	0 - 1	0.6	[24,27,30–32,41]
	Palmyrah	40 - 52	–	42 - 43	–	–	[26,51]
	Talipot	67 - 68	–	28 - 29	–	–	[26,51]
Stem	Barley straw	31 - 45	27 - 38	12 - 14	–	–	[28,33]
	Flax	64.1 - 81	11.62 - 20.6	2 - 3	1.72 - 4	1.5 - 1.7	[24,25,27,31,32,37,41]
	Hemp	63 - 75	10 - 22.4	3 - 10	0 - 1	0 - 3	[24,25,27,30– 32,41,46]
	Isora	74	–	23	–	1.09	[32]
	Jute	61 - 72	12 - 22.4	11.7 - 13.3	0.2 - 1.72	0.5	[24,25,27,29– 32,34,37,41,52]
	Kenaf	31 - 72	8 - 21.5	8 - 21.5	0.6 - 5	0.8	[24,30–32]
	Kudzu	33	11.6	14	–	–	[32]
	Miscanthus	38.2	24.3	25	–	4.2	[53]
	Nettle	47.63 - 86	10 - 18.9	8.15	8.11	1.95 - 4	[32,54]
	Petiole bark	46	–	12	–	–	[26]
	Ramie	68.6 - 76.2	13 - 16.7	0.6 - 1	1.9 - 2	0.3	[24,25,27,31,32]
	Rice straw	28 - 36	23 - 28	12 - 14	–	–	[28,33]
	Sorghum	12.4 - 27	10.2 - 25	4.8 - 11	–	–	[28,33,55]
	Sunn hemp	41 - 48	8.3 - 13	22.7	–	–	[32]
Wheat straw	33 - 51	15 - 32	12 - 20	8	–	[27,28,32,33,38,41]	
Wood	Hardwood	45 - 50	20 - 25	20 - 25	–	–	[38]
	Softwood	35 - 58	18 - 30	17 - 34	0 - 3	–	[30,38,46]

1.3. Flax fibres

Flax (*Linum usitatissimum L.*) is the oldest fibre used by humans about 10 000 – 8000 B.C. (Neolithic period). The oldest sample of textile, a fragment of white woven cloth of flax of about 10 000 years old, was found in Cayonu (Turkey). Egyptians are considered the first civilization that cultivated and produced fibres from flax. Flax technology was transferred to other civilizations by Phoenician sailors. With the conquest of America, Spanish brought to Europe cotton fibres. Cotton began to replace flax from the nineteenth century and since the twentieth century cotton and artificial fibres (viscose) replaced more intensively flax. Flax fibres were extensively used during the Second World War, principally in the manufacture of airplanes, parachutes and incendiary bombs [56]. Nowadays, flax fibres are used mainly in textile applications, but new sectors, such as composite manufacturing, are emerging (Fig. I - 7).

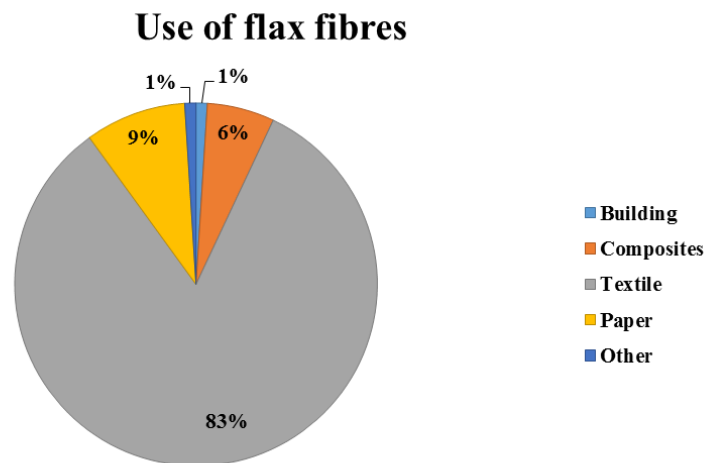


Fig. I - 7 Main applications sectors of flax fibres (taken from [57])

1.3.1. Flax structure

Flax fibres are obtained from the stem of the *Linum usitatissimum L.* Two main parts, separated by a cambium layer, can be observed in a flax stem cross section (Fig. I - 8): a central woody core and a surrounding cortex, which contain the bast fibres [58]. From the outside to the inside, flax stems are composed of [59,60]:

- The cuticula is a thin waxy layer localized at the edge of the stem surrounding the cortex. The main function of this layer is the protection against pathogens and water loss. A layer of epidermis, located underneath the cuticula, serves several functions such as water loss protection, gas exchange regulation and metabolic compounds secretion
- Bast fibres are surrounded by thin-walled parenchyma cells. These cells contain much chlorophyll, pectins and lignin material. The bast fibre layer contain between 15 and 40 weakly bonded fibre bundles, also called technical fibres. Each of these fibre bundles is composed of several elementary fibres with an average diameter of 15 μm and length of about 25 mm.
- The cambium layer separates the bast fibres from the central woody core. The cambium produces secondary tissues to transport nutrients.
- The woody core is composed by an external wood tissue, the xylem, and the pith, which surround the lumen, i.e. the central channel of the stem.

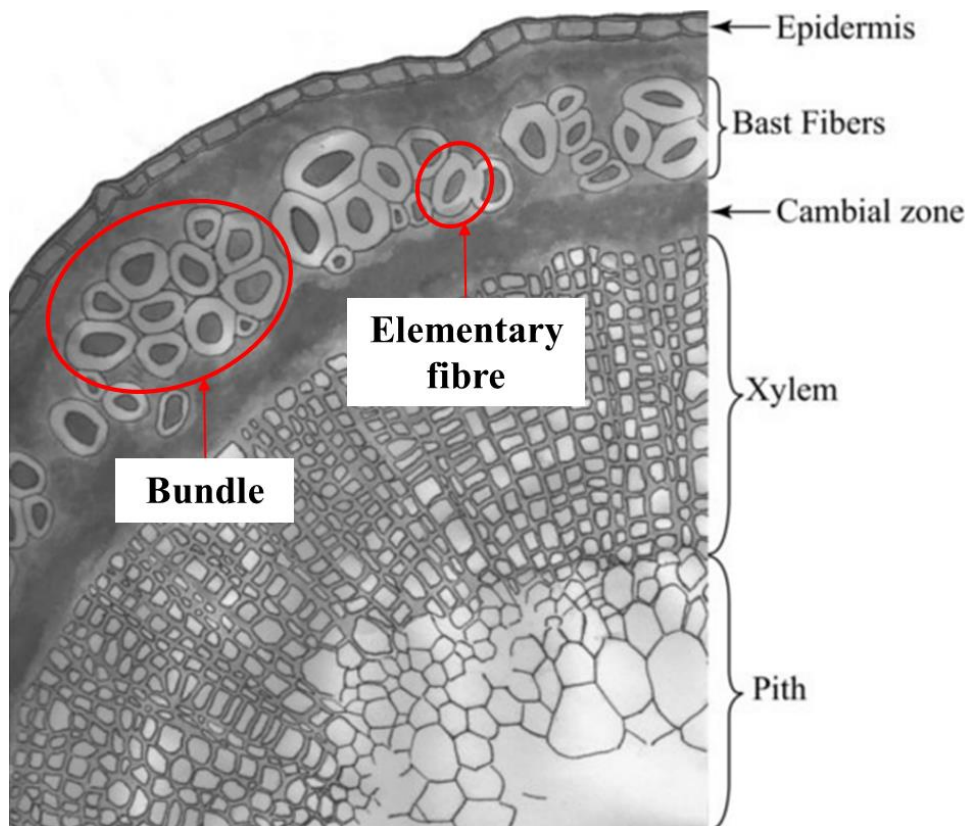


Fig. I - 8 Flax stem cross-section (adapted from [61])

1.3.2. From the stem to the final product: Flax fibre transformation steps

Flax undergoes a series of transformation steps from the stem to the final product (tow, slivers, roving, mat, yarns or fabrics). During the transformation process, several secondary products are obtained; therefore, an important amount of straw flax is required to obtain a high quality product, as slivers (Fig. I - 9).

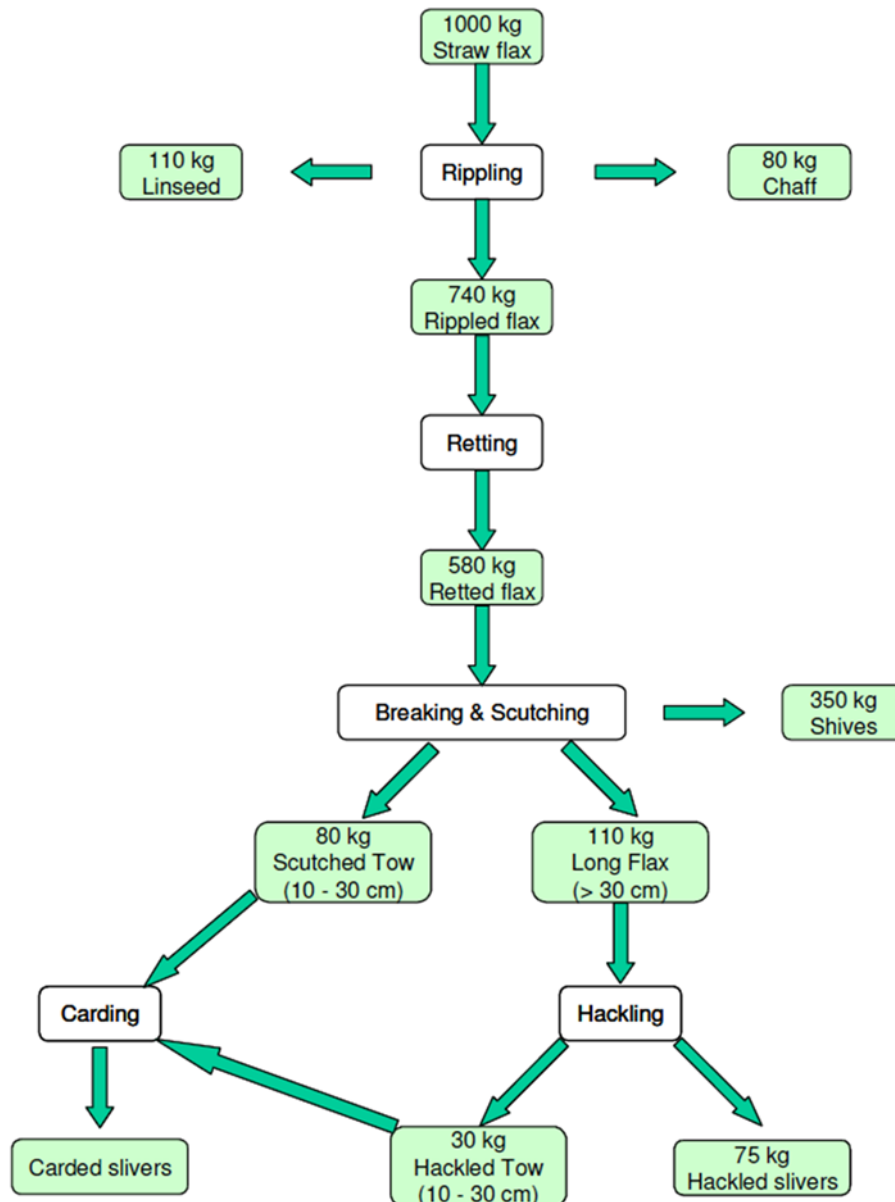


Fig. I - 9 Processing scheme for flax fibres, including the average yield after each stage (taken from [60])

When flax plants maturity is reached, flax stems are harvested pulling from soil (not cut) and stacked one beside the other. Then, flax transformation procedure (Fig. I - 9) begins [56]:

- In the first stage, flax plant is degummed. There are several degumming methods for flax plants (Fig. I - 10). Some of these methods, as water degumming, are harmful to the environment, and are not usually used nowadays. The most useful method to degum flax plants is the dew-retting in the countryside. This method consists in the degradation of the woody core by external agents, such as the sun, humidity and enzymes excreted by microorganisms. For an efficient degumming, plants are returned periodically (Fig. I - 11).

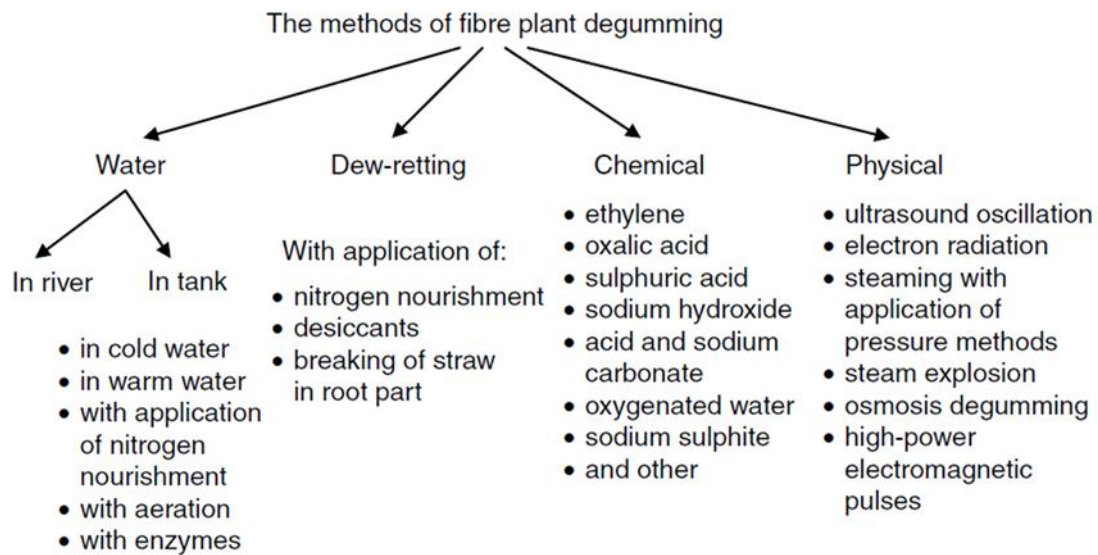


Fig. I - 10 The methods of fibre plant degumming (taken from [56])



Fig. I - 11 Flax fibre dew-retting process (taken from [56])

- The second step consists in the scutching process. At this step, the bast fibre is separated from the woody core. During this step, fibres are aligned and bent by mechanical process, which allows breaking the stems and retrieving bast fibres and shives.
- Once bast fibres are obtained, hackling or combing is carried out. This process allows preparing fibres for an effective and good quality spinning. The obtained products are: long straight fibre bundles (“line fibre”) and short tangled fibres (“tow fibres”).
 - With short tangled fibres (lower quality), carding is carried out. This process allows the orientation of short fibres. It is possible to obtain mats, tow, roving, yarns and fabrics of low-quality using these fibres.
 - With long straight fibre bundles (high quality), different processes can be carried out. Cottonization, for example, involves cutting and refining processes as well as the removal of impurities as much as possible, for a subsequent spinning by cotton process (short fibres) or wool process (long fibres). In thermoset composite applications, flax fabrics can be obtained from rovings or yarns.

1.3.3. Flax fibre properties

The bio-based nature, as well the physical and mechanical properties of flax fibres, makes them an attractive material to use in composite applications, in order to substitute common reinforcing materials as glass fibres. The main physical, morphological and mechanical properties of flax fibres and glass fibres are presented in Table I - 2.

Even though mechanical properties of glass fibres are usually much higher than those of flax fibres – tensile strength is around 2.5 times higher for E-glass, 3.5 times for R-glass and 2 times for D-glass in comparison with flax fibres; Young's modulus is around 1.2 and 1.5 times higher for E-glass and R-glass and similar for D-glass –, density of flax fibres is almost twice less than glass fibres. Taking this into account, when specific mechanical properties are compared, properties of flax fibres and glass fibres become closer: specific tensile strength is around 800 MPa/cm³/g, 1100 MPa/cm³/g, 1800 MPa/cm³/g and 1200 MPa/cm³/g for flax, E-glass, R-glass and D-glass fibres, respectively, while specific Young's modulus is around 40 GPa/ cm³/g, 28 GPa/ cm³/g, 34 GPa/ cm³/g and 26 GPa/cm³/g respectively. Lowering the overall density of the composites is also considered as a substantial advantage in many structural applications such as transportation for which decreasing the vehicle weight allows a significant gain in energy and less gas emission[62].

Table I - 2 Physical, morphological and mechanical properties of flax , E-glass, R-glass and D-glass fibres

	Properties	Flax	References	E-glass	R-glass	D-glass	References
Physical	Density (g/cm ³)	1.4 - 1.5	[63–66]	2.55 - 2.6	2.5	2.14	[67,68]
	Moisture content (wt. %)	8 - 12	[63,64]	<0.1	<0.1	<0.1	[67,68]
	Shape of cross-section	Round-oval / polygonal	[56]				
Morphological	Diameter of elementary fibre (µm)	10 - 80	[56,64,65,69]				
	Length of elementary fibre (mm)	27 - 36	[64,66]				
	Aspect ratio (d/l)	1258 - 1687	[64,66]				
	Wall thickness (µm)	5 - 10	[56]				
	Microfibrillar angle (°)	5 - 10	[63,64,66]				
	Tensile strength (MPa)	343 - 2000	[63–66,69,70]	2400 - 3500	4400	2500	[67,68]
Mechanical	Young's modulus (GPa)	12 - 103	[63–66,69,70]	70 - 73	85	55	[67,68]
	Ultimate elongation (%)	1 - 4	[63–66,69]	3 - 4	4.8	4.5	[67,68]

There are also other advantages of natural fibres compared to glass fibres, as mentioned in Table I - 3: for instance, natural fibres are renewable and biodegradable resources, and their use in industrial processes does not cause any significant risks regarding the abrasion and deterioration of the machines, which is the case when using glass fibres [68].

Table I - 3 Comparison between natural and glass fibres (taken from [68])

	Natural fibres	Glass fibres
Density	Low	Twice that of natural fibres
Cost	Low	Low, but higher than natural fibres
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO2 neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes

1.4. Thermoset agro-composites

1.4.1. Textile structures for composites reinforcement

1.4.1.1. Generalities

An important part of thermoset composites are using textile substrates as reinforcing elements. Some textile manufacturing techniques, used for technical textiles, have been adapted to composites textiles as reinforcing elements (Fig. I - 12) [71]. The main difference between 2D and 3D fabrics is their thickness. The use of techniques, such as the warp knitting allows to produce 3D fabrics with thickness ranging from 3 to 65 mm [72]. In laminate composites, 2D fabrics are mostly used. The three main techniques used for the manufacturing of fabrics intended for composite laminates are:

- ***Non-woven fabrics***: In non-woven fabrics, the bonding of fibres can be made by mechanical, chemical or thermal methods, replacing the weaving or knitting of yarns in conventional textiles. Non-woven fabrics are basically produced in two steps, i.e. web formation and web bonding, although modern technologies are based on a single-step processing. The main fabric structure obtained by this technique is the ***mat***, in which short fibres are randomly organized.
- ***Woven fabrics***: They are commonly manufactured by ***weaving*** processes. The bonding of fibres is carried out by interlacing yarns perpendicularly. This technique allows obtaining ***quasi-unidirectional fabrics (UD)*** and ***bi-axial fabrics (0°/90°, +/- 45°)***.
- ***Knitted fabrics***: The bonding consists in elaborating fabrics by loop yarn formation. Depending on how the yarns are supplied to the needles, two main techniques can be used: ***weft knitting*** and ***warp knitting***. ***Unidirectional (UD)***, ***bi-axial (0°/90°, +/- 45°)*** and ***multi-axial fabrics*** can be obtained using these techniques.

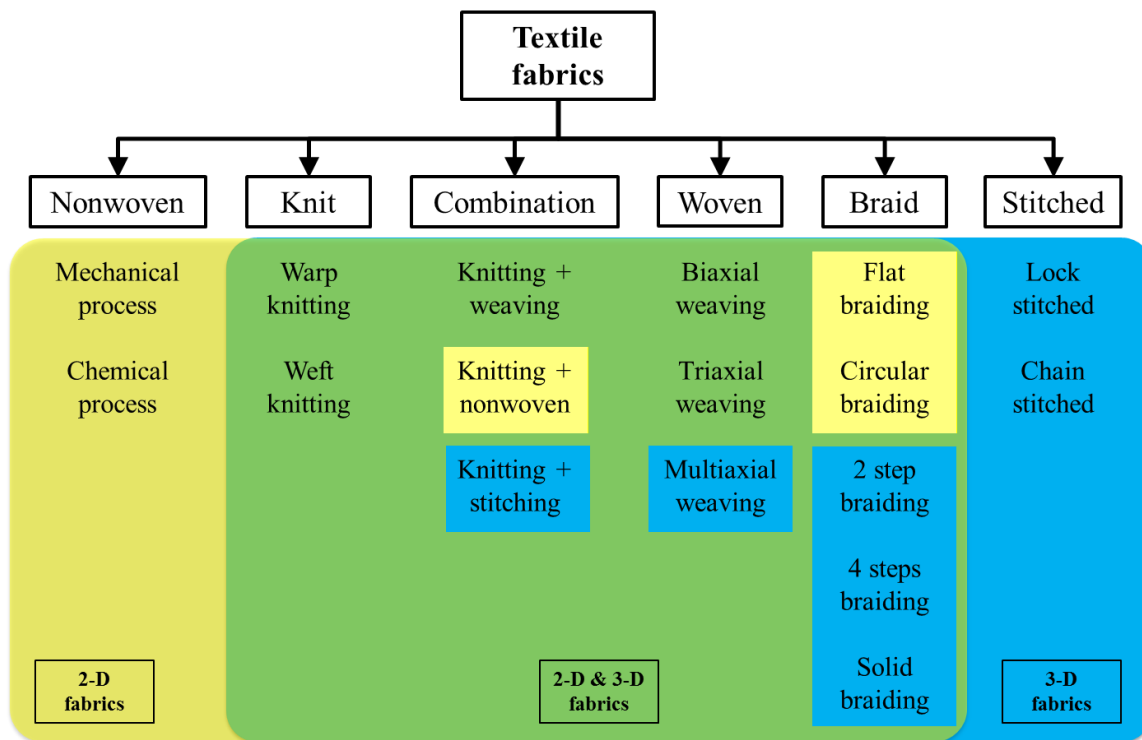
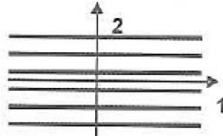
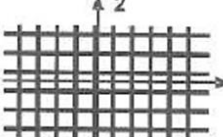
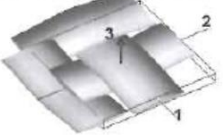
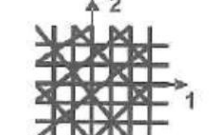

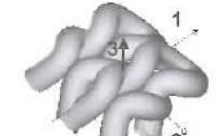


Fig. I - 12 Technical textile fabrics used as reinforcement in composites (adapted from [73])

Woven fabrics are the most used reinforcement in thermoset composite laminates and this kind of fabrics has been used in the framework of this doctoral thesis. A detailed description of the processing techniques and resulting fabric structures is given in section 1.4.1.2.

Depending on the kind of reinforcement and materials used, physical properties of composites will be completely different. Table I - 4 shows typical mechanical properties, i.e. E,G, “nu” of flax/epoxy composites. The alignment of the fibres in the mechanical stress direction improves drastically the properties of the composites.

Table I - 4 Typical values of engineering stiffness parameters (E,G, “nu”) of UD, cross-ply and textile flax/epoxy composites. Fibre volume fraction 60% (taken from [74])

Reinforcement	Image and coordinate system (for laminates: Axis 3 is normal to the image plane)	E11, E22 GPa	Flax/epoxy G12 GPa	ν_{12}
UD		39.5 4.4	2.4	0.311
Cross-ply 0-90		23 23	2.4	0.061
Plain woven, crimp 1.5%		15 15	2.2	0.023
Quasi-isotropic 0/45/-45/90		17 17	6.7	0.283
Tri-axial braid 0/60/-60 crimp braiding yarns 1%		17 15	5.8	0.267
Knitted jersey		6.5 6.0	2.7	0.301

1.4.1.2. Woven fabrics

In two-dimensional woven fabrics, yarns are interlaced and lie at right angles to each other. The yarns disposed in the length direction of the fabric are called *warp ends* or simply *ends*. The yarns perpendicularly disposed to the length direction are called *weft picks* or *picks* [75].

In the *weaving* process, one yarn is required for each warp end. The number of yarns can be very important, depending on fabric size and yarn count. In order to increase the productivity and the quality control, a previous step of *warping* (Fig. I - 13) is required. This step consists in unwinding the yarns from bobbins and rewinding it simultaneously on a weaver's beam,

controlling yarn tension and yarn breaks. During the warping process, yarns can be sized in order to reduce wear, tear or breaks during *weaving*.

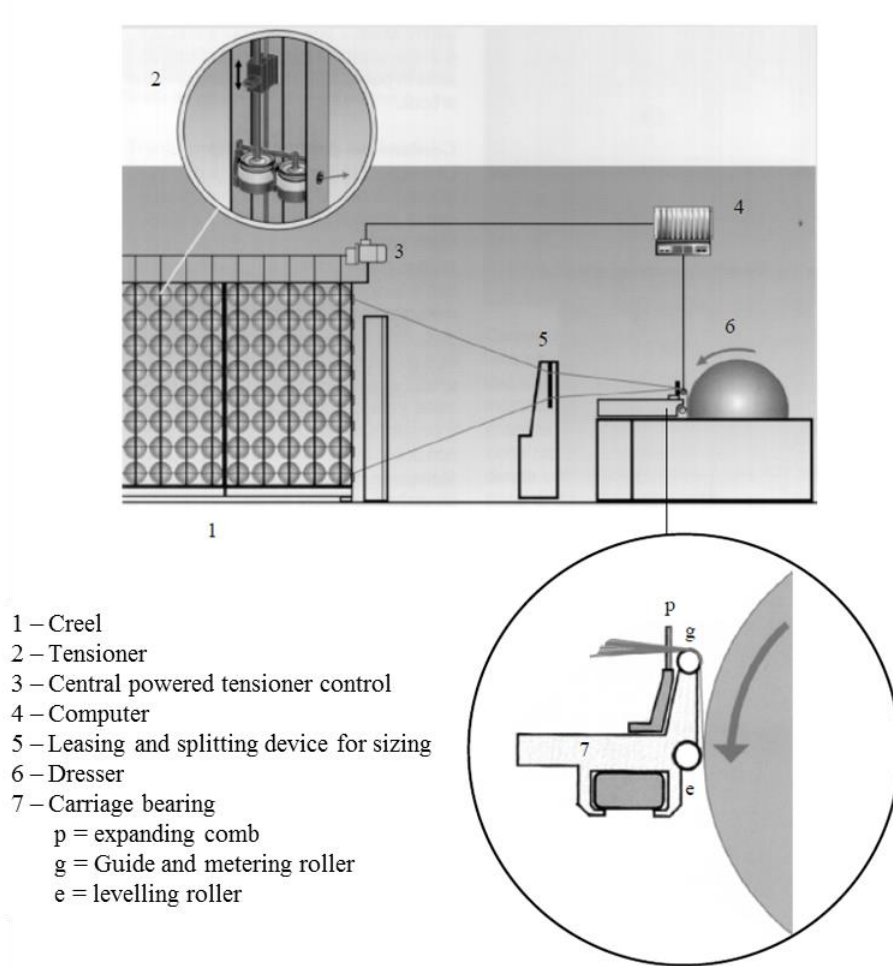


Fig. I - 13 Schematic representation of the warping machine and process (taken from [76])

A schematic representation of a simple loom weaving machine is shown in Fig. I - 14. Once warping and, eventually, sizing are carried out, warp ends yarns are guided through the loom. Woven fabrics are produced by interlacing warp ends yarns with weft picks yarn. Ends are selected to the front or to the back of the fabric using the heddles. The areal density of fabric is obtained by the yarn count, warp let-off velocity, fabric take-down velocity and pressure of the shuttle on the fabric. The weft pick yarn is introduced through the ends using a weft-insertion system.

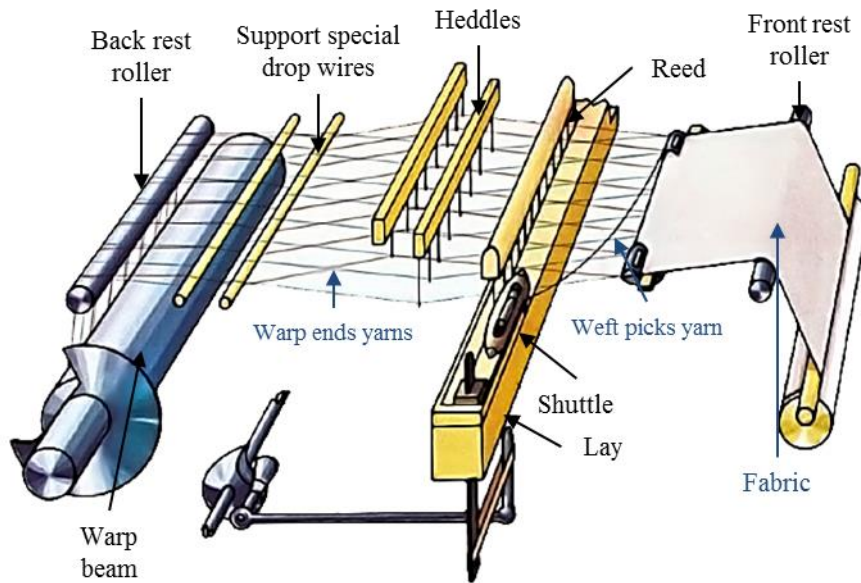


Fig. I - 14 Schematic representation of a loom weaving machine (taken from [77])

There are a huge number of structures that can be produced by weaving. Regarding the two-dimensional woven technical fabrics, the basic structures are (i) the *plain weave fabrics* (Fig. I - 15) that represent at least 90% of technical two –dimensional woven fabrics, (ii) the *rib fabrics and mat weave fabrics* (Fig. I - 16) obtained by simple modification of plain weave fabrics as shown in Fig. I - 16, (iii) the *twill fabrics* (Fig. I - 17) that produce diagonal lines on the face of fabrics and (iv) *satins and sateens* (Fig. I - 18) that produce a smooth fabric surface by a high number of ends with respect to the number of picks (satin) or vice versa (sateen) [75].

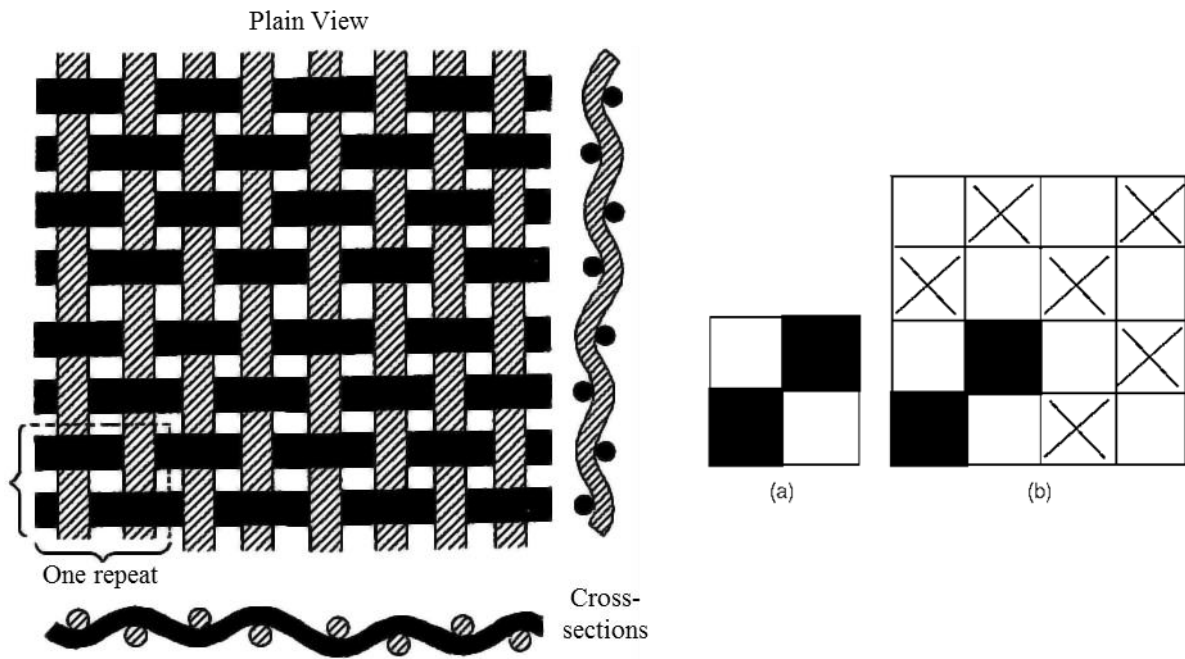


Fig. I - 15 Plain fabric and schematic representation of a) one repeat and b) four repeats (taken from [75])

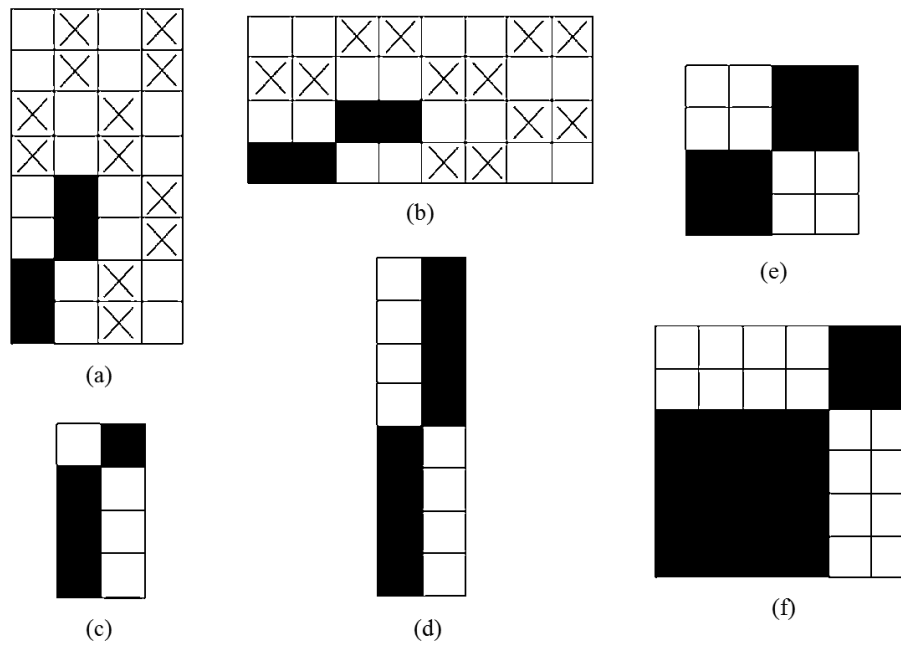


Fig. I - 16 Rib fabrics: a) 2/2 warp rib (four repeats), b) 2/2 weft rib (four repeats), c) 3/1 warp rib (one repeat), d) 4/4 warp rib (one repeat) and matt fabrics: e) 2/2 mat and f) 4/2 mat (taken from [75])

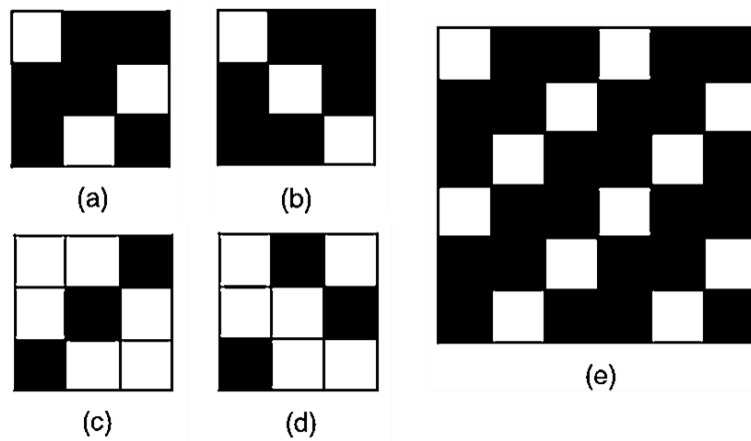


Fig. I - 17 3x3 Twill weaves: a) 2/1 twill with Z twill line, b) 2/1 twill with S twill line, c) 1/2 twill with Z twill line, d) 1/2 twill with S twill line and e) four repeats of (a) (2/1 twill with Z twill line) (taken from [75])

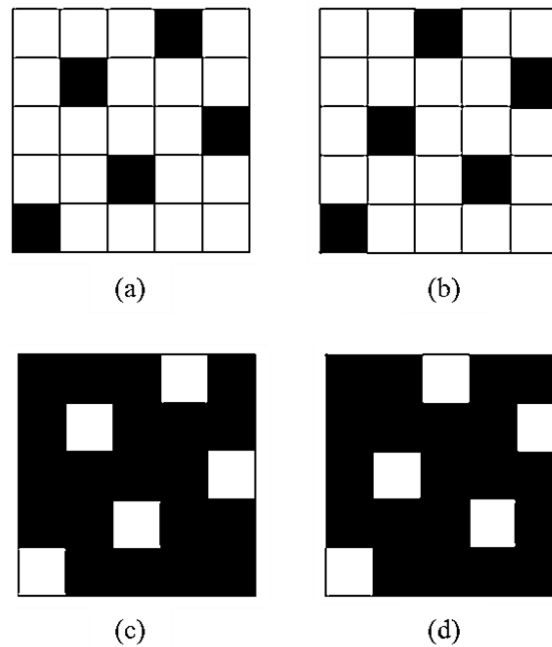


Fig. I - 18 End weft sateen: a) 5-end and 2 steps sateen , b) 5-end and 2 steps sateen; and 5-end warp satin: d) 5-end and 2 steps satin and d) 5-end and 3 steps satin (taken from [75])

1.4.1.3. Unidirectional (UD) fabrics

In some industrial applications in which mechanical stress direction can be controlled, and in research works dealing with the analysis of mechanical properties of composites, it is necessary to manufacture composites with anisotropic properties. This requires that the reinforcing fibres are aligned in the same direction, forming a unidirectional composite laminate. The quality of fibre/matrix interface, for example, can be directly related to the

transverse mechanical properties of unidirectional composites [78], thus supporting the interest in making these types of composites in the present research work.

It should be mentioned that there are different methods of manufacturing UD composites that do not directly require prior manufacture of UD fabrics, such as pultrusion [65], filament winding or drumwinding [79]. For research purposes, some authors also reported manufacturing procedures based on a manual alignment of the fibres to obtain UD flax fibre reinforced composites [79,80].

The unidirectional fabrics, or rather quasi-unidirectional fabrics (Fig. I - 19), are fabrics that have a major part of fibres aligned in the longitudinal direction and a small fraction of yarns or fibres intertwined with the longitudinally aligned fibres [81].

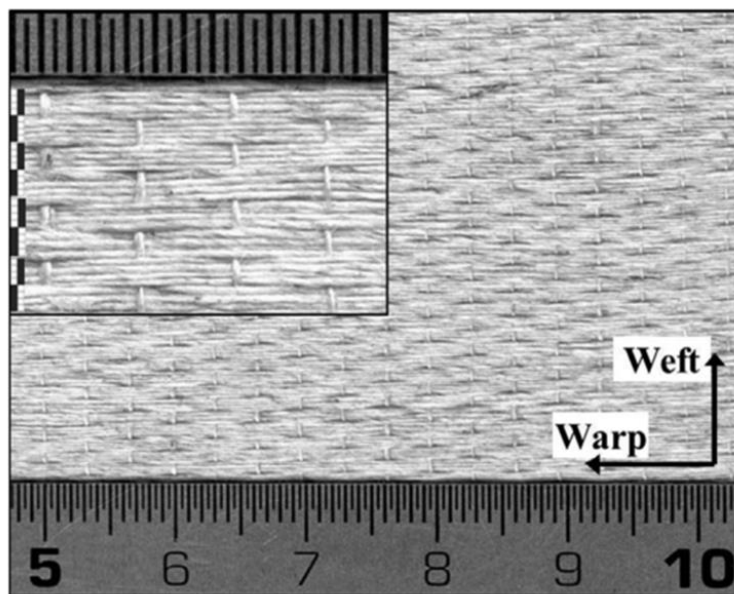


Fig. I - 19 Quasi-unidirectional flax woven fabric (LINEO - FLAXPLY UD 180) (taken from [81])

The manufacturing of composite materials can be carried out using different techniques, depending on the kind of reinforcement and the kind of matrix. In the next section, the main processes applied to thermoset composite laminates will be exposed.

1.4.2. Main processes for thermoset composites production

Fabrication processes depend directly on the nature of both the resin and the reinforcement used. In the case of thermoplastic composites, the matrix is generally in solid state at room temperature. The polymer matrix should thus be molten to be further impregnated (case of long fibres and fabrics) or compounded (case of short fibres) with the fibres and fabrics. In the case of thermoset composites, the resin can be found in solid, liquid or pasty states. In contrast with thermoplastic composites, the irreversible formation of three-dimensional networks with covalent bonds during curing does not allow a subsequent thermoforming for thermoset composites. Depending on the state of the resin, different processes can be used to prepare thermoset composite laminates [82]:

- Atmospheric moulding processes: hand lay-up, spray lay-up
- Liquid moulding: RRIM, RTM, impregnation, infusion, etc.
- Solid-state moulding: compression and injection, SMC, BMC, ZMC, etc.
- Prepreg systems
- Bag moulding
- Filament winding
- Centrifugal moulding
- Continuous sheet manufacture
- Pultrusion
- Sandwich composites, etc.

In literature, the most common processes used for the analysis of composite properties based on liquid resins, as epoxy or unsaturated polyester systems, are: thermo-compression process after hand or spray lay-up [69,83–88], infusion process [89–91] and vacuum bag moulding process after hand or spraylay-up [92]. These three processes will be detailed in the following. In the experimental part of the present research work, only the thermo-compression process will be used.

1.4.2.1. Thermo-compression process

The thermo-compression process (Fig. I - 20) requires a preliminary step of hand or spray lay-up impregnation of the fibre fabric plies with the resin. Then, the impregnated plies are stacked one after the other, and the resulting non-cured composite laminate is introduced in a mould that has been previously treated with a demoulding agent or an anti-adherent film. Depending on the resin curing temperature, composites are pressed and heated at the same time to polymerize the resin. Often, a post-curing at higher temperature can be carried out so as to complete polymerization of the resin system, while limiting stress accumulation within the composite laminate upon curing.

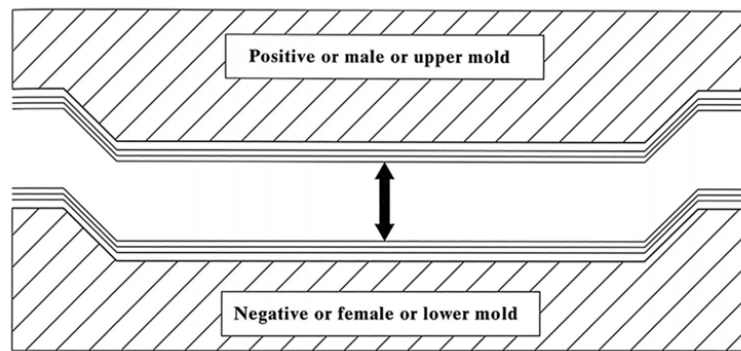


Fig. I - 20 Principle of the thermo-compression moulding after hand lay-up (taken from [67])

Table I - 5 presents the advantages and drawbacks of thermo-compression process over other thermoset composites elaboration processes.

Table I - 5 Advantages and drawbacks of thermo-compression process (adapted from [67])

Advantages	Drawbacks
<i>Technics</i>	
Estheticize of surfaces if a demoulding agent is used	Limitation in the part design by the thermo-press dimensions
Better cohesion of the composite and less imperfections due to pressure	Risks of sliding of layers in the mould
Suitable for thick parts	
Adapted for prototypes and small series	
<i>Production</i>	
	Limited production output
	High costs of two parts mould and thermo-press

1.4.2.2. Vacuum-assisted resin infusion process

The infusion process (Fig. I - 21) is carried out in several steps. The fabrics layers are stacked one over another on a mould previously treated with a demoulding agent or an anti-adherent film. A peel ply and a resin flow mesh are then laid over the surface. A tube system for the resin introduction and another for the air extraction are placed on the surface. A plastic bag is finally used to cover the surface. The plastic bag is perforated by the resin and vacuum connectors, and sealed to the mould surface, in order to produce vacuum inside the bag. Once these preparation steps are carried out, a pump extract the air inside the bag and the resin flows and diffuses within the fabrics by the vacuum effect. Finally, resin can be cured in an oven, an auto-clave or at room temperature.

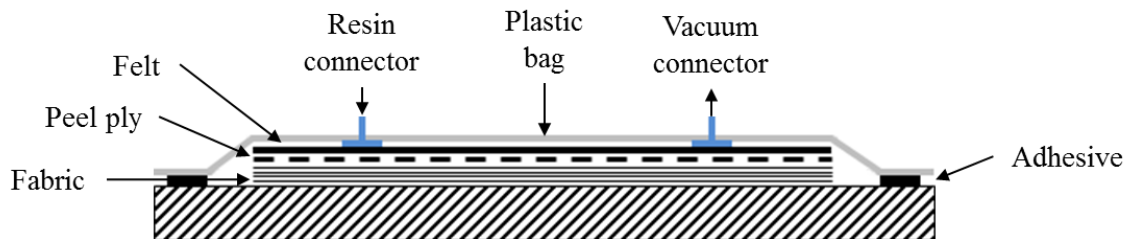


Fig. I - 21 Principle of infusion process

The advantages and drawbacks of infusion process over other thermoset composites elaboration processes are shown in Table I - 6.

Table I - 6 Advantages and drawbacks of infusion process (adapted from [67])

Advantages	Drawbacks
	<i>Technics</i>
Better degassing under vacuum: less bubbles and voids	Limited to very low viscosity resins
Adaptable for different size and shape	Control of polymerization kinetics during the infusion step
	Not suitable for Honeycombs sandwich structure
	<i>Production</i>
Low costs due to one part mould: the upper part is replaced by plastic film	

1.4.2.3. Vacuum bag moulding process after hand or spray lay-up

Vacuum bag moulding process after hand lay-up (Fig. I - 22) and vacuum bag infusion process are very similar. The only difference in between is how the resin impregnates the

fabrics. In vacuum bag moulding, a pre-impregnation of the fabrics is necessary. Resin is applied by hand or sprays lay-up to each fibre fabrics plies and then all impregnated fabrics are laid on a mould. A peel ply and a felt is deposited over the fabric surface. In this case, as fabrics are impregnated, only a vacuum connector is required. The plastic bag is used to cover the components and make the vacuum, like in the infusion process. The air inside the plastic bag and the exceeded resin are then extracted within the felt under vacuum. The resin can be finally cured in an oven, an auto-clave or at room temperature.

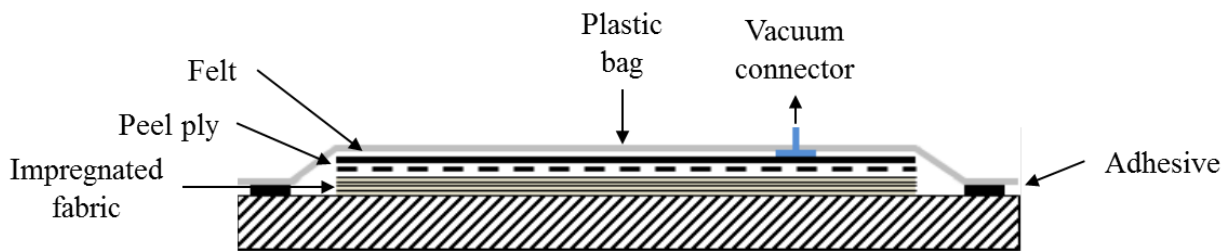


Fig. I - 22 Principle of vacuum bag moulding process after hand lay-up

The advantages and drawbacks of this process are similar to these of the infusion process [67].

1.4.1. Physical and mechanical properties of thermoset agro-composites

Numerous studies were carried out to compare glass and natural fibres reinforced composites and their physical and mechanical properties, as shown in Table I - 7 for epoxy resin, E-glass fibre / epoxy and flax fibre / epoxy composites. Mechanical properties of composites depend, among other factors, on the fibre content and the porosity rate [93]. According to these studies, the mechanical properties of the composites are greatly influenced by the fibre type. The longitudinal tensile mechanical properties of epoxy resin were considerably increased by the introduction of fibres. The tensile strength of pure epoxy resins increased from around 70 MPa to 380 - 1057 MPa and 120 - 268 MPa when reinforced with glass fibres and flax fibres, respectively. This increase was more important for glass/epoxy composites, due to the higher tensile strength properties of glass fibres in comparison with flax fibres. In the transversal direction, the mechanical properties are mostly governed by the matrix properties and the quality of the interface between the fibres and matrix. Accordingly, the pronounced difference between flax/epoxy and glass/epoxy mechanical properties observed in these studies could be

mainly attributed to a weaker fibre/matrix interface in the case of flax/epoxy composite, although lower transverse mechanical properties of flax fibres as compared to glass fibres are also expected. This behaviour is commonly observed in agro-composites, and represents a strong limitation to the use of these materials as replacement of glass fibres based composites. As it will be discussed in the following section, many authors investigated different strategies to modify the fibre/matrix interface in order to improve the mechanical properties of natural fibres reinforced composites.

Table I - 7 Physical and mechanical properties of epoxy resin, glass fibres / epoxy and flax fibres / epoxy composites

		Epoxy	E-Glass / Epoxy	Flax /epoxy
References		[79,85,92,94,95]]	[83,85,95]	[79,83,92]
<i>Physical properties:</i>				
	Density (g/cm³)	1.16 – 1.2	1.79 – 2.15	1.28
	T_g (°C)	120		
	Fibre content (Vol. %)	-	42.5 – 69.8	40 – 55.1
	Diameter fibre (mm)	-	0.017	0.708
	Porosity (Vol. %)		1.3 – 3.8	1.3
<i>Mechanical properties</i>				
Longitudinal tension	Tensile strength (MPa)	70 – 73	380 – 1057	120 – 268
	Young's modulus (GPa)	3.2 – 3.5	21.9 – 49.9	5.5 – 32
	Elongation at break (%)	2.5 – 4.5	2.16 – 2.18	3 – 3.8
Transverse tension	Tensile strength (MPa)	-	40.7 – 48	10 – 18
	Young's modulus (GPa)	-	14.1 – 18.3	4
	Elongation at break (%)	-	0.26 – 0.41	
Longitudinal 3 points bending	Flexural strength (MPa)	82 – 120	1654	218 – 282
	Flexural modulus (GPa)	2.9	50.2	18 – 23
	Elongation at break (%)	3.8 – 6.5	3.34	
Transverse 3 points bending	Flexural strength (MPa)	-	92.9	8 – 27
	Flexural modulus (GPa)	-	17	0.4 – 1.3
	Elongation at break (%)	-	0.57	

1.5. Interface modification on plant fibres – epoxy composites

In general, the mechanical properties of composites depend on the intrinsic mechanical properties of the reinforcement, the matrix and finally the stress transfer between fibres and matrix. The fibre/matrix stress transfer occurs across the interface/interphase in between, the latter having thus a key role in the final composite properties [96].

Unlike glass or carbon fibres, plant fibres have a heterogeneous macroscopic and microscopic composite structure. As previously detailed in section 1.2.1, at the macroscopic level, tow or yarns of plant fibres are composed of elementary fibres linked together by a pectin-rich matrix (middle lamellae) that form fibre bundles, also called technical fibres (Fig. I - 23). At the microscopic level, elementary fibres are characterized by a very complex cell wall structure in which each biopolymer is organized in several layers. At this scale, a composite consisting of highly crystalline cellulose microfibrils embedded in an amorphous matrix of hemicelluloses and lignin is observed [70].

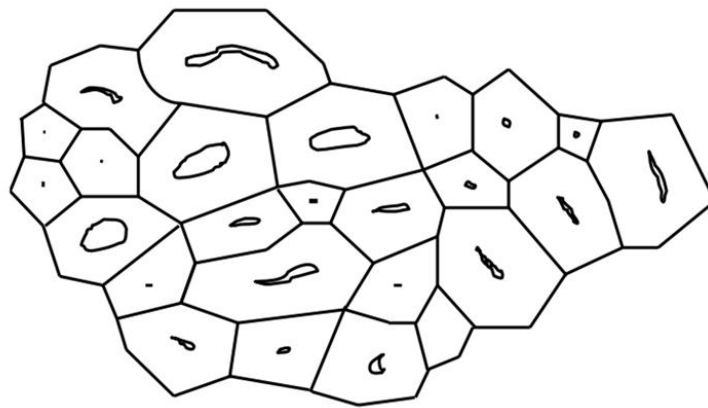


Fig. I - 23 Section of a bundle of elementary fibres in flax. Each elementary fibre is delimited by the middle lamellae

One of the main limitations in the use of plant fibres as reinforcement in composites is the low compatibility between the fibre and the matrix. To improve this compatibility and enhance the mechanical interlocking and chemical interactions at the fibre/matrix interface, the fibre surface can be modified by physical or chemical methods. These treatments could modify (i) physical aspects, such as fibre roughness, (ii) physico-chemical aspects, such as the fibre surface tension, as well as (iii) chemical aspects, such as the grafting of functionalizing molecules at the fibre surface so as to chemically bind fibres and matrix [4]. This state of the art will be focused on chemical treatments of plant fibres dedicated to epoxy resin based composites. Among them, alkali, silane, acetylation and others treatments will be exposed.

1.5.1.1. Alkaline treatment

The alkaline treatment, also called alkalization or mercerization, cannot be considered as a functionalization treatment of natural fibres, because no functional groups are added at the

fibre surface. For this treatment, sodium hydroxide is diluted in aqueous solution and then, fibres are treated with the alkaline solution at defined times and concentrations in order to extract a part of lignin, pectins, hemicelluloses and waxes [27]. Simultaneously, depending on alkaline solution concentration, the crystalline structure of cellulose can be modified, and a cellulose I / cellulose II transition occurs at high alkaline concentration [22, 39]. Several authors have observed a smoothing of fibre surfaces for agave and flax [44,92,97], as can be observed in Fig. I - 24. This treatment is often used as a preliminary step prior to functionalization of fibre surfaces with reactive molecules or oligomers. Alkalization can thus be considered as a fibre pre-treatment intended to prepare fibre surfaces [98].

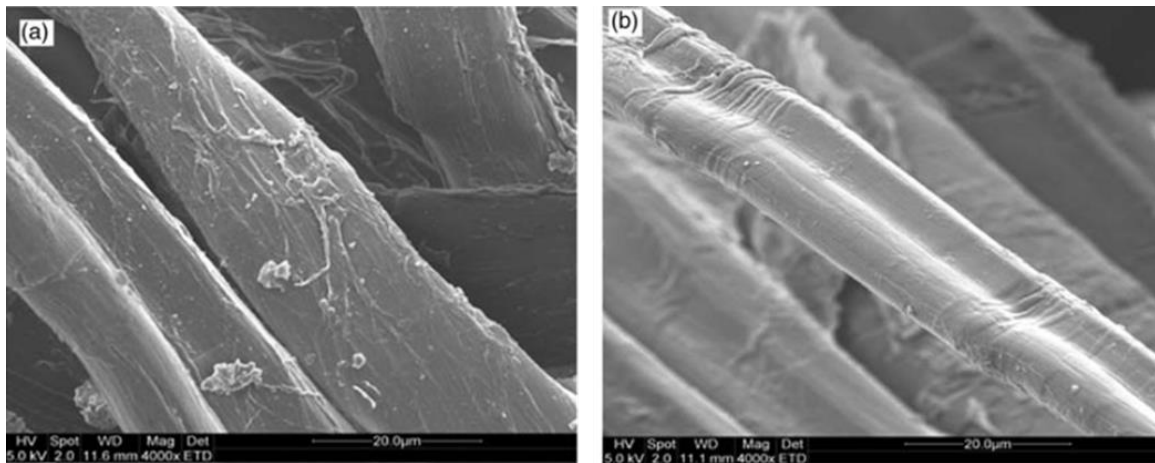


Fig. I - 24 Surface morphology of untreated and alkali-treated single fibre yarns: (a) untreated flax and (b) treated flax (taken from [92])

Van de Weyenberg et al. [79] have treated flax fibres by alkaline solutions to produce unidirectional flax fibre/epoxy composites, and have studied the resulting mechanical properties. The authors have compared three fibre treatment processes with two kinds of flax fibres: (i) discontinuous treatment with flax slivers, (ii) semi-continuous treatment and (iii) continuous treatment with flax roving. In the first treatment process, flax slivers were aligned in a frame and soaked in three different concentrations of alkali solution (1%, 2% and 3% w/w) for 20 min at room temperature. Fibres were washed in 1 L of water at room temperature, and neutralized with 20 drops of HCl 0.1M in order to remove excessive NaOH. Finally, fibres were dried in an oven at 80°C for 8 h and then, composite elaboration was carried out by film stacking method. In the semi-continuous treatment, flax fibre roving was immersed in an alkali bath at 8% for 20 min, and 13% and 23% for 2 min at room

temperature. The washing of fibres and drying were carried out in the same conditions as for fibre slivers. In this case, resin pre-impregnation was carried out using a drumwinder installation. In the continuous process, fibre roving was treated and resin pre-impregnation occurred in a full continuous process (Fig. I - 25). The treatment was applied in alkaline baths at 0%, 4%, 6%, 8% and 12% through by the roving for 45 s. Yarn tension was controlled by adjusting the velocity of rolls. Fibres were dried successively at 250°C, 260°C and 120°C, as it is shown in Fig. I - 25. Then fibres were pre-impregnated with resin using a drumwinder. With regard to the mechanical properties, a three-point bending test in longitudinal and transverse direction was used to analyse the resulting composite mechanical properties. Table I - 8 shows the results obtained in this work. Authors found an increase of the three-point bending properties (longitudinal and transverse) with the discontinuous process, supposedly due to an improvement of the fibre/matrix adhesion. Concerning the lower mechanical properties obtained with the continuous processes, authors justified the results by the inefficiency of the rinsing section.

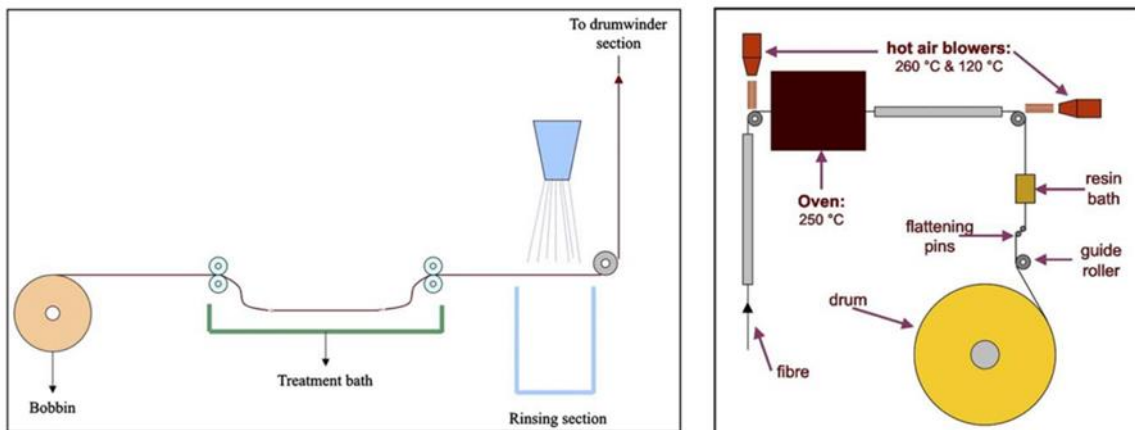


Fig. I - 25 Treatment, rinsing, drying and resin application in the fully continuous production set-up (taken from [79])

Table I - 8 Three-point bending test properties of epoxy based composites reinforced with alkali treated flax fibre (by discontinuous, semi-continuous and continuous processes) (taken from [79])

Process	Treatment time	NaOH solution (wt.%)	Fibre fraction in composite (%v/v)	Longitudinal		Transverse	
				σ_L (MPa)	E_L (MPa)	σ_T (MPa)	E_T (MPa)
Discontinuous	Untreated		40	218 ± 18	18 ± 3	8 ± 4	0.4 ± 0.2
	20 min	1	40	237 ± 12	23 ± 1	20 ± 4	2.3 ± 0.2
	20 min	2	40	261 ± 13	20 ± 2	15 ± 2	1.1 ± 0.1
	20 min	3	40	283 ± 20	22 ± 2	19 ± 4	1.2 ± 0.1
Continuous	Untreated		48	282 ± 11	23 ± 1	27 ± 3	1.3 ± 0.2
	45 s	0	42	256 ± 5	22 ± 2	36 ± 1	2.9 ± 0.6
	45 s	4	53	283 ± 10	25 ± 1	35 ± 2	3.6 ± 0.3
	45 s	8	17	132 ± 6	8.3 ± 0.5	20 ± 1	2.2 ± 0.1
	45 s	12	25	50 ± 4	2.7 ± 0.3	-	-
Semi-continuous	20 min	8	35	258 ± 11	22.8 ± 0.6	38 ± 2	4.1 ± 0.1
	2 min	13	49	284 ± 8	26 ± 1	21 ± 4	1.2 ± 0.2
	2 min	23	47	240 ± 11	22 ± 1	19 ± 5	1.1 ± 0.2

Yan et al. [92] have applied an alkali treatment on flax, linen and bamboo fabrics and yarns, and then analysed the mechanical properties on the resulting natural fibre/epoxy composites. Fabrics have been pre-washed three times with cold water to remove contaminants and dried at room temperature for 48 h. The alkali treatment was applied to fabrics in a 5 wt.% alkaline solution for 30 min at 20°C. Fabrics were then washed ten times with cold water and three more times with distilled water. Finally, fabrics were dried at 80°C for 24 h. Tensile tests were performed on single yarns and natural fibre/epoxy composites and three-point bending tests were performed on composites. A reduction of tensile failure stress was observed on single yarns for flax (untreated: 1.43±0.09 MPa – treated: 1.22±0.05 MPa), linen (untreated: 1.35±0.04 MPa – treated: 1.17±0.13 MPa) and bamboo (untreated: 1.26±0.1 MPa – treated: 0.85±0.09 MPa). A decrease in Young's modulus of single yarns (flax untreated: 16.4±0.4 MPa – flax treated: 13.8±0.5 MPa, linen untreated: 12.3±0.6 MPa – linen treated: 10.7±0.4 MPa and bamboo untreated: 5.4±0.4 MPa – bamboo treated: 3.9±0.3 MPa) was also measured. A moderate increase in tensile strength was observed for flax/epoxy composites (6.4%) and linen/epoxy composites (1.1%). However, an important decrease of bamboo/epoxy composites tensile strength was measured (-22.7%). Tensile Young's modulus decreases for all composites (flax/epoxy: -12.3%, linen/epoxy: -15.6% and bamboo/epoxy: -8.2%). In contrast, flexural mechanical properties of flax/epoxy, linen/epoxy and bamboo/epoxy were increased with alkali treatment by about 16%, 17% and 14%,

respectively, as concerns the bending strength, and by about 7%, 9% and 6%, respectively, as concerns the flexural modulus.

Other authors have treated plant fibres with alkali solutions in order to improve mechanical properties of plant/epoxy composites [99–105].

1.5.1.2. Acetylation treatment

The acetylation treatment is obtained by esterification of acidic groups with hydroxyl groups of natural fibres. As a result of this treatment, fibre surface is smoother, and at the same time, a reduction in the amount of voids increasing the interlocking with the matrix [2]. Fig. I - 26 shows an example of acetylation of a fibre using acetic anhydride. This treatment is considered as a hydrophobization treatment.

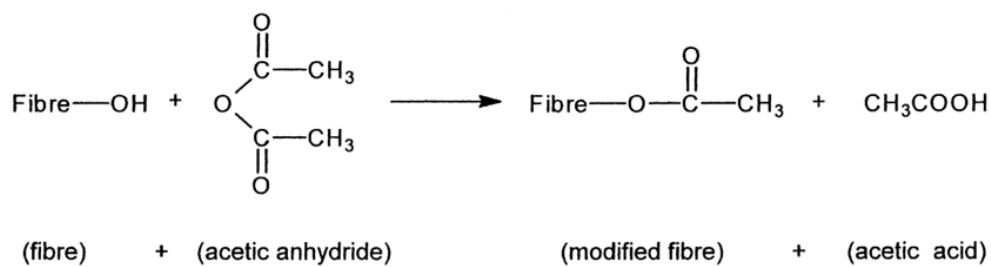


Fig. I - 26 Plant fibres reaction with acetic anhydride (taken from [106])

Rong et al. [98] analysed, among other treatments, the effect of acetylation treatments with acetic acid on sisal fibres and sisal/epoxy composites. The treatment was carried out after an alkali pre-treatment in a solution of sodium hydroxide at 18% for 5 min at room temperature. Then, fibres were washed, neutralized in a 2.5 wt.% H₂SO₄ solution and air dried. Fibres were acetylated by soaking it in 50% acetic acid aqueous solution for 5 min, then washed in water and air dried. Tensile and flexural mechanical properties were determined for sisal/epoxy composites. An increase of the tensile strength and elongation at break was reported while a decrease of the Young's modulus was observed. The authors also observed an increase in flexural strength and modulus, which was attributed to the formation of strong interfacial interactions.

1.5.1.3. Silane treatments

In their review, Xie et al. [5] reported that different silanes can be used with natural fibres, depending on the targeted matrices. Table I - 9 shows that epoxy matrix can potentially react with amino or glycidoxy functions of APS and GPS silanes if grafted on natural fibre surfaces.

Table I - 9 Chemical structures, organofunctionalities and target polymer matrix of several silanes (adapted from [5])

Structure	Functionality	Abbreviation	Target matrix
$(R^*O)_3Si-(CH_2)_3-NH_2$ $R^* = \text{-methyl or ethyl}$	Amino	APS	Epoxy Polyethylene Butyl rubber Polyacrylate PVC
$(RO)_3Si-CH=CH_2$	Vinyl	VTS	Polyethylene Polypropylene Polyacrylate
$(RO)_3Si-(CH_2)_3-OOC(CH_3)C=CH_2$	Methacyl	MPS	Polyethylene Polyester
$(RO)_3Si-(CH_2)_3-SH$	Mercapto	MRPS	Natural rubber PVC
$(RO)_3Si-(CH_2)_3-O-CH_2CHCH_2O$	Glycidoxy	GPS	Epoxy Butyl rubber Polysulfide
$R_2-Si-Cl_2$	Chlorine	DCS	Polyethylene PVC
VTS grafted plastics	Vinyl	VSP VSPE	Polypropylene Polyethylene
$(RO)_3-Si-C_6H_4-SO_2-N_3$	Azide	ATS	Polypropylene Polyethylene Polystyrene
$(RO)_3Si-(CH_2)_{15}CH_3$	Alkyl	HDS	Polyethylene Natural fibres

A huge number of papers focused on organosilanes molecules applied onto plant fibres in order to improve the interfacial properties in agro-composites[25,48,97,107–110]. In all cases, four successive treatment steps were described:

- Hydrolysis (Fig. I - 27 (a)): Silanes are hydrolysed in water or water/ethanol mixtures with catalyst (acid or base), forming silanol groups.
- Self-condensation (Fig. I - 27 (b)): Condensation between silanols groups of silane molecules is occurring. To prevent a fast self-condensation, an acid pH environment is used.

- Adsorption (Fig. I - 27 (c)): A physical absorption of silanols through hydrogen bonding with hydroxyl groups present at the natural fibre surface occurred.
- Grafting (Fig. I - 27 (d)): covalent -Si-O-C- bonds can be formed between hydroxyl groups and silanol groups when water is removed at a raised temperature. It should be noticed that the -Si-O-C- bonds are not stable towards hydrolysis.

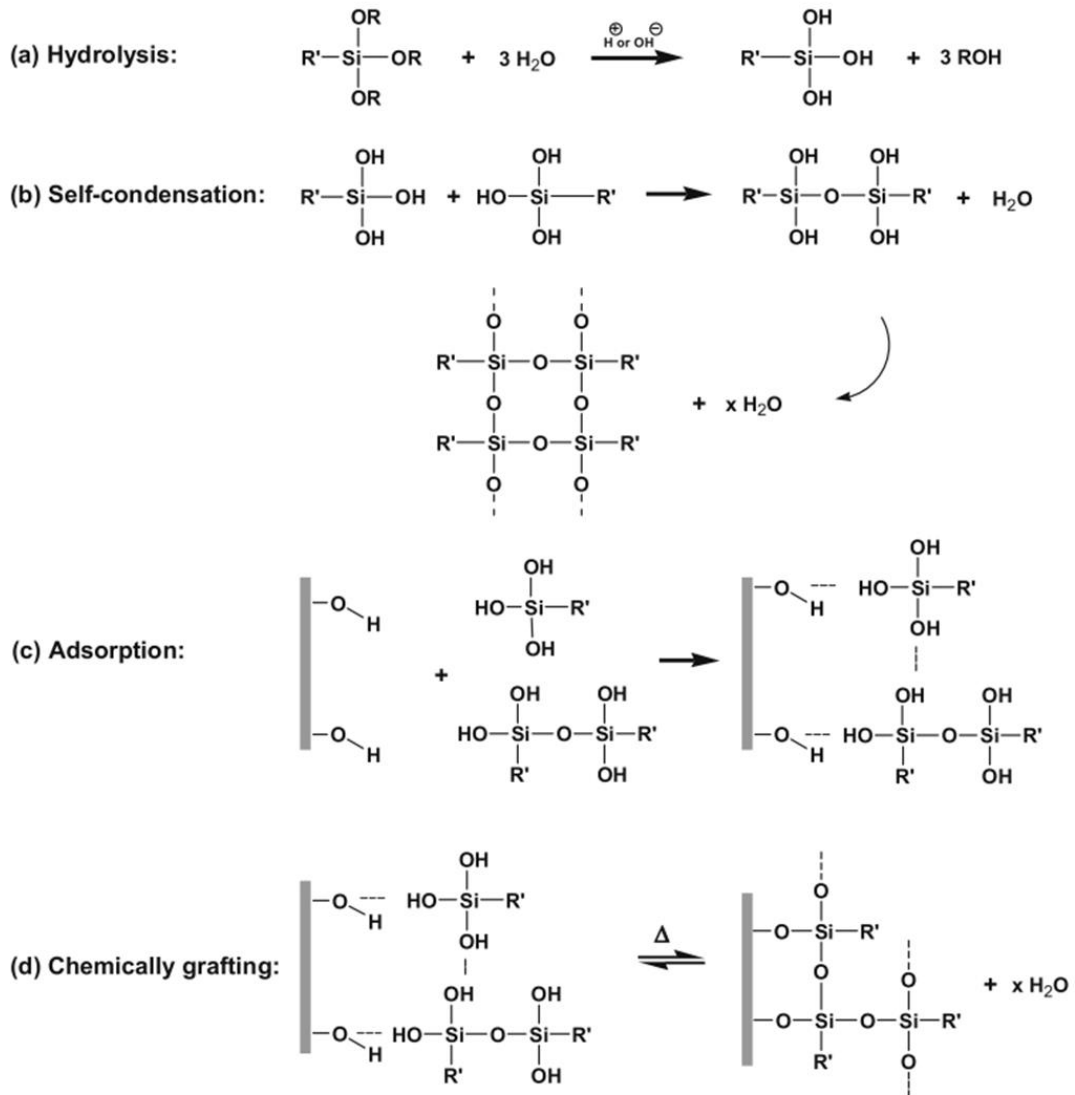


Fig. I - 27 Interaction of silanes with natural fibres by hydrolysis, condensation and chemical grafting processes (taken from [5])

Van de Weyenberg et al. [111] analysed the effect of silane treatment on the mechanical properties of flax fibres/epoxy composites. The authors applied a solution of 3-amino-propyltrimethoxysilane (APS) at 1% in water/acetone (50/50 v/v) to flax fibres for 2h at room

temperature and dried it during 8h at 80°C. A three point bending test was performed and longitudinal and transverse flexural strengths and modulus were determined. The authors observed an improvement of both longitudinal and transverse properties, i.e. longitudinal strength (about 4%), and modulus (about 45%), transverse strength (about 115%) and modulus (about 400%).

Other papers reported the combination of silane treatments with different pre-treatments in order to increase the surface roughness of the fibre and therefore to improve the chemical interactions as well as the mechanical interlocking between the fibres and the epoxy resin. Bisanda et al. [86] analysed the effect of silane treatment on the mechanical and physical properties of sisal/epoxy composites. In a first step, short fibres were dewaxed by soaking in a solution of benzene and denatured alcohol (1:1) for 24 h, washed in alcohol and then in demineralized water. In a second step, fibres were mercerized in a 0.5 N solution of sodium hydroxide for 72 h, washed with demineralized water and dried. Finally, a solution of 5% w/w of 3-amino-propyltriethoxysilane (APS) diluted in denatured alcohol and 0.1 M of ceric ammonium nitrate (catalyser) was used to treat the fibres. The treatment was carried out by soaking 150g of mercerized fibres in 1500 ml of silane solution for 24 h at room temperature. Fibres were then washed with distilled water and dried. Sisal/epoxy composites were prepared using a thermo-compression process at 60°C for 2 h, 80°C for 2 h more and then post-cured at 100°C overnight. The authors observed a decrease of the moisture absorption on silane treated fibres (Fig. I - 28), and also a decrease of water absorption for silane treated fibres based composites (Fig. I - 29). Compressive strength and flexural tests were performed in order to analyse the resulting mechanical properties for the treated composites. A significant increase in the compressive strength was observed for the combined mercerization and silane treatment (Untreated: 120 MPa, Mercerized + Silane: 184.8 MPa). Furthermore, the loss of compressive strength in water immersion was less pronounced for treated composites (Untreated: 62.53 MPa and Mercerized + Silane: 98.53 MPa). Besides, the flexural strength was little modified by the fibre treatment (Untreated: 266.5 MPa, Mercerized + Silane: 244.5 MPa; Untreated: 221.7 MPa, Mercerized + Silane: 237.2 MPa after ageing in water). The same trends were observed for flexural modulus at the initial state (untreated: 15.93 GPa, Mercerized + Silane: 17.36 GPa) and after ageing in water (untreated: 9.15 GPa, Mercerized + Silane 12.33 GPa).

The authors considered that this improvement was due to a better interfacial bonding by the use of silane and by the lower water absorption of composites with silane treated fibres.

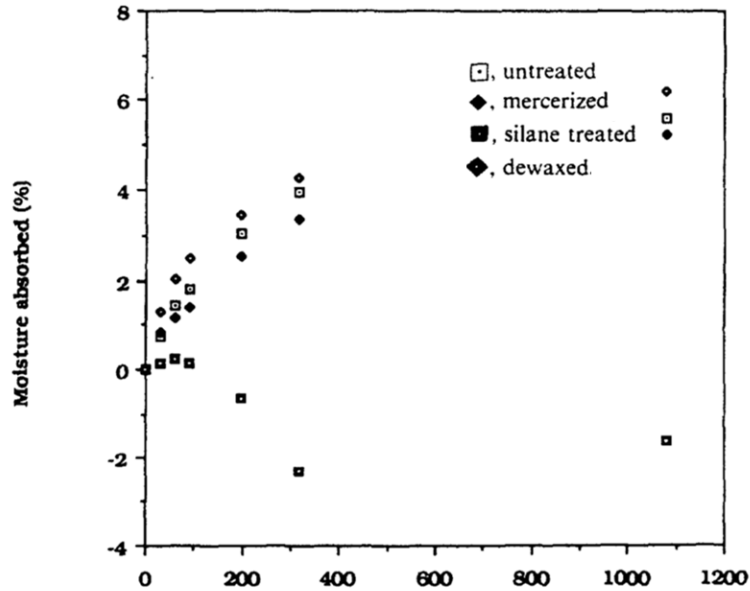


Fig. I - 28 Effect of fibre treatment on moisture absorption, at 20°C and 65% RH (taken from [86])

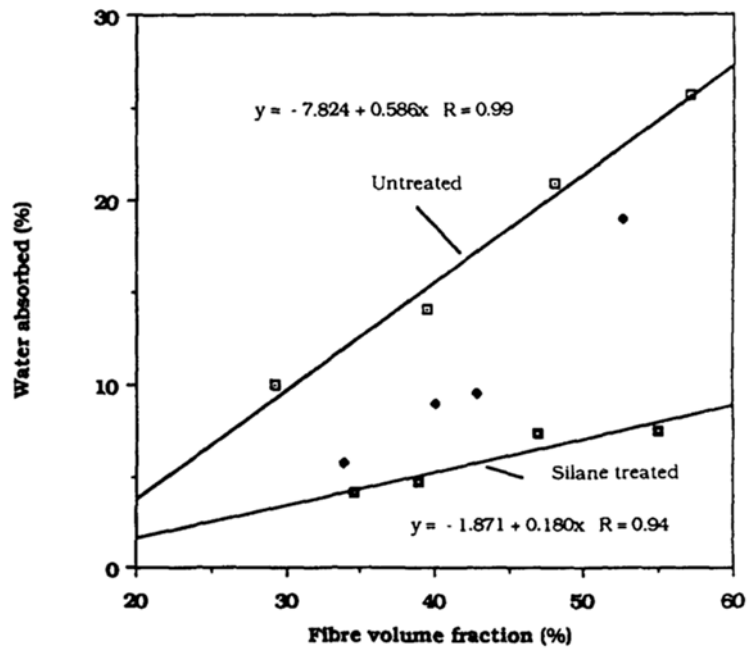


Fig. I - 29 Effect of fibre treatment on the resistance of sisal/epoxy composites to water absorption (taken from [86])

Doan et al. [112] studied the surface properties and interfacial adhesion in jute fibre/epoxy composites. In this study, the authors compared with three different silane treated fibres based composites. Fibres were treated through different ways : (i) fibres were pre-treated with NaOH at 1% for 4 h in immersion and then washed; (ii) pre-treated fibres were afterwards treated with a mixture of 3-aminopropyl-triethoxy-silane (APS) at 1%, prepared in acidified water (pH 4.5), and a water based epoxy solution (ED); (iii) pre-treated fibres were also treated with an aqueous solution of 3-phenyl-aminopropyl-trimethoxy-silane (PAPS) at 1% (pH 2.9). The authors observed a smooth surface for untreated fibres, which was explained by the presence of different components on the fibre surface, such as waxes, fats, lignin, pectin and hemicellulose. In the case of alkaline pre-treated fibres, the surface was more grooved due to the partial removal of pre-mentioned components. And for the treated fibres, the silane treatment acts as a coating, and fibre surface is re-smoothed. This was more noticeable in the case of the PAPS treatment. A modification of polar and dispersive surface energy was reported from the untreated to pre-treated and treated fibres. An increase in polar and dispersive surface energy was observed for pre-treated fibres. The authors observed that the increase in the dispersive surface energy was higher for treated fibres but polar dispersion was reduced in consideration with untreated fibres, as it can be observed in Fig. I - 30. The interfacial adhesion strength was evaluated by single fibre pull-out test. Interfacial shear strength between untreated jute fibres and the epoxy matrix is 49 ± 9 MPa. An increase of around 40% (61 ± 12 MPa) was observed for alkaline pre-treated sisal fibres. In the case of silane treated sisal fibres, the increase was around 49% for NaOH/APS-ED treatment and 46% for NaOH/PAPS treatment, respectively. These results demonstrate that a combined alkaline + APS silane treatment is able to improve the interfacial shear strength due to the synergistic effect of physico-chemical interactions and mechanical interlocking.

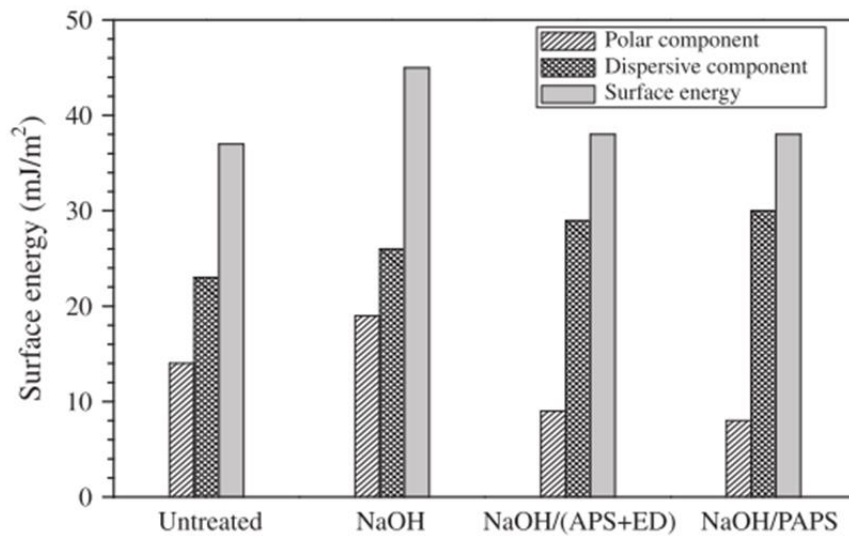


Fig. I - 30 Surface energy of untreated and treated jute fibres (taken from [112])

Other studies with 3-amino-propyltriethoxysilane (APS) [113] and 3-glycidoxypropyltrimethoxysilane (GPS) [113,114] were carried out on micro-fibrillated cellulose and natural fibres epoxy composites, showing an hydrophobization and an enhancement in mechanical properties.

1.5.1.4. Other treatments

In literature, it is possible to find other treatments used in order to improve the mechanical properties of composites by the increase of interface adhesion. For example, Rong et al. [98] compared a cyanoethylation treatment with alkali, acetylation and silane treatments, and a combination of these treatments on sisal fibres based epoxy composites. As mentioned above, Van de Weyenberg et al. [111] treated flax fibres with sodium hydroxide and silane solution, but also with acetone and with Araldite LY 5052 epoxy and HY 5052 hardener (CIBA) diluted in acetone; by combination of treatments (alkali + epoxy), an improvement around 40% of longitudinal bending strength and 60% of stiffness was obtained. Ishak et al. [115] analysed the effect of sea water treatment on the mechanical properties of palm fibre/epoxy composites: the treatment was carried out for 30 days, so as to extract the outer layer of hemicellulose and pectin and improve the interfacial bonding between fibre and matrix. Authors showed that sea water treated fibres have higher mechanical properties than untreated composites except for flexural strength at 20% fibre content. Lu et al. [113], besides silane

treatments (APS and GPS), carried out treatments with a titanate coupling agent on microfibrillated cellulose, for the preparation of epoxy based composites reinforced with cellulose fibres from lodge pole pine (50%), white spruce (40%) and Douglas fir (10%). Authors observed that titanate coupling gave the most hydrophobic surface in comparison with APS and GPS treatment, possibly due to the lower polarity of the alkyl chain of the titanate modifier. The storage modulus of composites at 30°C was increased from 3.11 GPa to 3.45 GPa for titanate treatment, higher than APS and GPS treatments at similar temperature.

1.6. Conclusions

In this chapter, the most important features of natural fibres and particularly flax fibres, as the chemical composition, structure and transformation steps, have been addressed. Considering the industrial interest in making composites reinforced with natural fibres, details about thermoset agro-composites manufacturing, key factors influencing plant fibres compatibility with polymer matrix, as well as chemical treatment strategies to modify fibre/matrix interfaces and their effect on fibre and composite properties, have been exposed.

Regarding the flax stem transformation steps, studies about the evolution of chemical composition upon processing have not been carried out. In particular, chemical composition of flax fibres is usually known at the end of the different processing steps, but its evolution upon processing is unknown. As an example, flax slivers processing involves a mixing step in order to homogenize the fibre composition. The influence of this mixing step on the chemical composition has not been analysed yet. These analyses are of great interest; as it would on one hand, give information about the homogenization quality of the final fibre products, and secondly, give valuable information about the natural fibre characteristics in view of their subsequent (pre)treatment. Chemical modifications and fibre reactivity are indeed expected to be greatly influenced by factors such as chemical compositions of the fibres. These aspects will be addressed in the experimental part of this doctoral thesis.

In numerous studies, rovings as well as yarns or fabrics were pre-treated and/or treated to be used as reinforcement in agro-composites. These works showed how pre-treatments can improve the mechanical interlocking between the fibre and the matrix and how functionalization with selected molecules can improve fibre/matrix physicochemical interactions. It was also shown that pre-treatment can be an effective strategy to extract chemical components from the fibre, and enhance the efficiency of the further functionalization treatment. It is noticeable that the fibre treatments reported in literature for epoxy based agro-composites are principally carried out with amino-silanes (APS) molecules with or without a combined alkaline pre-treatment. With the initial goal set by the French Environment and Energy Management Agency (ADEME), to seek functionalization solutions that respect the environment, the research, development and application of new bio-molecules will be investigated in the present doctoral thesis.

1.7. References

- [1] M. John, R. Anandjiwala, Recent developments in chemical modification and characterization of natural fiber reinforced composites, *Polym. Compos.* 29 (2008) 187–207. doi:10.1002/pc.20461.
- [2] M.M. Kabir, H. Wang, K.T. Lau, F. Cardona, Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview, *Compos. Part B Eng.* 43 (2012) 2883–2892. doi:10.1016/j.compositesb.2012.04.053.
- [3] S. Kalia, B.S. Kaith, I. Kaur, Pretreatments of Natural Fibers and their Application as Reinforcing Material in Polymer Composites — A Review, *Polym. Eng. Sci.* (2009). doi:10.1002/pen.
- [4] O. Faruk, A.K. Bledzki, H.-P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000–2010, *Prog. Polym. Sci.* 37 (2012) 1552–1596. doi:10.1016/j.progpolymsci.2012.04.003.
- [5] Y. Xie, C. a. S. Hill, Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review, *Compos. Part A Appl. Sci. Manuf.* 41 (2010) 806–819. doi:10.1016/j.compositesa.2010.03.005.
- [6] J.E.G. Van Dam, Environmental benefits of natural fibre production and use, *Proc. Symp. Nat. Fibres.* (2009) 3 – 18.
- [7] K. Jayaraman, Manufacturing sisal-polypropylene composites with minimum fibre degradation, *Compos. Sci. Technol.* 63 (2003) 367–374. doi:10.1016/S0266-3538(02)00217-8.
- [8] M.J. John, S. Thomas, Biofibres and biocomposites, *Carbohydr. Polym.* 71 (2008) 343–364. doi:10.1016/j.carbpol.2007.05.040.
- [9] M.B. Sticklen, Plant genetic engineering for biofuel production: towards affordable cellulosic ethanol., *Nat. Rev. Genet.* 9 (2008) 433–443. doi:10.1038/nrg2336.
- [10] R. a. Festucci-Buselli, W.C. Otoni, C.P. Joshi, Structure, organization, and functions of cellulose synthase complexes in higher plants, *Brazilian J. Plant Physiol.* 19 (2007) 1–13. doi:10.1590/s1677-04202007000100001.
- [11] M. Jarvis, Chemistry: cellulose stacks up., *Nature.* 426 (2003) 611–612. doi:10.1038/426611a.
- [12] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Cellulose: Fascinating Biopolymer and Sustainable Raw Material, *Angew. Chemie Int. Ed.* 44 (2005) 3358–3393. doi:10.1002/anie.200460587.

- [13] T. Heinze, K. Petzold-Welcke, J.E.G. van Dam, Polysaccharides: Molecular and Supramolecular Structures. Terminology, in: Eur. Polysacch. Netw. Excell., Springer Vienna, Vienna, 2012: pp. 23–64. doi:10.1007/978-3-7091-0421-7_3.
- [14] A.S. Mamman, J.M. Lee, Y.C. Kim, I.T. Hwang, N.J. Park, Y.K. Hwang, et al., Furfural: Hemicellulose/xylose-derived biochemical, Biofuels, Bioprod. Biorefining. 2 (2008) 438–454. doi:10.1002/bbb.95.
- [15] H.V. Scheller, P. Ulvskov, Hemicelluloses, Annu. Rev. Plant Biol. 61 (2010) 263–289. doi:10.1146/annurev-arplant-042809-112315.
- [16] W. Boerjan, J. Ralph, M. Baucher, Lignin biosynthesis., Annu. Rev. Plant Biol. 54 (2003) 519–546. doi:10.1146/annurev.arplant.54.031902.134938.
- [17] Z. Yinghuai, K. Tang, N. S., Applications of Ionic Liquids in Lignin Chemistry, in: Ion. Liq. - New Asp. Futur., InTech, 2013: pp. 315–346. doi:10.5772/51161.
- [18] E. Adler, Lignin chemistry?past, present and future, Wood Sci. Technol. 11 (1977) 169–218. doi:10.1007/BF00365615.
- [19] A. Tejado, C. Peña, J. Labidi, J.M. Echeverria, I. Mondragon, Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis, Bioresour. Technol. 98 (2007) 1655–1663. doi:10.1016/j.biortech.2006.05.042.
- [20] A.G.J. Voragen, G.-J. Coenen, R.P. Verhoef, H.A. Schols, Pectin, a versatile polysaccharide present in plant cell walls, Struct. Chem. 20 (2009) 263–275. doi:10.1007/s11224-009-9442-z.
- [21] W.G.T. Willats, L. McCartney, W. Mackie, J.P. Knox, Pectin: cell biology and prospects for functional analysis, Plant Mol. Biol. 47 (2001) 9–27. doi:10.1023/A:1010662911148.
- [22] A. Gutiérrez, J.C. Del Río, F.J. González-Vila, F. Martín, Analysis of lipophilic extractives from wood and pitch deposits by solid-phase extraction and gas chromatography, J. Chromatogr. A. 823 (1998) 449–455. doi:10.1016/S0021-9673(98)00356-2.
- [23] G. Marques, J.C. del Río, A. Gutiérrez, Lipophilic extractives from several nonwoody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching., Bioresour. Technol. 101 (2010) 260–7. doi:10.1016/j.biortech.2009.08.036.
- [24] a. K. Mohanty, M. Misra, G. Hinrichsen, Biofibres, biodegradable polymers and biocomposites: An overview, Macromol. Mater. Eng. 276-277 (2000) 1–24. doi:10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W.

- [25] A.K. Bledzki, S. Reihmane, J. Gassan, Properties and modification methods for vegetable fibers for natural fiber composites, *J. Appl. Polym. Sci.* 59 (1996) 1329–1336. doi:10.1002/(SICI)1097-4628(19960222)59:8<1329::AID-APP17>3.0.CO;2-0.
- [26] K.G. Satyanarayana, K. Sukumaran, P.S. Mukherjee, C. Pavithran, S.G.K. Pillai, Natural fibre-polymer composites, *Cem. Concr. Compos.* 12 (1990) 117–136. doi:10.1016/0958-9465(90)90049-4.
- [27] L.Y. Mwaikambo, M.P. Ansell, Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization, *J. Appl. Polym. Sci.* 84 (2002) 2222–2234. doi:10.1002/app.10460.
- [28] C. Ververis, K. Georghiou, N. Christodoulakis, P. Santas, R. Santas, Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production, *Ind. Crops Prod.* 19 (2004) 245–254. doi:10.1016/j.indcrop.2003.10.006.
- [29] S. Jain, R. Kumar, U.C. Jindal, Mechanical behaviour of bamboo and bamboo composite, *J. Mater. Sci.* 27 (1992) 4598–4604. doi:10.1007/BF01165993.
- [30] S.S. Sathishkumar TP, Navaneethakrishnan P, E. Al., Characterization of new cellulose *sansevieria ehrenbergii* fibers for polymer composites, *Compos. Interfaces.* 20 (2013) 575–593. doi:10.1080/15685543.2013.816652.
- [31] I.M. De Rosa, C. Santulli, F. Sarasini, Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated *Phormium tenax* leaf fibers, *Mater. Des.* 31 (2010) 2397–2405. doi:10.1016/j.matdes.2009.11.059.
- [32] M.J. John, R.D. Anandjiwala, Recent developments in chemical modification and characterization of natural fiber-reinforced composites, *Polym. Compos.* 29 (2008) 187–207. doi:10.1002/pc.20461.
- [33] N. Reddy, Y. Yang, Biofibers from agricultural byproducts for industrial applications, *Trends Biotechnol.* 23 (2005) 22–27. doi:10.1016/j.tibtech.2004.11.002.
- [34] J. Prachayawarakorn, S. Chaiwatyothin, S. Mueangta, A. Hanchana, Effect of jute and kapok fibers on properties of thermoplastic cassava starch composites, *Mater. Des.* 47 (2013) 309–315. doi:10.1016/j.matdes.2012.12.012.
- [35] B.M.D. Dauda, E.G. Kolawole, Processibility of Nigerian kapok fibre, *Indian J. Fibre Text. Res.* 28 (2003) 147–149.
- [36] M. Sreekala, M. Kumaran, S. Joseph, Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance, *Appl. Compos. Mater.* 7 (2000) 295–329. <http://www.springerlink.com/index/w414808601377162.pdf> (accessed November 23, 2012).

- [37] Wang Yueping, Wang Ge, Cheng Haitao, Tian Genlin, Liu Zheng, Xiao Qun Feng, et al., Structures of Bamboo Fiber for Textiles, *Text. Res. J.* 80 (2010) 334–343. doi:10.1177/0040517509337633.
- [38] P. McKendry, Energy production from biomass (part 1): Overview of biomass, *Bioresour. Technol.* 83 (2002) 37–46. doi:10.1016/S0960-8524(01)00118-3.
- [39] R. Sun, J. M. Fang, a. Goodwin, J. M. Lawther, a. J. Bolton, Fractionation and characterization of polysaccharides from abaca fibre, *Carbohydr. Polym.* 37 (1998) 351–359. doi:10.1016/S0144-8617(98)00046-0.
- [40] P. Ramadevi, D. Sampathkumar, C.V. Srinivasa, B. Bennehalli, Effect of alkali treatment on water absorption of single cellulosic abaca fiber, *BioResources.* 7 (2012) 3515–3524.
- [41] F. Le Digabel, L. Avérous, Effects of lignin content on the properties of lignocellulose-based biocomposites, *Carbohydr. Polym.* 66 (2006) 537–545. doi:10.1016/j.carbpol.2006.04.023.
- [42] A. El Oudiani, Y. Chaabouni, S. Msahli, F. Sakli, Physico-chemical characterisation and tensile mechanical properties of *Agave americana* L. fibres, *J. Text. Inst.* 100 (2009) 430–439. doi:10.1080/00405000701863350.
- [43] K. Mysamy, I. Rajendran, Investigation on Physio-chemical and Mechanical Properties of Raw and Alkali-treated *Agave americana* Fiber, *J. Reinf. Plast. Compos.* 29 (2010) 2925–2935. doi:10.1177/0731684410362817.
- [44] A.E.O. Ben Sghaier, Y. Chaabouni, S. Msahli, F. Sakli, Morphological and crystalline characterization of NaOH and NaOCl treated *Agave americana* L. fiber, *Ind. Crops Prod.* 36 (2012) 257–266. doi:10.1016/j.indcrop.2011.09.012.
- [45] M. Idicula, A. Boudenne, L. Umadevi, L. Ibos, Y. Candau, S. Thomas, Thermophysical properties of natural fibre reinforced polyester composites, *Compos. Sci. Technol.* 66 (2006) 2719–2725. doi:10.1016/j.compscitech.2006.03.007.
- [46] A. Thygesen, J. Oddershede, H. Lilholt, A.B. Thomsen, K. Ståhl, On the determination of crystallinity and cellulose content in plant fibres, *Cellulose.* 12 (2005) 563–576. doi:10.1007/s10570-005-9001-8.
- [47] R.A. Cruz, A.M. Mendoza Mtz., T. Heinze, Synthesis and characterization of graft copolymers from natural fibers, *Int. J. Polym. Mater.* 51 (2002) 661–674. doi:10.1080/714975799.
- [48] A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo, P.J. Herrera-Franco, Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites, *Compos. Part B Eng.* 30 (1999) 309–320. doi:10.1016/S1359-8368(98)00054-7.

- [49] S.M. Sapuan, A.R. Mohamed, J.P. Siregar, M.R. Ishak, Cellulose Fibers: Bio- and Nano-Polymer Composites, (2011) 325–343. doi:10.1007/978-3-642-17370-7.
- [50] S.C. Saha, B.K. Das, P.K. Ray, S.N. Pandey, K. Goswami, SEM Studies of the Surface and Fracture Morphology of Pineapple Leaf Fibers, *Text. Res. J.* 60 (1990) 726–731. doi:10.1177/004051759006001205.
- [51] K.G. Satyanarayana, K.K. Ravikumar, K. Sukumaran, P.S. Mukherjee, S.G.K. Pillai, a. G. Kulkarni, Structure and properties of some vegetable fibres - Part 3 Talipot and palmyrah fibres, *J. Mater. Sci.* 21 (1986) 57–63. doi:10.1007/BF01144699.
- [52] M.D. Judd, B.A. Plunkett, M.I. Pope, The thermal decomposition of calcium, sodium, silver and copper(II) acetates, *J. Therm. Anal.* 6 (1974) 555–563. doi:10.1007/BF01911560.
- [53] T. De Vrije, G.G. De Haas, G.B. Tan, E.R.P. Keijsers, P.A.M. Claassen, Pretreatment of Miscanthus for hydrogen production by Thermotoga elfii, *Int. J. Hydrogen Energy.* 27 (2002) 1381–1390. doi:10.1016/S0360-3199(02)00124-6.
- [54] G. Huang, Nettle (*Urtica cannabina* L) fibre, properties and spinning practice, *J. Text. Inst.* 96 (2005) 11–15. doi:10.1533/joti.2004.0023.
- [55] E. Billa, D.P. Koullas, B. Monties, E.G. Koukios, Structure and composition of sweet sorghum stalk components, *Ind. Crops Prod.* 6 (1997) 297–302. doi:10.1016/S0926-6690(97)00031-9.
- [56] R.M. Kozasowski, M. Mackiewicz-Talarczyk, A.M. Allam, Bast fibres: flax, in: *Handb. Nat. Fibres*, Elsevier, 2012: pp. 56–113. doi:10.1533/9780857095503.1.56.
- [57] C.E.L.C, Master of linen, (2010). www.masteroflinen.com (accessed August 4, 2015).
- [58] C.W. Hock, Microscopic structure of flax and related bast fibers, *J. Res. Natl. Bur. Stand.* (1934). 29 (1942) 41. doi:10.6028/jres.029.024.
- [59] D.E. Akin, Flax - Structure, Chemistry, Retting and Processing, in: J. Müsig (Ed.), *Ind. Appl. Nat. Fibres Struct. Prop. Tech. Appl.*, Wiley, 2010: pp. 89 – 108.
- [60] I. Van de Weyenberg, Flax Fibres As a Reinforcement for Epoxy Composites, Katholieke Universiteit Leuven, 2005.
- [61] D.D. Stokke, Q. Wu, G. Han, *Introduction to Wood and Natural Fibers Composites*, Wiley, 2013.
- [62] S. V. Joshi, L.T. Drzal, a. K. Mohanty, S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites?, *Compos. Part A Appl. Sci. Manuf.* 35 (2004) 371–376. doi:10.1016/j.compositesa.2003.09.016.

- [63] D.B. Dittenber, H.V.S. Gangarao, Critical review of recent publications on use of natural composites in infrastructure, *Compos. Part A Appl. Sci. Manuf.* 43 (2012) 1419–1429. doi:10.1016/j.compositesa.2011.11.019.
- [64] G. Cicala, G. Cristaldi, A. Latteri, Composites Based on Natural Fibre Fabrics, in: P.D. Dubrovski (Ed.), *Woven Fabr. Eng.*, InTech, 2010: pp. 317 – 342.
- [65] H.L. Bos, K. Molenveld, W. Teunissen, a. M. Van Wingerde, D.R. V Van Delft, Compressive behaviour of unidirectional flax fibre reinforced composites, *J. Mater. Sci.* 39 (2004) 2159–2168. doi:10.1023/B:JMSC.0000017779.08041.49.
- [66] A. Bledzki, J. Gassan, Composites reinforced with cellulose based fibres, *Prog. Polym. Sci.* 24 (1999) 221–274. <http://www.sciencedirect.com/science/article/pii/S0079670098000185> (accessed September 23, 2013).
- [67] M. Biron, Composites, in: *Thermosets Compos.*, Elsevier, 2013: pp. 299–473. doi:10.1016/B978-1-4557-3124-4.00006-7.
- [68] P. Wambua, J. Ivens, I. Verpoest, Natural fibres: Can they replace glass in fibre reinforced plastics?, *Compos. Sci. Technol.* 63 (2003) 1259–1264. doi:10.1016/S0266-3538(03)00096-4.
- [69] G. Coroller, A. Lefeuvre, A. Le Duigou, A. Bourmaud, G. Ausias, T. Gaudry, et al., Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional composite, *Compos. Part A Appl. Sci. Manuf.* 51 (2013) 62–70. doi:10.1016/j.compositesa.2013.03.018.
- [70] C. Baley, Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase, *Compos. - Part A Appl. Sci. Manuf.* 33 (2002) 939–948. doi:10.1016/S1359-835X(02)00040-4.
- [71] A.R. Horrocks, S.C. Anand, *Handbook of technical textiles*, 2000.
- [72] Xiaohua Ye, Hong Hu, Xunwei Feng, Development of the Warp Knitted Spacer Fabrics for Cushion Applications, *J. Ind. Text.* 37 (2008) 213–223. doi:10.1177/1528083707081592.
- [73] S.L. Ogin, Textil-reinforcing composites materials, in: *Handb. Compos.*, 2000: pp. 264–281.
- [74] J. Baets, S. V. Lomov, Architecture of textile reinforcements and properties of composites, in: *Flax Hemp Fibres a Nat. Solut. Compos. Ind.*, JEC Composites, 2012: pp. 61 – 70.
- [75] W.S. Sounhem, Technical fabric structures - 1. Woven fabrics, in: A.R. Horrocks, S.C. Anand (Eds.), *Handb. Tech. Text.*, 2000: pp. 62 – 94.

- [76] G. Castelli, S. Maietta, G. Sigrisi, I.M. Slaviero, Reference Books of Textile Technology: Weaving, 2000.
- [77] F.E. Lockuán Lavado, La industria textil y su control de calidad, 2012.
- [78] A. Bergeret, P. Krawczak, Liaison renfort / matrice. Comportement des composites, Tech. L'ingénieur. 33 (2014) 0–19.
- [79] I. Van de Weyenberg, T. Chi Truong, B. Vangrimde, I. Verpoest, Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment, Compos. Part A Appl. Sci. Manuf. 37 (2006) 1368–1376. doi:10.1016/j.compositesa.2005.08.016.
- [80] C. Baley, Y. Perrot, F. Busnel, H. Guezenoc, P. Davies, Transverse tensile behaviour of unidirectional plies reinforced with flax fibres, Mater. Lett. 60 (2006) 2984–2987. doi:10.1016/j.matlet.2006.02.028.
- [81] B. Vanleeuw, V. Carvelli, M. Barburski, S.V. Lomov, A.W. van Vuure, Quasi-unidirectional flax composite reinforcement: Deformability and complex shape forming, Compos. Sci. Technol. 110 (2015) 76–86. doi:10.1016/j.compscitech.2015.01.024.
- [82] M. Biron, Thermoset Processing, in: Thermosets Compos., Elsevier, 2014: pp. 269–297. doi:10.1016/B978-1-4557-3124-4.00005-5.
- [83] S. Liang, P.B. Gning, L. Guillaumat, A comparative study of fatigue behaviour of flax/epoxy and glass/epoxy composites, Compos. Sci. Technol. 72 (2012) 535–543. doi:10.1016/j.compscitech.2012.01.011.
- [84] H. Dhakal, Z. Zhang, M. Richardson, Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites, Compos. Sci. Technol. 67 (2007) 1674–1683. doi:10.1016/j.compscitech.2006.06.019.
- [85] K. Benzarti, L. Cangemi, F. Dal Maso, Transverse properties of unidirectional glass/epoxy composites: Influence of fibre surface treatments, Compos. Part A Appl. Sci. Manuf. 32 (2001) 197–206. doi:10.1016/S1359-835X(00)00136-6.
- [86] E. Bisanda, M. Ansell, The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites, Compos. Sci. Technol. 41 (1991) 165–178. <http://www.sciencedirect.com/science/article/pii/026635389190026L> (accessed September 11, 2014).
- [87] P. Niedermann, G. Szebényi, A. Toldy, Characterization of high glass transition temperature sugar-based epoxy resin composites with jute and carbon fibre reinforcement, Compos. Sci. Technol. 117 (2015) 62–68. doi:10.1016/j.compscitech.2015.06.001.

- [88] R. Matadi Boumbimba, C. Froustey, P. Viot, P. Gerard, Low velocity impact response and damage of laminate composite glass fibre/epoxy based tri-block copolymer, *Compos. Part B Eng.* 76 (2015) 332–342. doi:10.1016/j.compositesb.2015.02.007.
- [89] K. Zhang, Y. Gu, M. Li, Z. Zhang, Effect of rapid curing process on the properties of carbon fiber/epoxy composite fabricated using vacuum assisted resin infusion molding, *Mater. Des.* 54 (2014) 624–631. doi:10.1016/j.matdes.2013.08.065.
- [90] Y. Gu, X. Tan, Z. Yang, M. Li, Z. Zhang, Hot compaction and mechanical properties of ramie fabric/epoxy composite fabricated using vacuum assisted resin infusion molding, *Mater. Des.* 56 (2014) 852–861. doi:10.1016/j.matdes.2013.11.077.
- [91] C. Xia, S.Q. Shi, L. Cai, Vacuum-assisted resin infusion (VARI) and hot pressing for CaCO₃ nanoparticle treated kenaf fiber reinforced composites, *Compos. Part B Eng.* 78 (2015) 138–143. doi:10.1016/j.compositesb.2015.03.039.
- [92] L. Yan, N. Chouw, X. Yuan, Improving the mechanical properties of natural fibre fabric reinforced epoxy composites by alkali treatment, *J. Reinf. Plast. Compos.* 31 (2012) 425–437. doi:10.1177/0731684412439494.
- [93] B. Madsen, A. Thygesen, H. Lilholt, Plant fibre composites - porosity and volumetric interaction, *Compos. Sci. Technol.* 67 (2007) 1584–1600. doi:10.1016/j.compscitech.2006.07.009.
- [94] M. Assarar, D. Scida, A. El Mahi, C. Poilâne, R. Ayad, Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax-fibres and glass-fibres, *Mater. Des.* 32 (2011) 788–795. doi:10.1016/j.matdes.2010.07.024.
- [95] S. Deng, L. Ye, Y.-W. Mai, Influence of fibre cross-sectional aspect ratio on mechanical properties of glass fibre/epoxy composites I. Tensile and flexure behaviour, *Compos. Sci. Technol.* 59 (1999) 1331–1339. doi:10.1016/S0266-3538(98)00168-7.
- [96] G. Cooper, A. Kelly, Role of the interface in the fracture of fiber-composite materials, *Interfaces Compos.* (1969) 90 – 106.
- [97] T. Thamae, C. Baillie, Influence of fibre extraction method, alkali and silane treatment on the interface of Agave americana waste HDPE composites as possible roof ceilings in Lesotho, *Compos. Interfaces.* 14 (2007) 821–836. doi:10.1163/156855407782106483.
- [98] M.Z. Rong, M.Q. Zhang, Y. Liu, G.C. Yang, H.M. Zeng, The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites, *Compos. Sci. Technol.* 61 (2001) 1437–1447. doi:10.1016/S0266-3538(01)00046-X.

- [99] J. Gassan, A.K. Bledzki, Possibilities for improving the mechanical properties of jute/epoxy composites by alkali treatment of fibres, *Compos. Sci. Technol.* 59 (1999) 1303–1309. doi:10.1016/S0266-3538(98)00169-9.
- [100] D. Bachtiar, S.M. Sapuan, M.M. Hamdan, The effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites, *Mater. Des.* 29 (2008) 1285–1290. doi:10.1016/j.matdes.2007.09.006.
- [101] D. Bachtiar, S.M. Sapuan, M.M. Hamdan, The Influence of Alkaline Surface Fibre Treatment on the Impact Properties of Sugar Palm Fibre-Reinforced Epoxy Composites, *Polym. Plast. Technol. Eng.* 48 (2009) 379–383. doi:10.1080/03602550902725373.
- [102] K. Mylsamy, I. Rajendran, Influence of alkali treatment and fibre length on mechanical properties of short Agave fibre reinforced epoxy composites, *Mater. Des.* 32 (2011) 4629–4640. doi:10.1016/j.matdes.2011.04.029.
- [103] K. Mylsamy, I. Rajendran, The mechanical properties, deformation and thermomechanical properties of alkali treated and untreated Agave continuous fibre reinforced epoxy composites, *Mater. Des.* 32 (2011) 3076–3084. doi:10.1016/j.matdes.2010.12.051.
- [104] B.F. Yousif, A. Shalwan, C.W. Chin, K.C. Ming, Flexural properties of treated and untreated kenaf/epoxy composites, *Mater. Des.* 40 (2012) 378–385. doi:10.1016/j.matdes.2012.04.017.
- [105] G. Goud, R.N. Rao, Effect of fibre content and alkali treatment on mechanical properties of *Roystonea regia*-reinforced epoxy partially biodegradable composites, *Bull. Mater. Sci.* 34 (2011) 1575–1581. doi:10.1007/s12034-011-0361-4.
- [106] H.P.S.. Khalil, H. Ismail, H.. Rozman, M.. Ahmad, The effect of acetylation on interfacial shear strength between plant fibres and various matrices, *Eur. Polym. J.* 37 (2001) 1037–1045. doi:10.1016/S0014-3057(00)00199-3.
- [107] M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne, Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading, *Compos. Sci. Technol.* 67 (2007) 1627–1639. doi:10.1016/j.compscitech.2006.07.003.
- [108] E. Bisanda, The effect of alkali treatment on the adhesion characteristics of sisal fibres, *Appl. Compos. Mater.* 7 (2000) 331–339. <http://www.springerlink.com/index/1117454654123170.pdf> (accessed January 28, 2013).
- [109] A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo, P.J. Herrera-Franco, Chemical modification of henequén fibers with an organosilane coupling agent, *Compos. Part B Eng.* 30 (1999) 321–331.

- [110] N. Le Moigne, M. Longerey, J.-M. Taulemesse, J.-C. Bénézet, A. Bergeret, Study of the interface in natural fibres reinforced poly(lactic acid) biocomposites modified by optimized organosilane treatments, *Ind. Crops Prod.* 52 (2014) 481–494. doi:10.1016/j.indcrop.2013.11.022.
- [111] I. Van de Weyenberg, J. Ivens, A. De Coster, B. Kino, E. Baetens, I. Verpoest, Influence of processing and chemical treatment of flax fibres on their composites, *Compos. Sci. Technol.* 63 (2003) 1241–1246. doi:10.1016/S0266-3538(03)00093-9.
- [112] T.-T.-L. Doan, H. Brodowsky, E. Mäder, Jute fibre/epoxy composites: Surface properties and interfacial adhesion, *Compos. Sci. Technol.* 72 (2012) 1160–1166. doi:10.1016/j.compscitech.2012.03.025.
- [113] J. Lu, P. Askeland, L.T. Drzal, Surface modification of microfibrillated cellulose for epoxy composite applications, *Polymer (Guildf)*. 49 (2008) 1285–1296. doi:10.1016/j.polymer.2008.01.028.
- [114] N. Sgriccia, M.C. Hawley, M. Misra, Characterization of natural fiber surfaces and natural fiber composites, *Compos. Part A Appl. Sci. Manuf.* 39 (2008) 1632–1637. doi:10.1016/j.compositesa.2008.07.007.
- [115] M.R. Ishak, Z. Leman, S.M. Sapuan, M.Y. Salleh, S. Misri, The Effect of Sea Water Treatment on the Impact and Flexural Strength of Sugar Palm Fibre Reinforced Epoxy Composites, *Int. J. Mech. Mater. Eng.* 4 (2009) 316–320.

Chapter II:

From sliver to yarns: chemical and mechanical properties through the different transformation steps of flax fibres

2.1. Description of the successive transformation steps from flax silver to flax yarns

It is well known that the properties of flax fibres depend on either their genotype, production environment or their maturity and on what transformation steps they have followed from the stems to the final sub-products or products [1,2]. As a consequence in order to reduce flax fibres intrinsic variability from a year, a maturity and a growing to others, flax stems are usually mixed all together previously to further manufacturing steps.

A general description of the transformation steps undergone by flax from the stem to the fibre was exposed in chapter 1.3.2. For this study, stem was scutched and hackled in order to obtain the slivers and then a combination of 12 different slivers were mixed, stretched and slightly twisted before testing as it was shown in Fig. II - 1.

In this chapter, the influence of successive transformation steps from doubled flax silvers to low twisted and twisted flax yarns on the flax visual aspect, their biochemical composition, their moisture content and their mechanical properties were studied. This study aims to understand further properties obtained on epoxy/flax fibres composites.

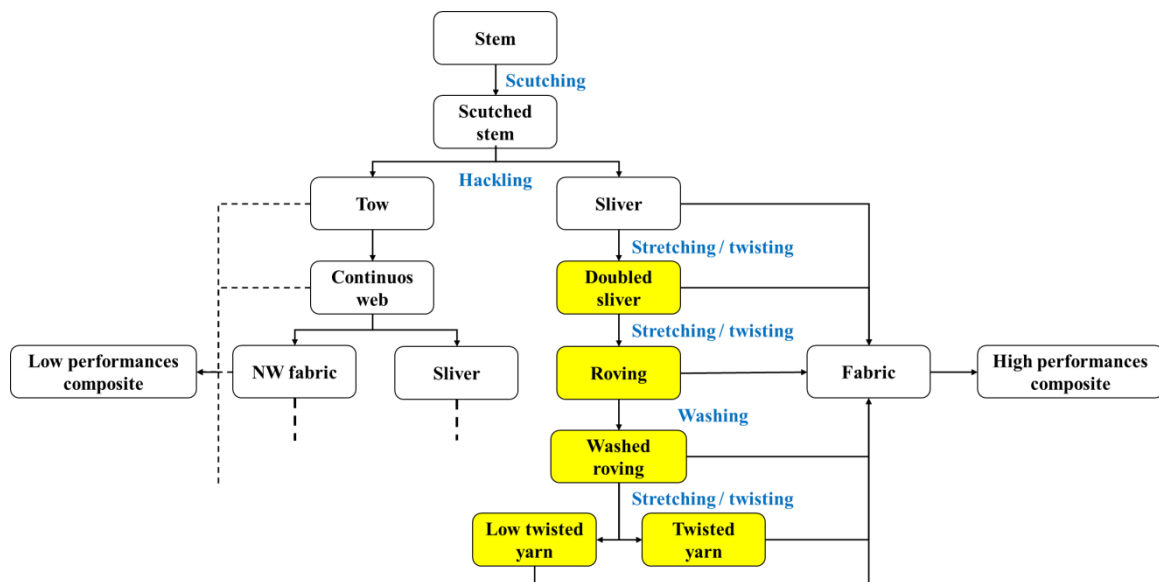


Fig. II - 1 Transformation steps of flax fibres from sliver to yarns that are analysed in this study

2.2. Materials and experimental methods

2.2.1. Materials

Two batches of flax fibre provided by Fibre Recherche Developpement (FRD, France) were obtained by mixing 12 different doubled slivers for homogenization. Stretching, twisting and washing steps were carried out by manufacturing companies unrelated to this project.

A reference of short flax fibres, cut from a third sliver, was supplied also by Fibre Recherche Developpement (FRD, France).

All chemical products of this chapter were provided by Fibre Recherche Developpement (FRD, France).

2.2.2. Visual aspect of flax fibres

A qualitative and descriptive visual analysis of fibres was carried out taking in consideration the adhesion between fibres, the fibre twist and the response to a weak hand manipulation.

2.2.3. Determination of biochemical composition of flax fibres by Van Soest method

The biochemical composition of flax fibres for each transformation step was quantified using Van Soest method [3]. This later is a gravimetric method using a semi-automatic FIBRE THERM – GERHARDT® extractor (Fig. II - 2) that determine precisely the biochemical composition of natural fibre, i.e. cellulose, hemicellulose, lignin, cell (including protein, fat and soluble carbohydrate or pectin) and ash contents according to the schematic procedure shown in Fig. II - 3.



Fig. II - 2 Semi-automatic FIBRE THERM – GERHARDT® extractor used to determine the biochemical composition of flax fibres

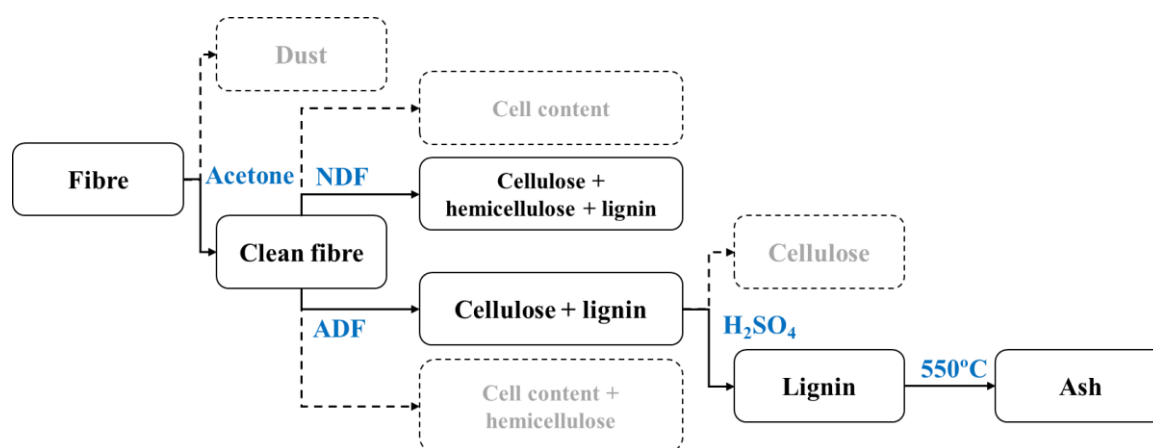


Fig. II - 3 Schematic procedure of Van Soest method [3]

Van Soest method [3] could be divided in four steps:

- *Fibre cleaning*

In order to avoid the degradation or loss of components by milling, 5 g of fibres were cut using scissors at around 2 mm in length. Then fibres were cleaned with acetone for 3 min and filtered. This process was carried out 3 times and then fibres were dried for 16 h at 60°C. Dried fibres were placed on a desiccator for 30 min at 35% humidity and 20°C before weighting.

- *Determination of hemicellulose content through neutral and acid detergent based extractions*

The first step of the extraction process consisted on one hand in the removal of the cell content (proteins, fats and soluble carbohydrates) by neutral detergent solution (NDS) obtaining as residual part the neutral detergent fibre (NDF) containing the cellulose, the hemicellulose and the lignin; and on the other hand, in the extraction of the cell content and hemicellulose by acid detergent solution (ADS) obtaining as residual part the acid detergent fibre (ADF) containing the cellulose and the lignin from the cleaned fibre. NDF extraction was carried out introducing around. Then filter bags were introduced in the semi-automatic FIBRE THERM – GERHARDT® extractor and NDS solution was applied for 1h at 80°C followed by a rinsing at 95°C and other with cold water. Filter bags were introduced in an oven for 16h at 105°C and then 30 min in a desiccator at 20°C and 35% of humidity. Loss of mass was then measured in order to determine the NDF content. For ADF extraction, also around 500 mg of cleaned and dried fibre in a FIBREBAG filter bag and weighted. An ADS solution was used in the extraction. The process was carried out as NDF extraction. Hemicellulose content was obtained by difference of mass between NDF and ADF.

- *Determination of cellulose and lignin content through sulfuric acid extraction*

Cellulose and lignin content were determined by dissolution of cellulose from ADF. For this extraction, four fibre bags containing ADF inside were introduced in a beaker of 250ml. Then 125ml of sulfuric acid at 72% were added and mixed slowly each 30 min in order to impregnate the fibres and extract the cellulose. 25ml more of acid were added each hour for two times. At 3 hours, bags were removed from the solution and rinsed 3 times with demineralised hot water and then with demineralised cold water. Fibre bags were introduced in an oven for 16 h at 105°C and then 30 min in a desiccator at 20°C and 35% of humidity. Loss of mass corresponds to cellulose and residual mass to lignin.

- *Determination of ash content through pyrolysis*

The inorganic residues or ashes were measured after combustion of lignin obtained after cellulose extraction. Combustion was carried out at 550°C for 1 h and then residue was introduced for 30 min in a desiccator at 20°C and 35% of humidity.

The bio-chemical analysis was carried out using two samples of each transformation step and batch.

2.2.4. Determination of lipophilic component of flax fibres by FT-IR

A qualitative analysis of the evolution of components through the different transformation steps was performed by Fourier Transform Infrared (FT-IR). FT-IR spectra were recorded using a Bruker IFS66 spectrometer in attenuated total reflectance (ATR) mode with a resolution of 2 cm^{-1} and 32 scans in the range 4000-400 cm^{-1} . All the spectra were normalized according to the band at 1202 cm^{-1} , corresponding to OH in plane bending of cellulose component [4].

2.2.5. Moisture content of flax fibres

Fibre moisture was analysed only for one batch (batch 1). Flax fibres were conditioned at 20°C and 60% humidity for 48h. Drying and measuring of moisture rate were performed using a halogen desiccator METTLER TOLEDO HB43-S Halogen. A mass of around 2.5 g of each step of fibre transformation from one batch was introduced in the balance and measured. Then fibres were dried at 105°C until mass loss was stabilized. Moisture rate was calculated between the initial mass and the final mass. For this test, two different measurements were carried out.

2.2.6. Linear density of flax fibres

For this analysis fibres were conditioned at 20°C and 60% humidity for 48h. From each transformation step and each batch, 10 pieces of 1 m long were cut. Then each piece was weighed. The linear density was measured in Tex. This unit consists in the mass of tow, threads, yarns, etc. in g divided by length unit in Km.

2.2.7. Tensile test of flax fibres

Tensile tests were carried out using a tensile set up INSTRON 5965 using a force captor of 5 KN and the yarn adapted jaws. The test was accomplished at 100mm/min with a distance between jaws at 500 mm and 0.5N of pre-charge. For this analysis fibres were conditioned at 20°C and 60% humidity for 48h. Ten samples of 1 m were used from each transformation step and batch.

2.3. Influence of the different transformation steps on the visual aspect of flax fibres

The visual aspect of flax fibres as a function of the different transformation steps (doubled silver, roving, washed roving, twisted and low twisted yarns) is presented on Fig. II - 4.

It can be observed that the doubled sliver (Fig. II - 4a) presents a high number of elementary fibres without any adhesion between each other. The sliver is easily defibrillated by hand manipulation in longitudinal or transverse directions. The roving (Fig. II - 4b) presents also a defibrillated visual aspect which is less pronounced than in the case of doubled sliver. Defibrillation was even produced easily by hand manipulation in transverse direction to the fibres, being much more difficult to defibrillate applying a force in fibre direction. Washed roving (Fig. II - 4c) diameter seems to be lower due to the better cohesion between fibres. Also a low twist was observed. Defibrillation was not easily produced by hand manipulation. In the last step, each batch presented two different products, a low twist yarn from the batch 1 (Fig. II - 4d) and a twisted yarn from the batch 2 (Fig. II - 4e). No differences are detected. In both cases yarn cohesion is high. As well, defibrillation was not produced by hand manipulation.

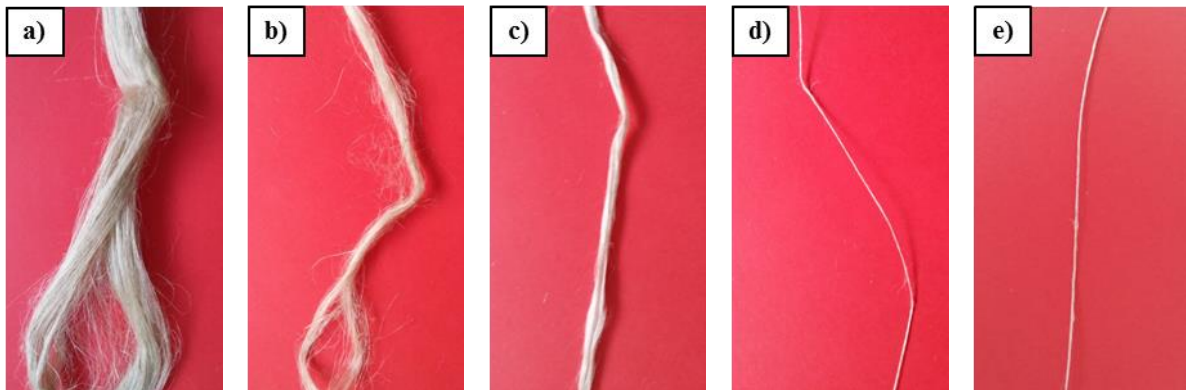


Fig. II - 4 Visual aspect of flax fibres according to the different transformation steps: a) doubled sliver (batch 1), b) roving (batch 1), c) washed roving (batch 1), d) low twisted yarn (batch 1) and e) twisted (batch 2)

2.4. Evolution of the biochemical composition measured by Van Soest method through the process transformation steps

The evolution on biochemical composition of flax fibres through the transformation steps is shown in Fig. II - 5 for batch 1 and Fig. II - 6 for batch 2. Both figures show the important

variability of the flax fibre biochemical composition depending on the transformations steps to which it had been submitted.

Mechanical transformation process, consisting in stretching and twisting of fibres, removed mainly the components at the flax fibre surface by mechanical friction. In the case of washing or chemical treatments, the extraction of components depends on the chemical solution and temperatures applied. In this case, washing treatment was carried out by industrial methods and the solution used was unknown for us. Otherwise, the main washing treatments industrially used, as desizing, mercerising, bleaching or optical brightening, do not modify cellulose content [5], for this reason, cellulose can be considered as the invariable component in the biochemical composition evolution.

From doubled sliver to low twisted yarn, cellulose composition was increased in about 7% (from 79.8 ± 0.36 to $87.0 \pm 0.68\%$) for batch 1. A similar increase is obtained from doubled silver ($81.3 \pm 0.56\%$) to twisted yarn ($88.8 \pm 0.28\%$) for batch 2. It can be noticed that no significant evolution occur either between doubled silver and roving or between washed roving and (low) twisted yarn, meaning that washing treatment is the main step influencing cellulose content by the extraction of mainly cell content and hemicellulose. Bourmaud et al. [6] studied the influence of washing treatments on the natural fibre components extraction. In the same way, the extraction of wall cell components by different washing treatments and its influence in the microstructure and interfacial behaviour will be studied in the chapter 3.

From the first analysed step to the last one, cell content, including proteins, fats and soluble carbohydrates (pectin), was decreased by about 55% (from 10.2 ± 0.03 to $5.5 \pm 0.23\%$) and 57% (from 10.6 ± 0.26 to $4.6 \pm 0.15\%$) for batch 1 and 2 respectively. Once more the washing step leads to the major decrease: 50% (from 9.4 ± 0.64 to $4.7 \pm 0.20\%$) for batch 1 and 42% (from 10.2 ± 0.04 to $5.9 \pm 1.90\%$) for batch 2. In this last case, a variation of fibre content was more important after washing treatment, which can be produced by non-homogeneity of fibre composites or errors during extraction or composition analysis, affecting to the final results.

Hemicellulose, lignin and ash contents are slightly decreased from $8.3 \pm 0.17\%$ to $6.2 \pm 0.58\%$, $1.7 \pm 0.32\%$ to $1.3 \pm 0.20\%$ and $0.4 \pm 0.11\%$ to 0.3 ± 0.13 respectively for batch 1 and from $6.3 \pm 0.39\%$ to $5.3 \pm 0.23\%$, $1.8 \pm 0.31\%$ to $1.3 \pm 0.01\%$ and $0.5 \pm 0.09\%$ to $0.5 \pm 0.06\%$

respectively for batch 2. Regarding the low differences between the first analysed step and the last one and the high variations between different samples of the same batch and step, it is in this case difficult to conclude about the major transformation step influencing the composition.

As cellulose is considered as non-extracted, the component content was calculated at the same cellulose rate. Table II - 1 Ratio between each component (hemicellulose, lignin and cell content) and cellulose through the flax process transformation step from sliver to yarns shows a ratio between each component (hemicellulose, lignin and cell content) and cellulose. The variation of components content between both batches was important for all process transformation steps. Discrepancies are less evident for lignin and cell content. Although fibres were mixed in between 12 different batches, the homogenization of flax fibres seems not to be optimized.

A homogenization of fibre biochemical composition between both batches was observed for (low) twisted yarn which is the last process transformation step. The variations between components of both batches was about 1.8% for cellulose, 0.9% for cell content, 0.9% for hemicellulose, 0.02% for lignin and 0.2% for ashes. Otherwise, the evolution of the biochemical composition was similar from the doubled sliver step to the roving step whatever the batch considered.

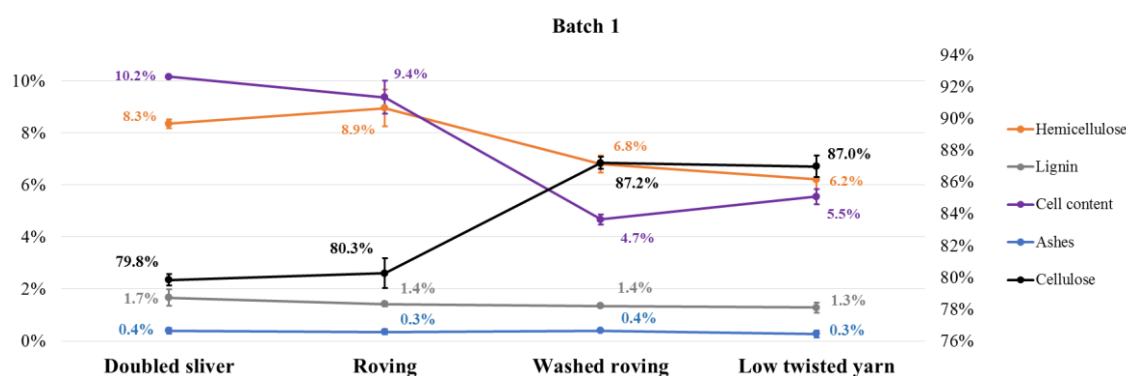


Fig. II - 5 Evolution of the biochemical composition through the flax process transformation steps from sliver to yarns (Batch 1)

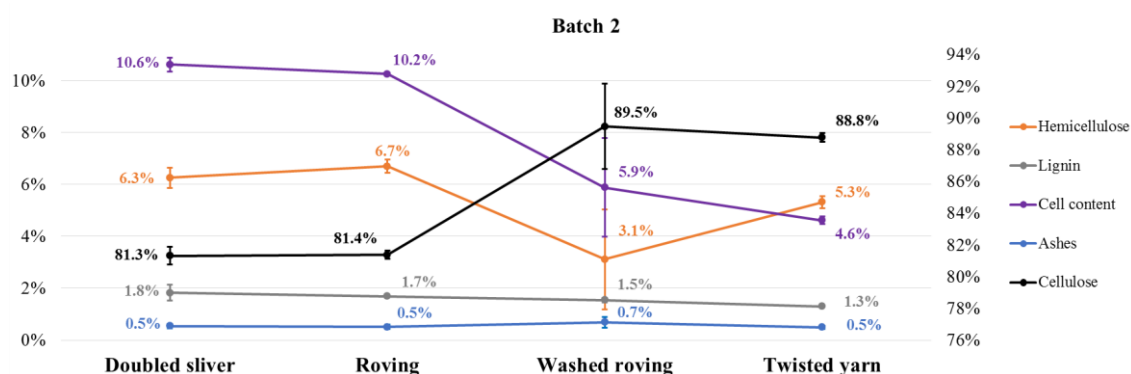


Fig. II - 6 Evolution of the biochemical composition through the flax process transformation steps from sliver to yarns (Batch 2)

Table II - 1 Ratio between each component (hemicellulose, lignin and cell content) and cellulose through the flax process transformation step from sliver to yarns

		Hemicellulose/cellulose (%)	Lignin/cellulose (%)	Cell content/cellulose (%)
Batch 1	Doubled sliver	10.5 ± 0.2	2.1 ± 0.4	12.7 ± 0.1
	Roving	11.1 ± 0.9	1.8 ± 0.1	11.7 ± 0.8
	Washed roving	7.8 ± 0.4	1.6 ± 0.0	5.4 ± 0.2
	Low twisted yarn	7.1 ± 0.7	1.5 ± 0.2	6.4 ± 0.3
Batch 2	Doubled sliver	7.7 ± 0.5	2.2 ± 0.4	13.1 ± 0.3
	Roving	8.2 ± 0.3	2.1 ± 0.0	12.6 ± 0.1
	Washed roving	3.5 ± 2.1	1.7 ± 0.1	6.6 ± 2.1
	Twisted yarn	6.0 ± 0.3	1.5 ± 0.0	5.2 ± 0.2

2.5. Evolution of the lipophilic content measured by FT-IR through the process transformation steps

2.5.1. Methodology

The Van Soest method [3] determined the biochemical composition (cellulose, hemicellulose, lignin, cell content and ashes) of flax fibres along the transformation steps. Other methods and standards can be used [7–13] and contents depend on the method employed. Generally, these methods consist in successive extractions of different components by chemical treatments. Tappi T264 standard [10] analysed the lipophilic components.

The chemical structure of the lipophilic components, i.e. fatty acids, aldehydes, aliphatic esters, aliphatic alcohols, alkanes, free sterols and sterol glycosides [14] are described in Chapter 1 Fig. 1-5. FT-IR can be used by analysis the evolution of peaks corresponding to CH₂ and sometimes CH₃ vibrations. In this way, Morvan et al. [15], analysed the waxed on flax fibres

by FT-IR using bands at 2850 cm^{-1} corresponding to the waxes (including in the lipophilic components).

2.5.2. Reference FT-IR spectra of lipophilic extractives, lignin, holocellulose and cellulose

A FT-IR analysis (Fig. II - 7) of each component extracted from a reference short flax fibre using Tappi T264 for lipophilic extractives, ASTM D1104-56 for holocellulose extraction, ASTM D1103-60 for cellulose extraction and the Van Soest method for lignin extraction was performed. The composition was pre-analysed (73.75% of cellulose, 11.85% of hemicellulose, 10.40% of lignin, 4% of lipophilic extractives). It will be shown in Chapter 3 (being put forward as part of a journal publication).

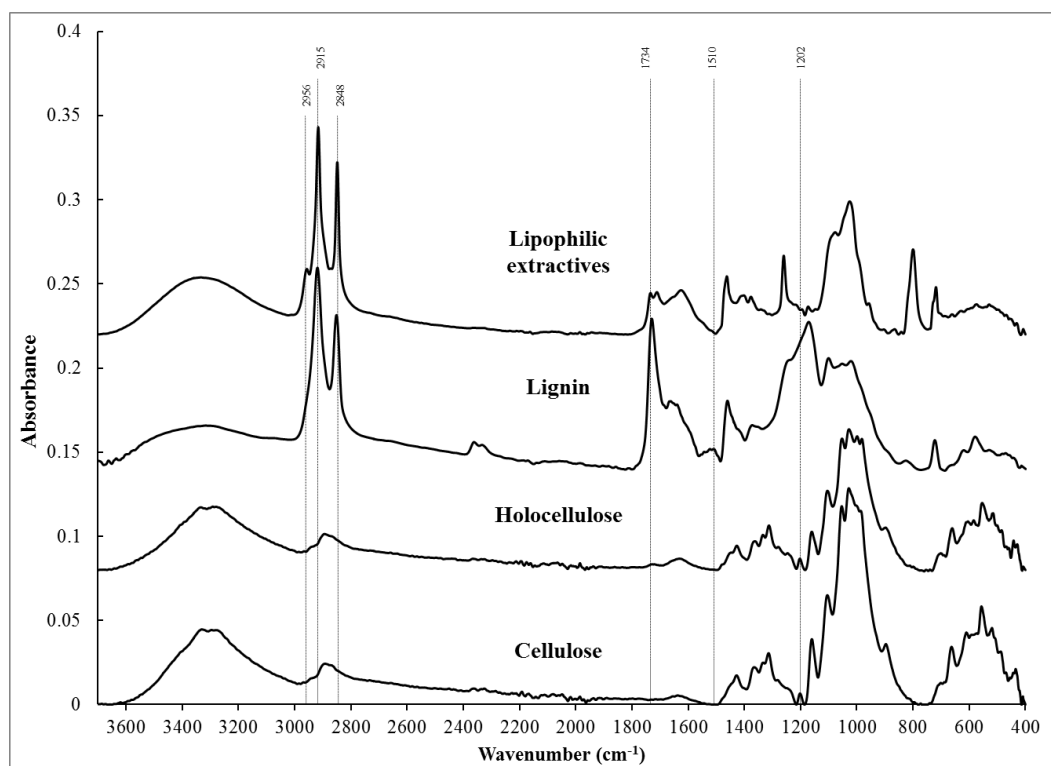


Fig. II - 7 FT-IR spectra of lipophilic extractives, lignin, holocellulose and cellulose extracted from a reference short flax fibre and characteristic vibration bands for lipophilic extractives and lignin

In the lipophilic extractives spectrum, three different characteristic peaks appears between 2800 and 3000 cm^{-1} , a peak at 2956 cm^{-1} , corresponding to antisymmetric CH_3 stretching, and two bands at 2915 and 2848 cm^{-1} , corresponding to asymmetric and symmetric CH_2 stretching respectively [16]. Asymmetric and symmetric CH_2 stretching bands were observed for lignin

too, as well as a peak at around 1735 cm^{-1} , related to saturated aliphatic and aromatic esters C=O stretching vibrations [16].

2.5.3. Evaluation of the lipophilic content according to the process transformation step

FT-IR spectra of the reference short flax fibre, the doubled sliver, roving, the washed roving, the (low) twisted yarn from batch 1 and 2 was depicted in Fig. II - 8. All spectra were adjusted using the peak at 1202 cm^{-1} corresponding to OH in plane bending vibrations of cellulose [4]. A variation of characteristics peaks for lipophilic extractives and lignin was observed depending on the considered transformation step. Bands corresponding to antisymmetric CH_3 stretching, at 2956 cm^{-1} was not easily observed.

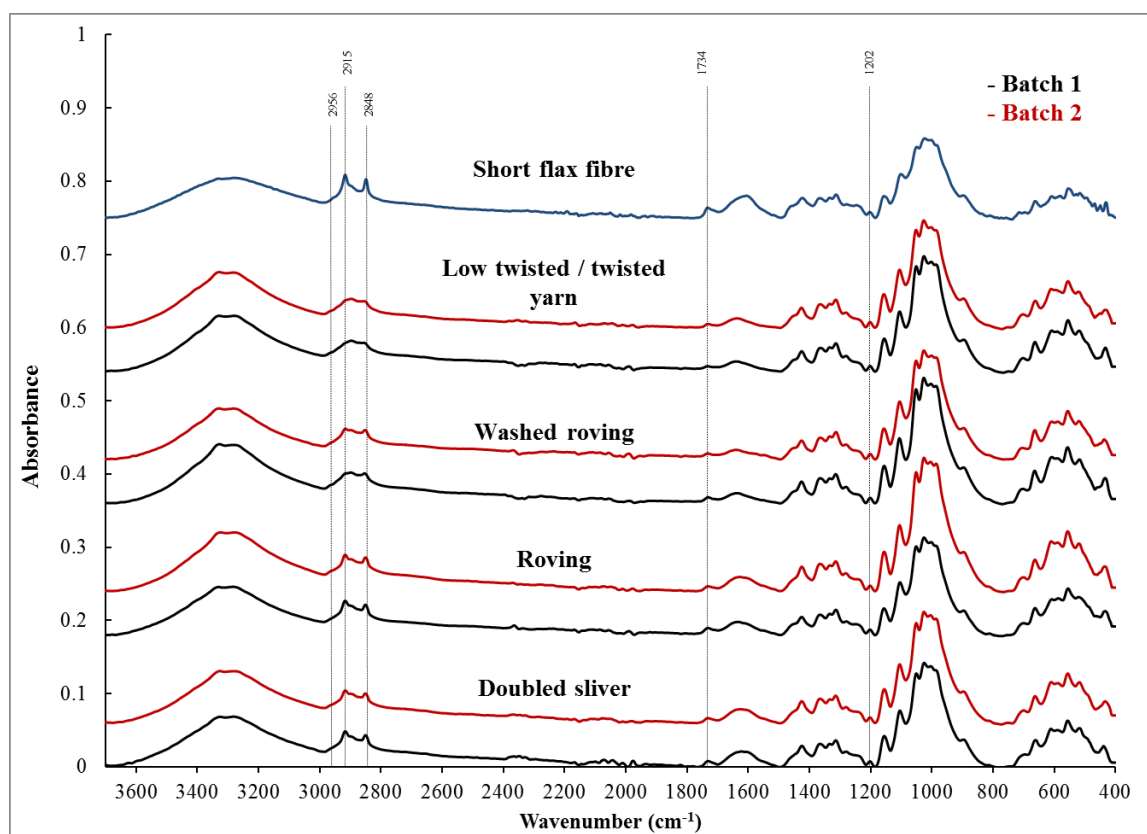


Fig. II - 8 FT-IR spectra of flax fibre doubled sliver, roving, washed roving, low twisted yarn and twisted yarn from batch 1 (black) and 2 (red)

In order to evaluate the lipophilic extractives content of the flax fibres through the different transformation steps, two ratios (corresponding to the quantity of lipophilic

extractives/cellulose) were determined: one between the band at 2915 cm^{-1} and the peak at 1202 cm^{-1} and the second between the band at 2845 cm^{-1} and the peak at 1202 cm^{-1} . Each ratio was multiplied by cellulose rate in order to obtain the intensity corresponding to the lipophilic extractives. Results are presented in Fig. II - 9 and Fig. II - 10. For both batches a low regular decrease was obtained. No sharp decrease was observed after the washing step as it was obtained previously for other components (hemicellulose, cell content). This technique does not allow to quantify the rate of lipophilic extractives on each sample, although the comparative with reference short flax fibres shows an equivalent ratio for doubled sliver and roving transformation steps with short flax fibre, whose lipophilic composition was around 4% and an impact on the extraction of this components, observed in Fig. II - 9, from the washed process. As it was observed for the other components, a homogenization of lipophilic extractives was obtained in the last transformation step.

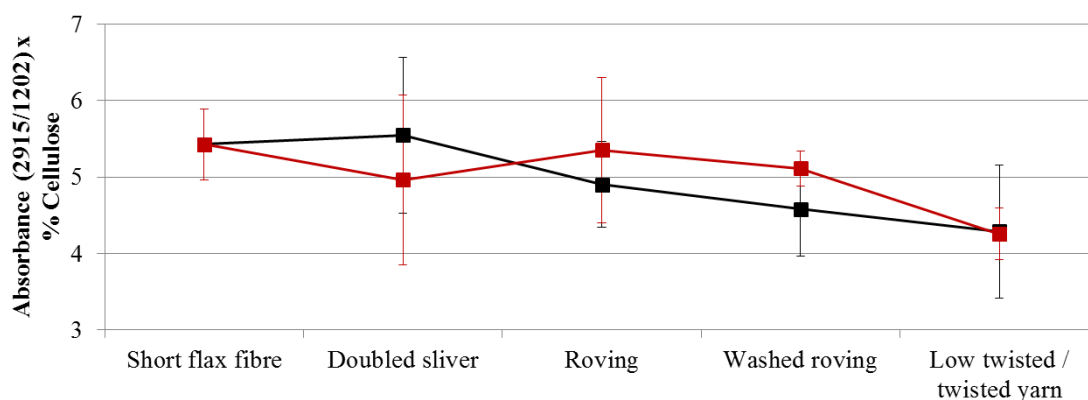


Fig. II - 9 Evolution of lipophilic components determined through the ratio between the FT-IR absorbance at 2915 and 1202 cm^{-1} multiplied by cellulose content as a function of the different transformation steps from doubled sliver to (low) twisted yarn for batch 1 (black) and batch 2 (red)

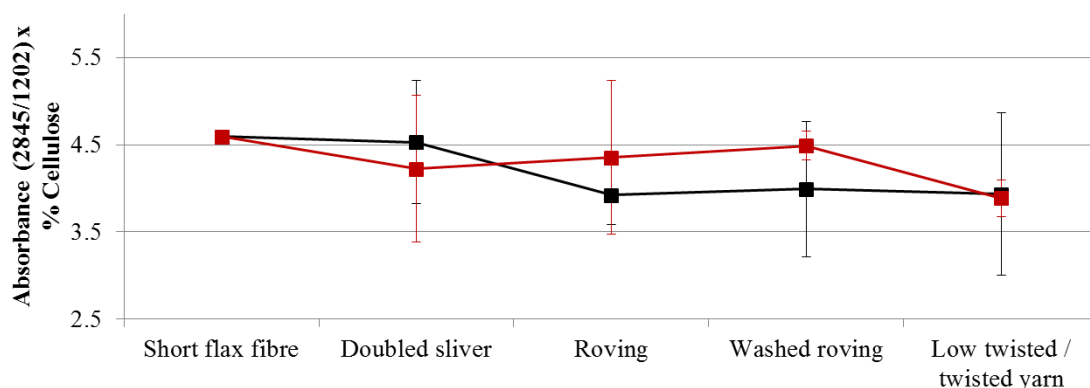


Fig. II - 10 Evolution of lipophilic components determined through the ratio between the FTIR absorbance at 2845 and 1202 cm^{-1} multiplied by cellulose content as a function of the different transformation steps from doubled sliver to (low) twisted yarn for batch 1 (black) and batch 2 (red)

The evolution of lignin composition can be also observed by FT-IR analysis through the band at 1734 cm^{-1} corresponding to alkyl ester groups [16]. Fig. II - 11 shows the evolution of the ratio between the FTIR absorbance at 1734 and 1202 cm^{-1} . In this case, as lignin content was known, values on biochemical composition of lignin were compared in the same figure. A slight decrease of the lignin content was observed from doubled sliver to the last transformation step, as it was shown in the bio-chemical composition obtained by Van Soest method.

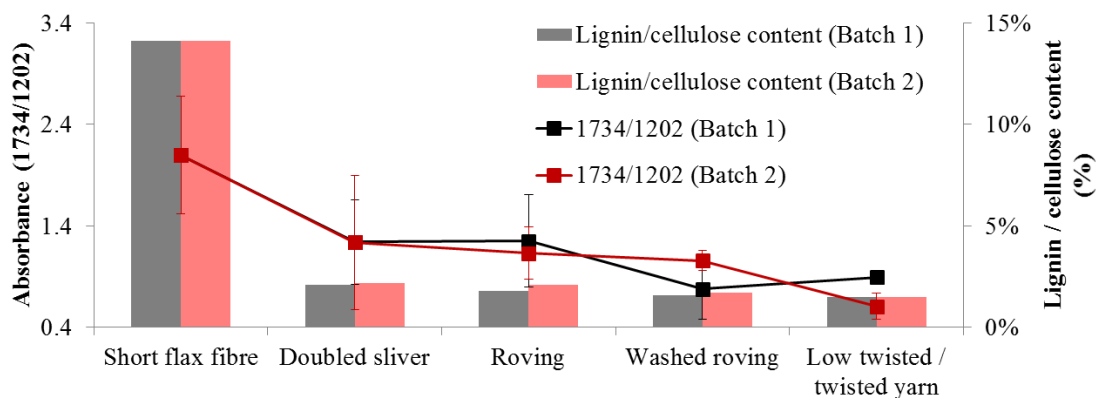


Fig. II - 11 Evolution of lignin/cellulose content determined through the ratio between the FT-IR absorbance at 1734 and 1202 cm^{-1} from doubled sliver to (low) twisted yarn compared with short flax fibre

2.6. Evolution of the flax fibre moisture content through the transformation steps

Fig. II - 12 shows the moisture content of flax fibres at each transformation step for batch 1. Variability high standard deviation in moisture content is observed for doubled sliver and

roving so that it was difficult to conclude. This high variation could be due an heterogeneous repartition of hydrophobic groups in cell content (e.g. fats) situated on the flax surface [15]. A slight decrease (about 2%) in moisture occurs for the last two transformation steps that could be related to the biochemical composition. A linear correlation between hemicellulose content and moisture content has been established as shown in Fig. II - 13. As hemicellulose is very hydrophilic component [17], its extraction could be responsible for the moisture variation.

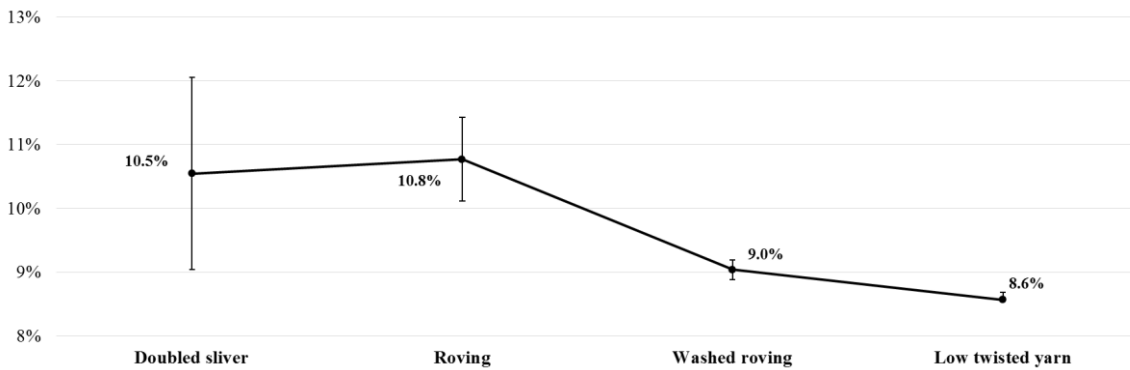


Fig. II - 12 Evolution of the flax moisture content as a function of the transformation process from doubled sliver to yarns (Batch 1)

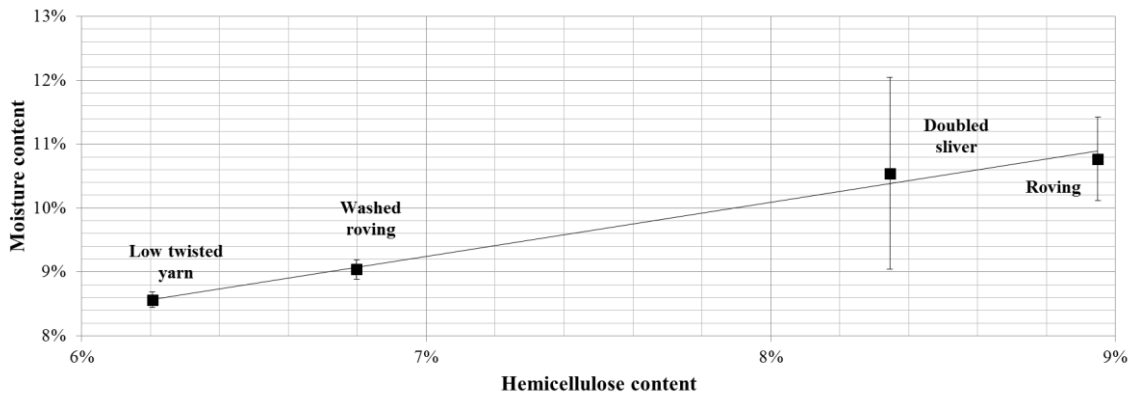


Fig. II - 13 Correlation between moisture and hemicellulose contents of flax fibres as a function of the manufacturing steps (Batch 1)

2.7. Mechanical properties of flax fibres

In Fig. II - 14, tensile strength curves for both batches and at the four transformation steps are presented. As section of samples cannot be measured by traditional methods (only estimated), curves were analysed in force-strain and then, using linear density previously measured,

ultimate stress was calculated in mN/Tex (Table II - 2 Ultimate force, linear density and ultimate stress of doubled sliver, roving, washed roving and yarns)

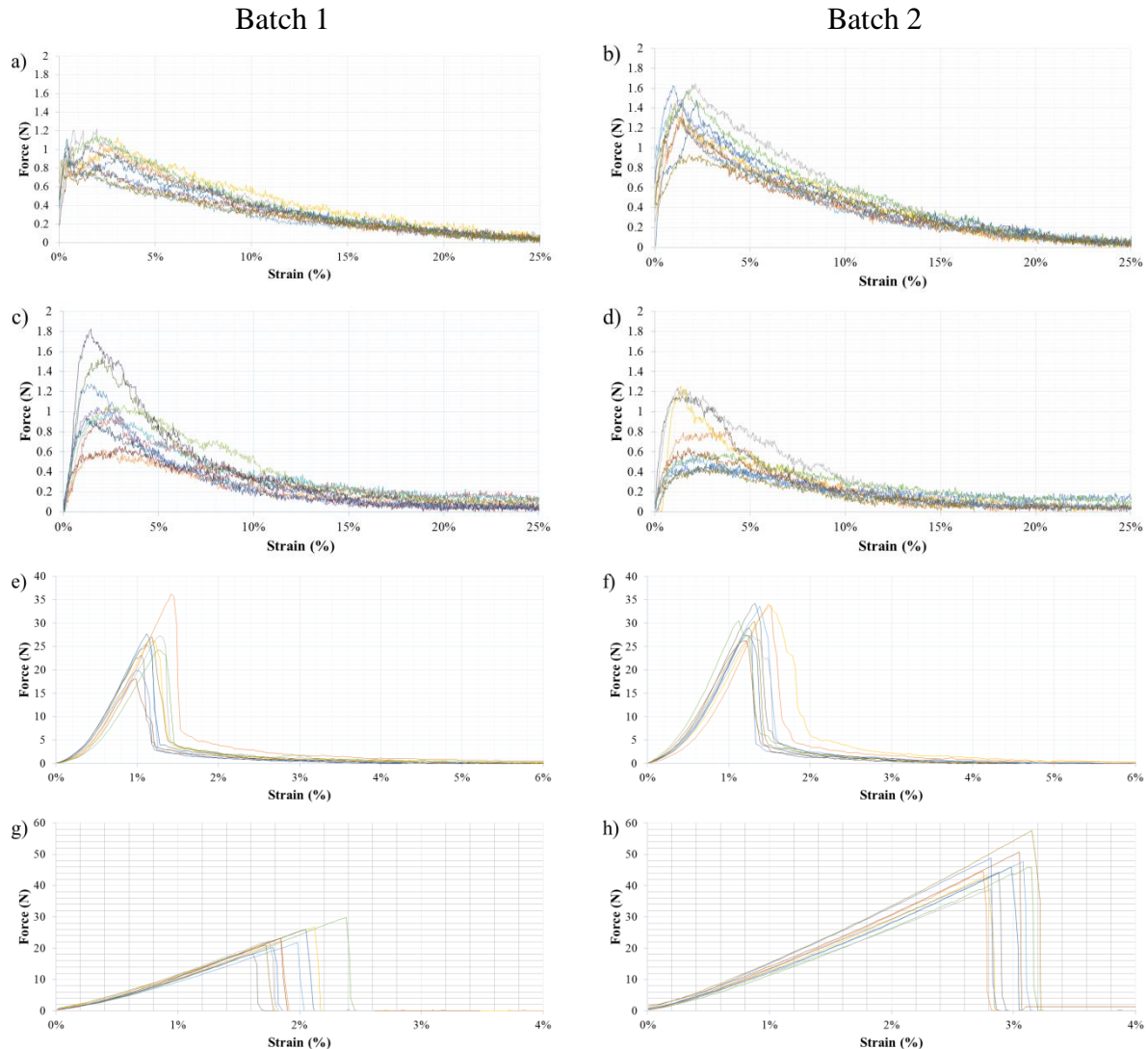


Fig. II - 14 Tensile strength curves in force-strain of (a) (b) doubled sliver, (c) (d) roving, (e) (f) washed roving and (g) (h) twisted yarn samples for batch 1 and 2

As concerns the doubled sliver samples, the maximal force is about 1 to 1.5 N for a deformation of about 2%. After that point, a slow and noisy decline of the curve is observed. This decline may be due to the friction between fibres and to the poor consistency of the doubled silver. As shown on Table 1, a linear density around 5000 Tex is obtained for both batches. For an equivalent linear density the ultimate stress of batch 2 seems to be higher than those of batch 1. As it was observed in Fig. II - 4, a low twist of the samples was observed for this sample, depending, the strength of fibres, on the friction between fibres and the adhesion between

unitary fibres by pectin cements. In this case, the cell content could be an influence on the variation between batch 1 and 2, as its composition was higher for batch 2.

Regarding roving sample, similar strength curves than those of doubled sliver samples was observed. The maximal force is about 0.5 to 2 N for a deformation of about 2%. After that point, a slow and noisy decline of the curve is also observed may be with a larger dispersion of the results. The linear density was decreased between doubled sliver and roving steps from about 5000 to about 700 Tex (719 ± 19 for batch 1 and 668 ± 9 for batch 2). The differences between linear densities from batch 1 to 2 may be produced by machine parameters during the stretching and twisting of fibres. For an equivalent linear density, the ultimate stress is increased between the two transformation steps (from 0.21 ± 0.01 mN/Tex to 1.51 ± 0.33 mN/Tex for batch 1 and from 0.28 ± 0.03 mN/Tex to 1.1 ± 0.33 mN/Tex for batch 2). Despite the extraction of cell content in both batches, an increment on the maximal strength was observed. In this case twist applied to the fibres, could increase the friction between fibres and consequently modify the maximal strength.

Concerning the washed roving samples, a stronger maximal strength was observed with an increment, compared to the previous step, of about 40% (from 1.51 ± 0.33 mN/Tex to 41.58 ± 4.87 mN/Tex) for batch 1 and 46% (from 1.1 ± 0.33 mN/Tex to 50.71 ± 3.09 mN/Tex) for batch 2. A low decrease was observed on the linear densities with a slight homogenization between batches (622 ± 20 Tex for batch 1 and 611 ± 13 for batch 2). As it was observed in 2.3, an adhesion between fibres can be appreciated. The increment of adhesion and, in consequence, the strong increment on the maximal strength can be justified by the high loss of non-cellulosic components, as pectin, which form a gel and produce interactions between the cellulose of different fibres.

As concerns the twisted yarn, a homogenization on linear density and composition was observed between batches. From the previous step, a decreasing in linear densities of about 6 times for both batches was observed (from 622 ± 20 Tex to 108 ± 3 Tex for batch 1 and from 611 ± 13 to 104 ± 4 Tex for batch 2). The important increment on the mechanical properties could be attributed essentially to the twist of yarns. In this way, it is possible to see a double maximal strength for batch 2 respected to batch 1, due to the difference of torsion.

Table II - 2 Ultimate force, linear density and ultimate stress of doubled sliver, roving, washed roving and yarns

	Doubled sliver		Roving		Washed roving		Low twisted yarn	Twisted yarn
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2
Ultimate force (N)	1.06 ± 0.07	1.43 ± 0.13	1.08 ± 0.23	0.73 ± 0.22	25.88 ± 3.03	31.03 ± 1.89	23.18 ± 2.13	46.47 ± 2.99
Linear density (Tex)	5066 ± 51	4952 ± 54	719 ± 19	668 ± 9	622 ± 20	611 ± 13	108 ± 3	104 ± 4
Maximal strength (mN/Tex)	0.21 ± 0.01	0.28 ± 0.03	1.51 ± 0.33	1.1 ± 0.33	41.58 ± 4.87	50.71 ± 3.09	215.2 ± 19.8	445.2 ± 28.6

2.8. Conclusion

This study analysed the evolution of visual aspect, bio-chemical composition, moisture absorption, linear density and mechanical properties of flax fibres through different transformation steps (doubled sliver, roving, washed roving and twisted yarn) for two different batches.

The chemical composition was carried out by Van Soest method and by FT-IR analysis. The evolution of the composition showed an important extraction of cell content and hemicellulose after the fibre washing. Lipophilic extractives content (e.g. fatty acids, aldehydes, aliphatic esters, aliphatic alcohols, was determined by FT-IR analysis. A low decrease in lipophilic extractives content was observed after the fibre washing. An estimation of the lipophilic extractives content was obtained by a comparison with a pre-analysed short flax fibre by TAPPI T-264 standard.

Through the different transformation steps, a decrease in the linear density (from about 5000 to 100 Tex) and an increment on the maximal strength related to a constant linear density (0.2 - 0.3 to 200 - 450 mN/Tex) were observed. The maximal strength, related to the friction and twist between fibres in the two first transformation steps analysed, was considerably increased after washing of fibres, probably due to the extraction of a part of non-cellulosic components and to the gelification and re-solidification of some pectin components during washing that produce an adhesions of fibres. The important effect of the torsion in the maximal strength of flax yarns was detected in the last transformation step, where, a homogenization of linear density and biochemical composition was produced.

2.9. References

- [1] El-Hariri DM, Hassanein MS, El-Sweify AHH. Evaluation of Some Flax Genotypes Straw Yield, Yield Components and Technological Characters. *J Nat Fibers* 2004;1:1–12.
- [2] Norton AJ, Bennett SJ, Hughes M, Dimmock JPRE, Wright D, Newman G, et al. Determining the physical properties of flax fibre for industrial applications: the influence of agronomic practice. *Ann Appl Biol* 2006;149:15–25.

- [3] Van Soest PJ, Robertson JB, Lewis BA. Methods for Dietary Fiber, Neutral Detergent Fiber, and Nonstarch Polysaccharides in Relation to Animal Nutrition. *J Dairy Sci* 1991;74:3583–97.
- [4] Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W. *Comprehensive Cellulose Chemistry: Volume I: Fundamentals and analytical Methods*. 1998.
- [5] K. Lacasse, W. Baumann. *Textile Chemicals: Environmental Data and Facts*. Springer. 2004.
- [6] Bourmaud A, Morvan C, Baley C. Importance of fiber preparation to optimize the surface and mechanical properties of unitary flax fiber. *Ind Crops Prod* 2010;32:662–7.
- [7] Hatfield RD, Junh H-JG, Ralph J, Buxtond DR, Weimera PJ. A Comparison of the Insoluble Residues Produced by the Klason Lignin and Acid Detergent Lignin Procedures. *J Sci Food Agric* 1994;65:51–8.
- [8] Prosky L, Asp NG, Schweizer TF, DeVries JW, Furda I. Determination of insoluble, soluble, and total dietary fiber in foods and food products: interlaboratory study. *J Assoc Off Anal Chem* 1988;71:1017–23.
- [9] Selvendran RR, Verne AVF V. The Chemistry and Properties of Plant Cell Walls and Dietary Fiber. In: Kritchevsky D, Bonfield C, Anderson JW, editors. *Diet. Fiber*, Boston, MA: Springer US; 1990, p. 1–13.
- [10] Tappi T-264 cm-07. Preparation of wood for chemical analysis. 2007.
- [11] ASTM D1104-56. Method of test for holocellulose in wood 1985.
- [12] ASTM D1103-60. Method of Test for Alpha-Cellulose in Wood 1985.
- [13] ASTM D1102-84. Standard Test Method for Ash in Wood 1985.
- [14] Marques G, del Río JC, Gutiérrez A. Lipophilic extractives from several nonwoody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching. *Bioresour Technol* 2010;101:260–7.
- [15] Morvan C, Andème-Onzighi C, Girault R, Himmelsbach DS, Driouich A, Akin DE. Building flax fibres: more than one brick in the walls. *Plant Physiol Biochem* 2003;41:935–44.
- [16] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. *The handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. California: Academic Press; 1991.
- [17] John MJ, Thomas S. Biofibres and biocomposites. *Carbohydr Polym* 2008;71:343–64.

- [18] Gardner DJ, Oporto GS, Mills R, Samir MASA. Adhesion and Surface Issues in Cellulose and Nanocellulose. *J Adhes Sci Technol* 2008;22:545–67.

Chapter III:
**Role of flax cell wall components on the
microstructure and transverse mechanical
behaviour of flax fabrics reinforced epoxy
biocomposites**

3.1. Introduction

Natural fibres are an interesting alternative to synthetic fibres in technical textiles and composite 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 [1–5]. Mechanical performances of natural fibre based composites are strongly influenced by the intrinsic mechanical properties of the fibres and matrices used but also by the fibre/matrix interfacial adhesion. Among all the natural fibres, flax fibres are nowadays the most advanced natural technical fibres. They indeed present high modulus and tensile stress [6,7]. 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 oriented along the fibre axis with an angle of roughly 5 to 10° for flax fibres [8–11] and embedded in a matrix of non-cellulosic components such as hemicellulose, lignin, pectin 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 organized, thus forming a multi-component and tri-dimensional fibrillar structure [12–14]. 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 [15]. The authors observed that flax stem surfaces in the epidermal region are mainly composed of pectin and lipophilic components, such as waxes. Underneath the epidermis, the internal zone rich in bast fibres, where cellulose is predominant, showed substantial amounts of pectin and some acetylated non-cellulosic polysaccharides, whereas lignin and non-cellulosic polysaccharides are much concentrated in the inner core tissues of the stem. These observations

showed that, in the case of flax fibres, bundles cohesion 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. [16] 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 their complex composite microstructure, several kinds of interfaces should thus be considered when incorporating flax fibres in a polymer matrix: (i) the interface between the individualized 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 them by removing impurities such as waxes and proteins to obtain yarns that are further arranged to form woven or non-woven fabrics [17,18]. Coroller et al. [19] 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 composite microstructure. Bourmaud et al. [20] investigated the effect of two “soft” water-washing treatments (72 hours at 23°C and 1 hour 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 hour, 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 hours. 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. [21] treated flax slivers with NaOH solutions at 1, 2 and 3 % for 20 minutes 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. A decrease of the fibre strength was also reported after alkalisation, supporting the hypothesis that the increase in composite mechanical properties was mainly due to a significant improved of interface quality. Yan et al. [22] carried out an alkali treatment, with 5 % w/w at 20°C for 30 minutes, on flax, linen and bamboo woven fabrics to improve the mechanical properties of epoxy composites manufactured by a vacuum bagging technique. The authors found a negative effect of the alkali treatment on the tensile strength and modulus of the flax, linen and bamboo single-strand yarns extracted from the fabrics. On the other hand, an increase in 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 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 chosen. It was treated by various aqueous and organic solvents of increasing solvation capacities, so as to extract gradually cell wall components from the fibres. Untreated and treated

flax fabrics were then processed by thermocompression with a low viscosity epoxy resin to obtain UD flax / epoxy biocomposites. The treated flax fibre fabrics were characterized 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.

3.2. Material and experimental methods

3.2.1. Flax fabrics, epoxy resin and chemicals

A UD flax tow woven fabrics 218 g/m² (FRD-UD41) was provided by Fibre Recherche Développement (FRD, France). Flax tows were not washed, treated or oiled for the production of woven fabrics in order to minimize 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 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 (purity, 96 %) 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, unstabilized), 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.

3.2.2. Chemical extraction treatments on flax woven fabrics

The extraction of flax cell walls components from flax fabrics was carried out by chemical treatments with increasing solvation capacities. Flax fabrics were immersed in the solutions in a 2 L round-bottomed flask for 1 hour at boil 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 1g/Kg of flax of HEDP, 3g/Kg of flax of non-ionic and anionic surfactants (70 wt % PEG, 30 wt % LAS), 2g/Kg of flax of NaOH [17]; (e) and (f) two aqueous alkali solutions , 1 and 5 % of NaOH, at 95°C. A special device was designed to avoid damaging the 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. Flax fabrics were gently deposited on a grid within the reactor and the stirring of the solutions was ensured by a magnetic stirrer below the grid. Each treatment was followed by a first demineralised water washing at 50°C for 10 minutes, 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 a rinsing at room temperature was carried out for each treated flax fabric.

3.2.3. 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 shown in Fig. III - 1. It should be noticed that variations in the biochemical composition may occur depending on the procedure used [23–26].

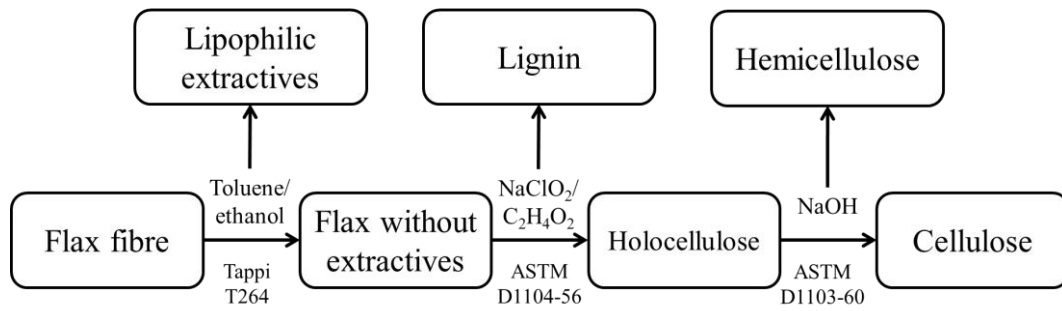


Fig. III - 1 Schema of the successive solvent extraction procedure used to analyse the biochemical composition of non-treated and treated flax fabrics

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 hours and then 6 hours with only ethanol solution. The obtained solution was evaporated with a rotary evaporator then dried in a vacuum oven at 60°C for 24h and the dry weight of lipophilic extractives was measured with an 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 hours 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 hour 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 an IR balance (Precisa XM66) at 105°C. Finally, pure α -cellulose was obtained by hemicellulose solubilization in sodium hydroxide solution and then acetic acid at 0.1M. The holocellulose sample obtained from the previous extraction step was introduced in a 250 ml beaker immersed in water at 20 ± 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 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 hour 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 neutralized cellulose. This was followed by demineralised water washing and filtering. The obtained pure cellulose sample was dried and weighed using an IR-balance (Precisa XM66) at 105 °C. Based on these weighed, 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 noticed that the procedure used 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 % [8,27–29]. As a consequence, the hemicellulose and lignin amounts were rather overestimated, and the lignin content in untreated flax fabrics was 6.2 % (see Table III - 2). As reviewed by Gorshkova et al. [30] lignin content may vary between 0.9 % and 5 % in literature, due to experimental difficulties in estimating cell wall phenolic components.

3.2.4. 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⁻¹ and 32 scans in the range 4000-400 cm⁻¹. All the spectra were normalized according to the band at 1200 cm⁻¹, assigned to OH in plane bending of anhydroglucose units in cellulose chains [12]. 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 component. Lipophilic extractives, holocellulose and cellulose were obtained from the solvent extraction procedure used for biochemical analysis (section 2.3). Lignin was obtained by the immersion of flax fabrics free of extractives for 3 hours in a solution of sulphuric acid 72 %, which was then filtered and washed with demineralised water in order to remove cellulose and hemicellulose components.

3.2.5. Dimension and density of flax yarns and fabrics

The chemical extraction treatments on flax woven fabric induce changes in their dimensions, caused by shrinkage in the warp and weft direction, and also in their areal density, caused by the loss of components and the shrinkage. Flax woven fabrics dimension 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, respectively. 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/m²) 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; weft yarns and warp yarns were cut to a length of 5x20 cm and 30x20 cm respectively. Three measurements were performed for each flax fabric sample.

3.2.6. 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 contact angle. Measurements were achieved three times for each sample.

3.2.7. Manufacturing of flax-epoxy composite plates

Untreated and treated UD flax woven fabrics were dried at 60°C for 24h in order to minimize the moisture content. 8 plies of UD flax woven fabric were 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 21h (curing 6h and post-curing 15h). The final composites thickness was adjusted at 3 ± 0.2 mm by the mean of a shim. Under the effect of pressure and temperature, the excess of resin flowed throughout the laminates.

3.2.8. Determination of fibre reinforcing rate and porosity

Discs of 25 mm diameter were cut from each UD flax-epoxy composite plates with a holesaw. The areal density (g/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 (ρ_f), epoxy resin (ρ_m) and composite plates (ρ_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 III - 1.

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

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

Based on these measurements, the fibre ($\%_{vf}$), matrix ($\%_{vm}$) and porosity ($\%_{vp}$) volume fractions were calculated using equations 1, 2 and 3 [34]:

$$\%_{0vf} = \%_{0mf} \cdot \frac{\rho_C}{\rho_f} \quad (\text{Eq.1})$$

$$\%_{0vm} = \%_{0mm} \cdot \frac{\rho_C}{\rho_m} \quad (\text{Eq.2})$$

$$\%_{0vp} = 1 - (\%_{0vf} + \%_{0vm}) \quad (\text{Eq.3})$$

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 Aphelion TM 3.2 (ADCIS) to determine both flax fibre size distribution and fibre dispersion. A multi scale analysis was performed: micrographs with a scale factor 95 (which cover the whole sample section) were used to evaluate fibre and yarn dispersion 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 binarized 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).

3.2.10. 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 N₂ as purging gas. T_g was determined from the cooling scan. Measurements were repeated twice for each sample.

3.2.11. 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 walls 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 [35,36], composite plates were cut to obtain specimens of 3 mm x 10 mm x 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 test 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.

3.3.Results and discussions

3.3.1. Influence of chemical extraction treatments on flax fabrics properties

3.3.1.1. 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 III - 2. Generally speaking, solvation capacity of the chemical extraction treatments can be ranged in three categories. The alkaline solutions, NaOH 1 % and 5 %, were the most efficient extraction treatments with 8.4 % and 10.4 % of non-cellulosic components removed from the flax woven fabrics, respectively. 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 toward hemicellulose with extraction yields of 19.7 %, 26 % and 27 %, respectively. Important amounts of hemicellulose were removed by NaOH 1 % and 5 % treatments, with high extraction yields of 36.1 % and 50.1 %, respectively. Similar conclusions can be drawn for the lignin extraction. NaOH 1 % and 5 % treatments exhibit a high solvation capacity toward lignin with extraction yields of 53.1 % and 64.6 %, respectively. Low extraction yields, not exceeding 5 %, were observed for ethanol, toluene/ethanol and water

treatments, attesting for their low solvation capacity toward 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 components. Besides, the toluene / ethanol mixture is classically used for the determination of the lipophilic extractives amounts [37]. Moderate extraction yields of 22.2 % to 25.9 % were obtained with the other treatments, 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.

Summarizing, the gradual increase of total extracts from 1.1 % to 10.4 % demonstrates that a gradient of solvation capacity of flax cell walls 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 treatments. 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)[38], 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 et al. (2002)[29] and Li et al. (2007)[39]. 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. [15], 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.

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

Treatment types		Untreated	Ethanol	Toluene / ethanol	Water	Surfactants	NaOH 1%	NaOH 5%
Total extracts (%)		-	1.1	3.8	3.8	4.7	8.4	10.4
Biochemical composition (%)	Cellulose	81.3	82.2	84.7	84.7	85.5	88.9	90.9
	Hemicellulose	11.1	11.0	9	8.3	8.2	7.4	5.8
	Lignin	6.2	6.1	6.0	5.9	5.1	2.9	2.2
	Lipophilic extractives	1.5	0.7	0.3	1.1	1.2	0.8	1.1
Extraction yield (%)	Hemicellulose	-	1.8	19.7	26.0	27.0	36.1	50.1
	Lignin	-	2.7	4.6	5.1	17.4	53.1	64.6
	Lipophilic extractives	-	50.5	77.1	25.9	22.2	47.7	22.9

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. III - 2, several vibration bands are common to each non-cellulosic component. However, the intense and narrow bands at 2915 and 2848 cm^{-1} , characteristic of asymmetric and symmetric CH_2 stretching vibrations [40], respectively, are mainly found in lipophilic extractives rich in aliphatic chains. The broad and intense vibration band around 1735 cm^{-1} , related to saturated aliphatic and aromatic esters $\text{C}=\text{O}$ stretching vibrations [40], is primarily found for lignin, although being also observed for lipophilic extractives due to the presence of ester waxes within flax fibres [16]. Besides, the weak band at 1510 cm^{-1} , corresponding to ester $\text{C}=\text{O}$ in aromatic compounds [40], 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.

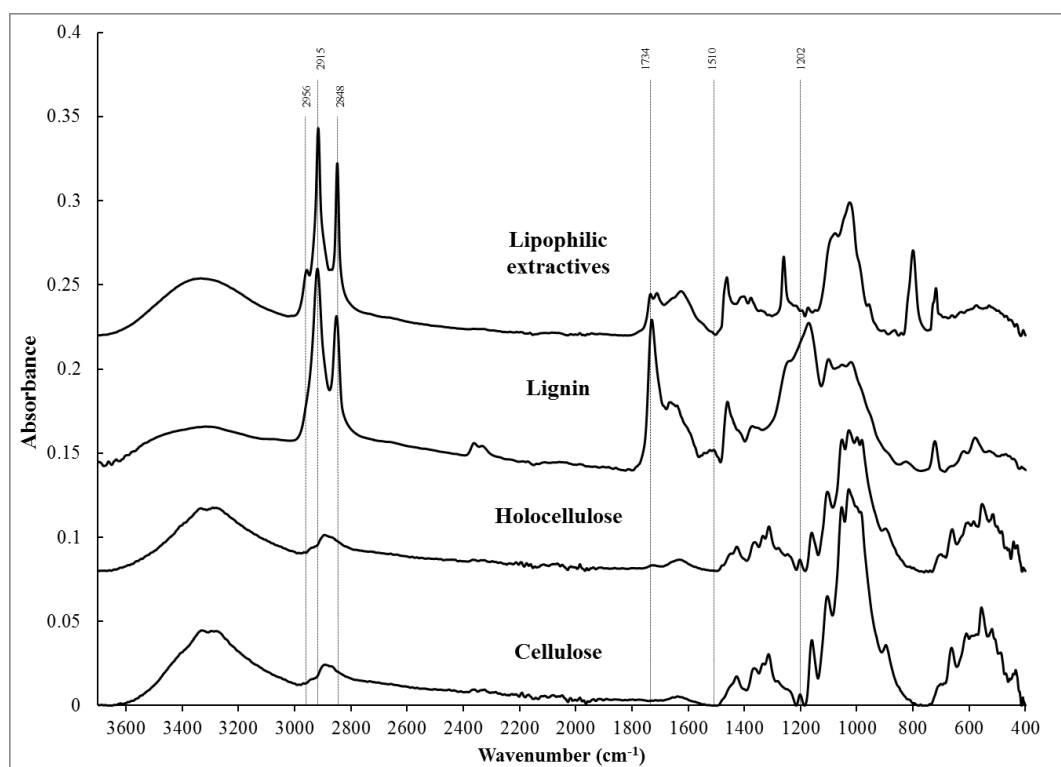


Fig. III - 2 FT-IR spectra of lipophilic extractives, lignin, holocellulose and cellulose and characteristic vibration bands for lipophilic extractives and lignin

Fig. III - 3 shows the FT-IR intensity ratios normalized by the band at 1202 cm^{-1} of untreated and treated flax fibre woven fabrics. A significant reduction in the intensity ratios for peaks located at 2915 and 2848 cm^{-1} (asymmetric and symmetric CH_2 stretching) is observed for ethanol and toluene/ethanol treated flax fabrics, and in a lesser extent after NaOH treatments. 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 toluene/ethanol extraction treatments were indeed found to be highly selective towards lipophilic extractives. The band located at 1735 cm^{-1} and corresponding to ester $\text{C}=\text{O}$ stretching, has almost disappeared after NaOH 1 and 5 % treatments, giving very low intensity ratios. This is in agreement with the biochemical analysis, which revealed a significant removal of lignin components from flax fabrics with NaOH treatments. Other treatments result in limited changes regarding the peak at 1735 cm^{-1} , thus suggesting that low amounts of lignin were removed.

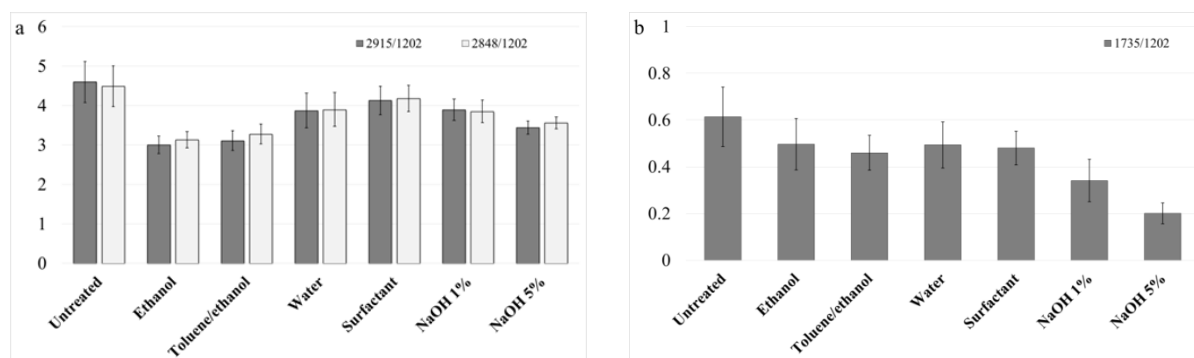


Fig. III - 3 FT-IR intensity ratios of (a) 2915 cm⁻¹ and 1202 cm⁻¹ bands and 2848 cm⁻¹ and 1202 cm⁻¹ bands (lipophilic extractives) and (b) 1735 and 1202 cm⁻¹ bands (lignin) as a function of the chemical treatments used

To conclude, 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 identifying quickly and efficiently the selective 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 treatments 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 within 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 within epoxy based biocomposites.

3.3.1.2. 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. III - 4, the initial water contact angle for untreated flax fibre fabrics is about 117.7° . The water droplet is stable until 10 seconds 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 enhances in turn 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 10.4 % of the total biomass for NaOH 5 % treatment (Table III - 2). This leads to a hydrophilic/hydrophobic balance which goes in the sense of an increased hydrophilicity in the case of NaOH 1 % and an increased hydrophobicity in the case of NaOH 5 %, i.e. lower and higher contact angles over time, respectively.

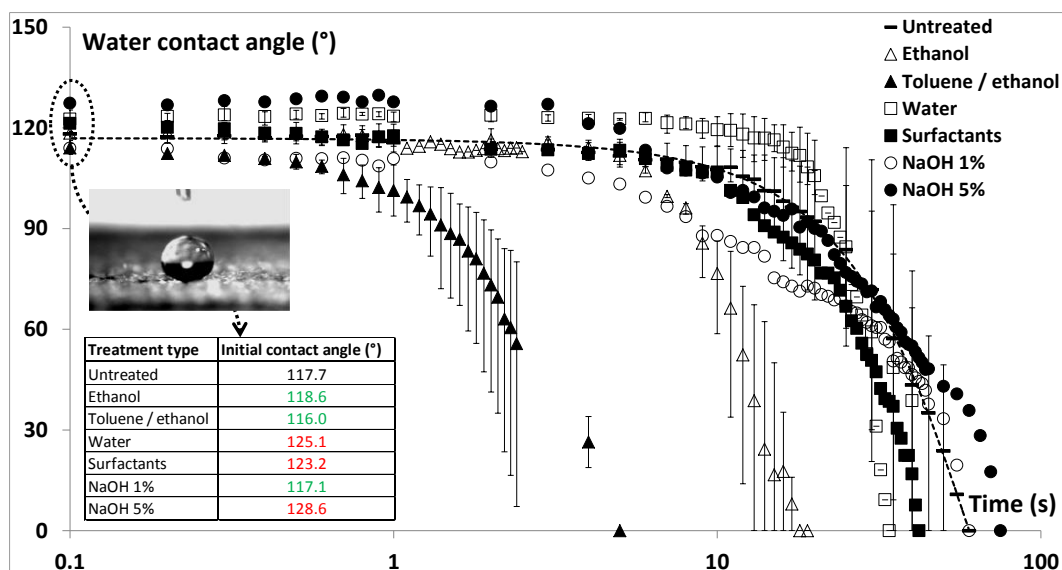


Fig. III - 4 Water contact angle kinetics for untreated (dashed line) and treated (open and closed symbols) flax fibre fabrics as a function of the chemical extraction treatments used

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 treatments, together with large amounts of hemicellulose and 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 an influence on the water contact angle measurements.

3.3.1.3. 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 III - 2), that is counterbalanced by a pronounced shrinkage effect, which modified their overall areal density. The dry linear density of 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 III - 3. Shrinkage consecutive 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. It results in an increase of the overall areal density of flax fabrics.

This increase was particularly significant for the toluene/ethanol treated fabrics (246.1 ± 3.7 g/m² versus 217.6 ± 5.6 g/m² for untreated fabrics), for which the extraction of non-cellulosic components was limited (3.8 %), and mostly involved lipophilic extractives and weakly bounded hemicelluloses. It seems like the removal of these components favoured the shrinkage of the fabrics, and hence hydrogen bonding between flax fibres within the yarns. Linear and insertion densities for both warp and weft 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/m² versus 217 ± 5.6 g/m² for untreated fabrics). In the case of surfactants and NaOH treatments, 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 10.4 % for NaOH 5 % 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 a slight decrease of the areal density was measured for this treated fabrics. So the removal of lipophilic extractives does not seem 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 hemicelluloses 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. On the other hand, 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.

Table III - 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		Insertion density		Relative amount of flax yarns		Dry areal density of flax fabrics (g/m ²)
	Warp (Tex)	Weft (Tex)	Warp (Tex)	Weft (Tex)	Warp (Tex)	Weft (Tex)	
Untreated	25.2 ± 0.8	88.8 ± 5.8	12.8	19	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	21	16.0	84.0	246.1 ± 3.7
Water	28.1 ± 1.4	100.1 ± 1.4	13.4	20	15.8	84.2	233.6 ± 2.2
Surfactants	27.9 ± 0.6	84.0 ± 5.0	13.2	20	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
NaOH 5 %	26.5 ± 0.5	83.7 ± 1.2	13.6	20.1	17.7	82.4	221.9 ± 1.2

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

Fig. III - 5 presents transverse cross sections of non-treated and treated flax fabrics reinforced composites at low magnification (~85x). 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. III - 5a). It is observed that for non-treated flax fabrics (Fig. III - 5a), yarns are easily identified and individualized 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 in comparison with the high dispersion observed for surfactants and NaOH treated fabrics, water treated fabrics being an intermediate case. As postulated above, these results support a prior decohesion of the yarns consecutive to high extraction yield treatments. This decohesion favours the dispersion of flax fibres and the diffusion of epoxy resin within the yarns between the elementary fibres during the thermocompression process to such an extent that it is no longer possible to visualize individual yarns in the case of NaOH treated fabrics (Fig. III - 5f and g).

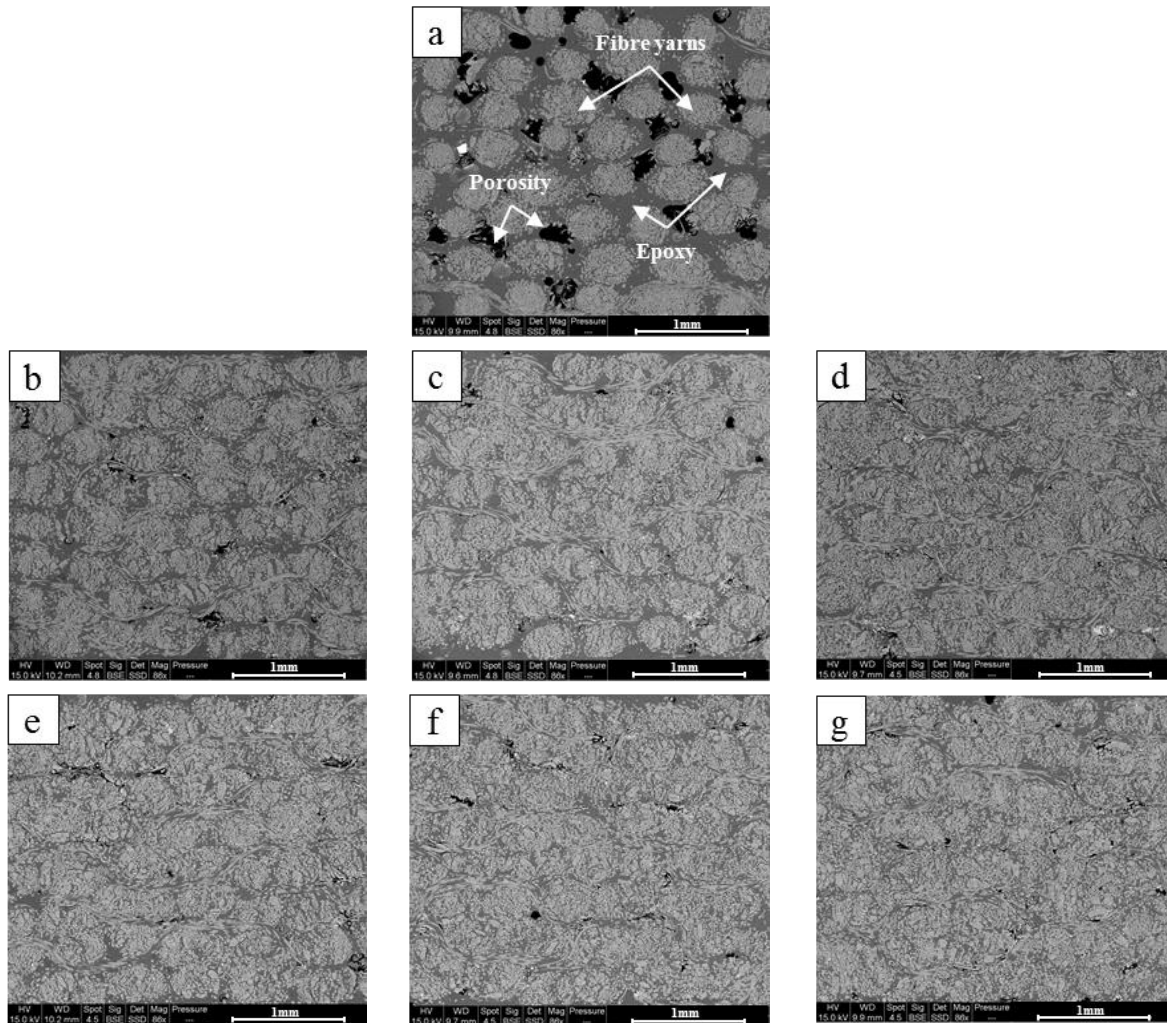


Fig. III - 5 SEM micrographs (85x) of transverse cross section of flax fabrics reinforced composites for the different treatments: (a) untreated, (b) ethanol, (c) toluene/ethanol, (d) water, (e) surfactants, (f) NaOH 1 %, (g) NaOH 5 %

To corroborate these qualitative observations, image analysis was performed on SEM micrographs, and the grey scale profiles were plotted across the section. Fig. III - 6a clearly shows that non-treated flax fabrics reinforced composites exhibit a periodic profile (average signal period 157 pixels, Fig. III - 6b) 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 individualized 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 the table of Fig. III - 6c). These results attest for the highest dispersion of flax yarns within the epoxy matrix. In the case of flax fabrics reinforced composites with NaOH 5 % treatment the periodic structure is

no longer observable since individual fibres are well dispersed in the 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 (see Fig. III - 6c). This supports that the chemical extractions achieved on flax fabrics are primarily responsible for the dispersion of the yarns in the epoxy resin during the thermocompression process.

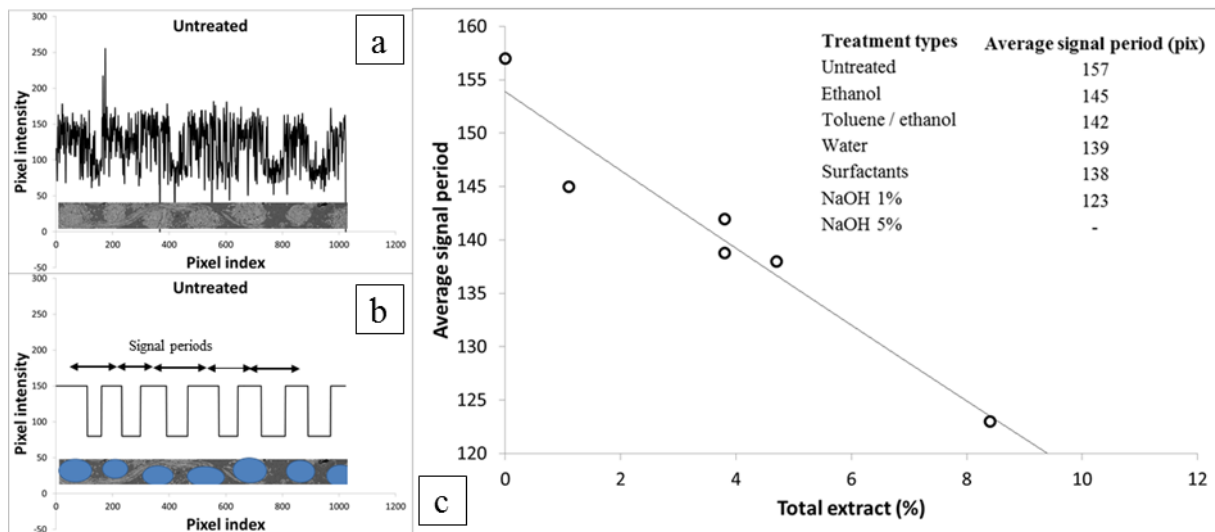


Fig. III - 6 Grey scale profile across the sections of flax fabrics reinforced composites for: (a) raw data, (b) normalized signal for untreated fabrics. Flax fibres correspond to pixel intensity of about 150 and epoxy resin corresponds to pixel intensity of about 8

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 decohesion, at the micrometric scale, of flax fibres bundles in elementary flax fibres (Fig. III - 7a). As discussed previously, the chemical extraction treatments applied on flax fabrics indeed involved the removal of several non-cellulosic components such as hemicelluloses 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 thermocompression process (Fig. III - 7b). When treated in toluene / ethanol (Fig. III - 7c) and NaOH 5 % (Fig. III - 7d), flax yarns exhibit a more dispersed

microstructure with higher proportions of elementary fibres and higher fractions of epoxy resin within the yarns.

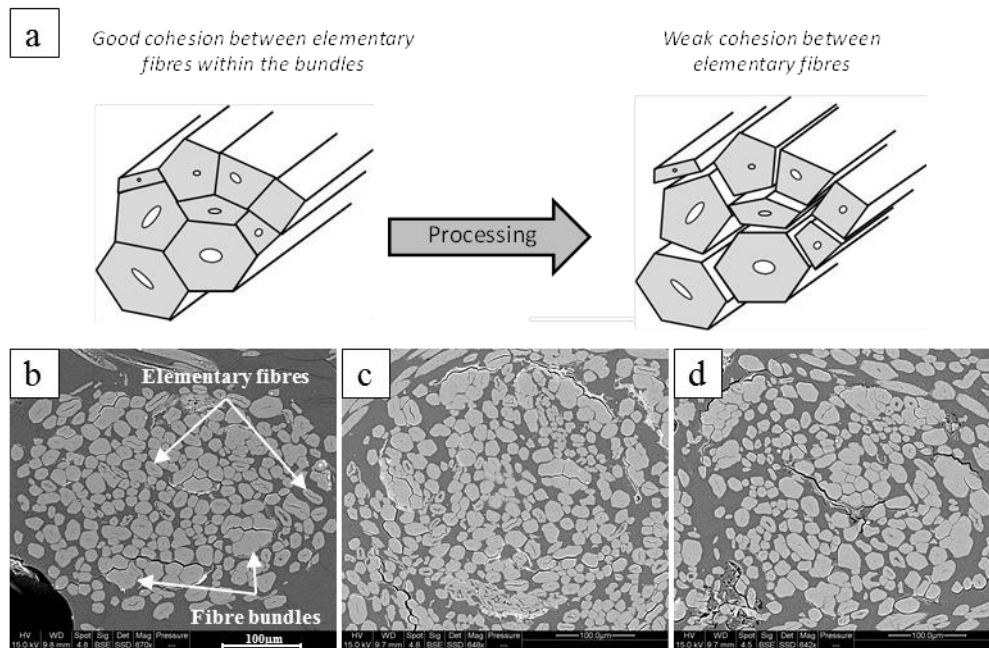


Fig. III - 7 Illustration of the dispersion states of fibre bundles within the epoxy matrix before and after the treatment and thermocompression processes; and SEM micrographs (670x) of flax yarns in transverse cross sections of flax fabrics reinforced composite

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. III - 8). 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 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 the ethanol, toluene/ethanol, water and NaOH 1 % treatments, and 39 % and 41 % for the surfactants and NaOH 5 % treatments, respectively. 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 of elementary fibres.

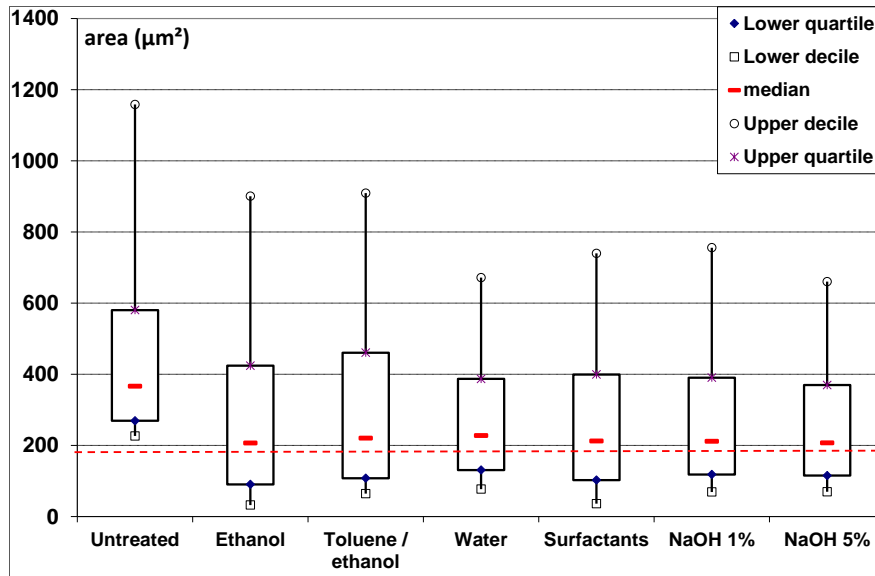


Fig. III - 8 Box plots of area distributions number weighted of flax objects within the yarns for untreated and treated flax fabrics reinforced composites. The dashed line stands for the typical section area of an elementary fibre

Concluding, 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 thermocompression process. According to the solvation capacity of the treatments towards flax cell walls 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 destroyed by the treatments and replaced by the formation of a greater interface between elementary fibres and epoxy matrix.

3.3.2.1. 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 influences greatly the mechanical performances of composites. As observed in Fig. III - 5 and Fig. III - 7, 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 [41]. 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. III - 9, the fibre volume fraction for untreated flax fabrics reinforced composite was around 45 %, and increased fibre rates 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 modify significantly the permeability of flax fabrics. It was observed that more resin has flowed throughout the laminates during the thermocompression process for treated flax fabrics. Besides, SEM micrographs in Fig. III - 7 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 III - 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. III - 5, the cross section of untreated flax fabrics reinforced composite show several black areas corresponding to macro-porosity, mostly localized between the yarns in rich-epoxy zones. It is well known that porosity is a weak spot in composites that originates from a bad impregnation of the resin within the fabrics during processing. Porosity found in natural fibres reinforced thermoset resins can be classify in four types from micro- to macro-porosity [42]: (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. III - 5 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. III - 9.

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 and exposes the surface hydroxyl groups (Fig. III - 4), appears to be efficient enough to improve the matrix impregnation and enhance the fibre dispersion and reinforcing rate, while reducing significantly the porosity. Improved fibres/matrix interactions through the esterification reaction between hydroxyl 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, fibre reinforcing rates and porosity being rather similar. Besides, it should be pointed out that at higher magnification, the micro-porosities originating from intrinsic fibre porosity and poor fibre / matrix interface are still observable on SEM micrographs in Fig. III - 7, whatever the treatment used.

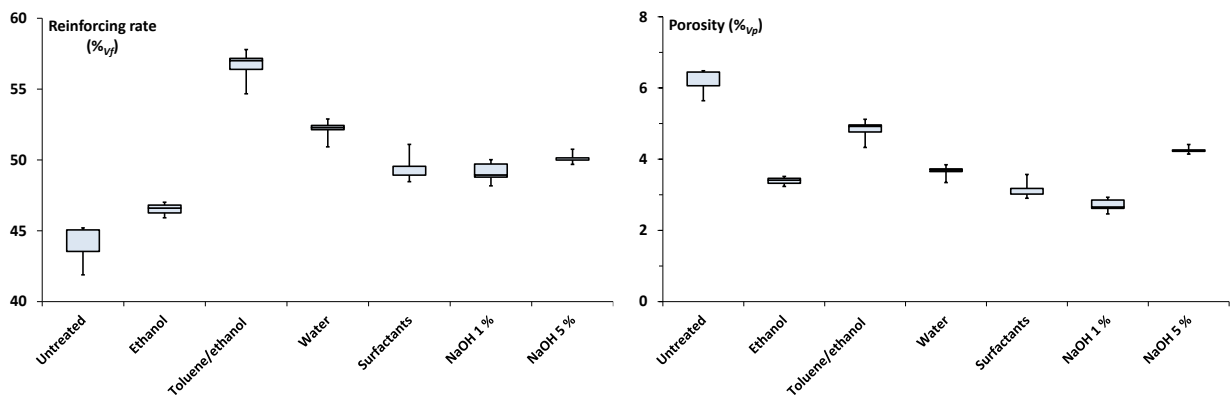


Fig. III - 9 Fibre reinforcing rates and porosity rates for untreated and treated flax fabrics reinforced composites as a function of the chemical extraction treatments used

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

Coroller et al. [19] 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 individualized elementary fibres (93 %) whereas Marilyn and Andrea flax fibres showed higher amounts of fibre bundles with fraction of individualized elementary fibres of 69 % and 74 %, respectively. This was explained by the hackling 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 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 enhance significantly the strength at break 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 [43] and their potential chemical interactions with epoxy.

3.3.3.1. 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 (even at a low level of applied strain), 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 individualized elementary fibres and epoxy matrix, and in between the elementary fibres within the fibre bundles. Benzarti et al. [44] 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 high 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. III - 10 for untreated and treated flax fabrics reinforced composites. Epoxy resin exhibits a brittle behaviour with a slightly marked deformation. In contrast, a large non-linear domain 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 lowered significantly the modulus, offset yield point ($R_{p0.2\%}$) and stress at break of the composites, the plastic deformation domain being slightly expanded.

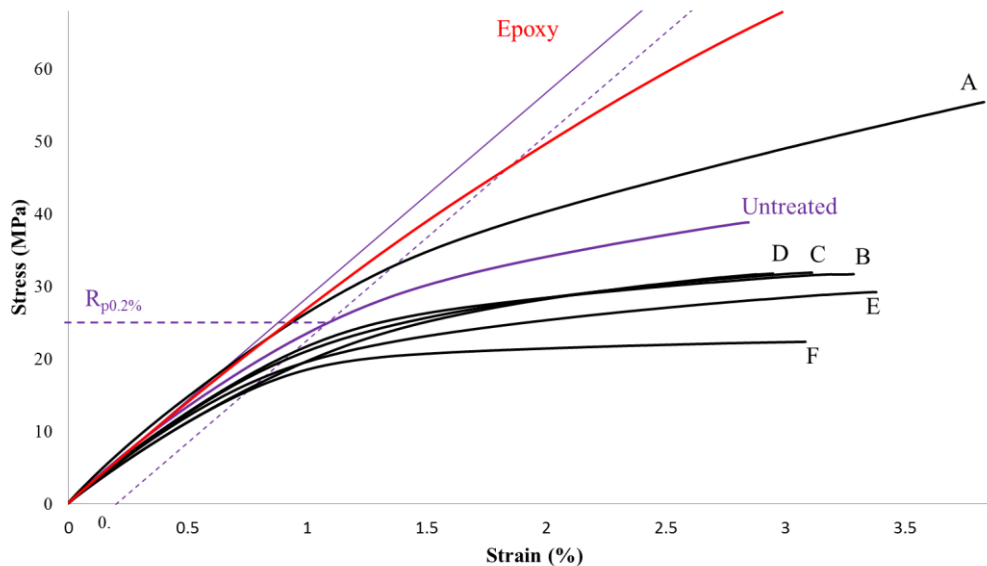


Fig. III - 10 Median strain/stress curves of transverse tensile tests for untreated and treated flax fabrics reinforced composites(A) Ethanol; (B) Toluene/ethanol; (C) Water; (D) Surfactants; (E) NaOH 1 % ; and (F) NaOH 5 %

Transverse mechanical properties of untreated and treated flax fabrics reinforced composites are given in Table III - 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 ± 2.7 MPa to 22.7 ± 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 ± 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 III - 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 the chemical treatments. Indeed, Yan et al. [22] 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 III - 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.

Table III - 4 Transverse mechanical properties of untreated and treated flax fabrics reinforced epoxy composites

Type of fibre treatment	Epoxy	Untreated	Ethanol	Toluene / ethanol	Water	Surfactants	NaOH 1%	NaOH 5%
Reinforcing rate (Vol. %)	-	44.2 ± 1.4	46.5 ± 0.5	56.6 ± 1.0	52.1 ± 0.6	49.5 ± 0.9	49.1 ± 0.6	50.1 ± 0.3
Warp reinforcing rate (Vol. %)	-	7.1	7.4	9.1	8.3	8.9	7.6	8.9
Weft reinforcing rate (Vol. %)	-	37.1	39.1	47.6	43.9	40.6	41.5	41.3
Porosity rate (Vol. %)	-	6.2 ± 0.3	3.4 ± 0.1	4.8 ± 0.3	3.7 ± 0.2	3.2 ± 0.2	2.7 ± 0.2	4.3 ± 0.1
T_g (°C)	91.7 ± 3.4	86.6 ± 1.4	94.8 ± 0.5	85.3 ± 1.8	83.6 ± 3.1	98.5 ± 4.1	82.7 ± 1.4	87.2 ± 2.9
Transverse Young modulus (MPa)	3135 ± 58	4642 ± 96	5037 ± 303	4027 ± 92	4309 ± 39	3810 ± 225	3973 ± 90	3907 ± 132
Offset yield point Rp_{0.2%} (MPa)	-	24.7 ± 0.8	29.9 ± 0.6	22 ± 0.3	20.9 ± 0.5	20.6 ± 0.9	19.3 ± 0.9	19.2 ± 1
Ultimate stress (MPa)	64.2 ± 4.0	38.8 ± 2.7	54.8 ± 1.8	31.0 ± 1.4	31.3 ± 1.4	31.2 ± 0.7	28.8 ± 0.9	22.7 ± 1.7
Ultimate strain (%)	2.7 ± 0.3	2.9 ± 0.2	3.8 ± 0.2	3.3 ± 0.2	3.0 ± 0.4	3.0 ± 0.6	3.2 ± 0.2	2.5 ± 0.3

As many parameters involved in the composite microstructure are varying (porosity, reinforcement rate, epoxy curing, fibre dispersion and intrinsic properties), thin Laminate Plate Theory (LPT) [45] 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. First of all, laminates are supposed to be an array of individual 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 III - 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 ν_{lt} , shear modulus G_{lt}) and the epoxy matrix was assumed to have isotropic elastic properties: elastic modulus $E = 3135$ MPa, Poisson's ratio

$\nu = 0.35$ [46]. 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 [47], assuming spherical shape macroporosities localized only within the matrix. Based on these assumptions, thin laminate plate theory [45] 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: $E_l / E_t = 7$ [48]. The resulting elastic longitudinal properties are summarized in Table III - 5 as a function of flax fabrics treatments. The estimated longitudinal modulus of flax fibres for untreated fabrics was 49.7 GPa, which is close to values found in literature for elementary flax tow fibres [49]. The results clearly show that chemical treatments deteriorate fibres elastic properties, with longitudinal and transverse Young moduli decreasing up to 26.3 GPa and 3.7 GPa, respectively, for surfactants treatments. In contrast, the ethanol treatment did not affect the longitudinal and transverse Young moduli up to 52.9 GPa and 7.5 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 transverse elastic response of fibres and bundles. For instance, Lefeuvre et al. (2015)[50] 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. Indeed, 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 cannot 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 ± 1.8 MPa, for the ethanol treated flax fabrics reinforced composite, while other treatments 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 induce a degradation of the fibres and strongly affect the transverse mechanical response of composites. Besides, it should be pointed out that the variations of a few degrees of the glass transition 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.

Table III - 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
NaOH 5 %	28.6±2.0	4.1±0.3

3.3.3.2. Fracture surface

Fig. III - 11 show transverse fracture surfaces observed by SEM of untreated and treated flax fabrics reinforced composites. Due to high reinforcing rates, 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 prints 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 ± 4.0 MPa versus 54.8 ± 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 NaOH 1 % and 5 %, seemed to produce a more pronounced decohesion of the elementary fibres within the yarns, which is related to the removal of interfibrillar components (pectic cements) and the weakening of the interface between the elementary fibres within the fibre bundles.

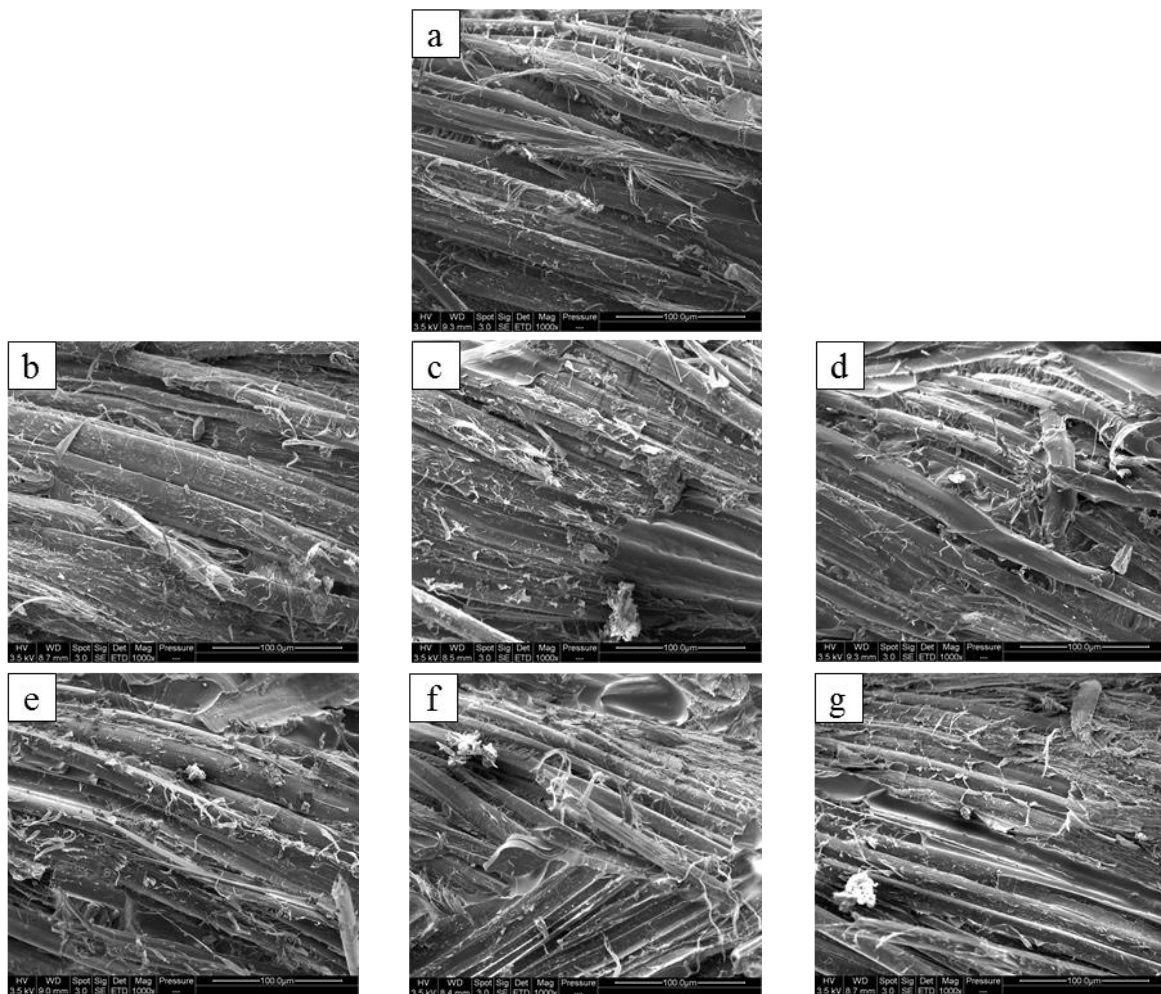


Fig. III - 11 SEM transverse fracture surfaces for flax fabrics reinforced composites according to the chemical treatments used : (a) untreated, (b) ethanol, (c) toluene/ethanol, (d) water, (e) surfactants, (f) NaOH 1% and (g) NaOH 5%

3.4. 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 the 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 treatments. Ethanol, toluene/ethanol and water treatments led to a softer extraction, mainly of lipophilic extractives and hemicelluloses. 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 turns the hydrophobic character of flax fabrics. As concerns NaOH treatments, large quantities of hydrophilic and hydrophobic components were removed leading to a hydrophilic/hydrophobic balance, with an increased hydrophilicity in the case of NaOH 1% and an increased hydrophobicity in the case of NaOH 5%. 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 hemicelluloses 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 treatments 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 thermocompression process. Moreover, the numerous interfibrillar interactions existing within the bundles were partially destroyed 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 improves the transverse mechanical strength of the composite, possibly 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 response of composites.

These results show that non-cellulosic components of flax fabrics 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.

3.5. References

- [1] J.R. Dufloy, D. Yelin, K. Van Acker, W. Dewulf, Comparative impact assessment for flax fibre versus conventional glass fibre reinforced composites: Are bio-based reinforcement materials the way to go?, *CIRP Ann. - Manuf. Technol.* 63 (2014) 45–48. doi:10.1016/j.cirp.2014.03.061.
- [2] S. V. Joshi, L.T. Drzal, a. K. Mohanty, S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites?, *Compos. Part A Appl. Sci. Manuf.* 35 (2004) 371–376. doi:10.1016/j.compositesa.2003.09.016.
- [3] N.P.J. Dissanayake, J. Summerscales, S.M. Grove, M.M. Singh, Life Cycle Impact Assessment of Flax Fibre for the Reinforcement of Composites, *J. Biobased Mater. Bioenergy.* 3 (2009) 245–248. doi:10.1166/jbmb.2009.1029.
- [4] A. Le Duigou, P. Davies, C. Baley, Replacement of Glass/Unsaturated Polyester Composites by Flax/PLLA Biocomposites: Is It Justified?, *J. Biobased Mater. Bioenergy.* 5 (2011) 466–482. doi:10.1166/jbmb.2011.1178.

- [5] A. Le Duigou, P. Davies, C. Baley, Environmental Impact Analysis of the Production of Flax Fibres to be Used as Composite Material Reinforcement, *J. Biobased Mater. Bioenergy*. 5 (2011) 153–165. doi:10.1166/jbmb.2011.1116.
- [6] C. Baley, Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase, *Compos. - Part A Appl. Sci. Manuf.* 33 (2002) 939–948. doi:10.1016/S1359-835X(02)00040-4.
- [7] O. Faruk, A.K. Bledzki, H.-P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000–2010, *Prog. Polym. Sci.* 37 (2012) 1552–1596. doi:10.1016/j.progpolymsci.2012.04.003.
- [8] A.K. Bledzki, S. Reihmane, J. Gassan, Properties and modification methods for vegetable fibers for natural fiber composites, *J. Appl. Polym. Sci.* 59 (1996) 1329–1336. doi:10.1002/(SICI)1097-4628(19960222)59:8<1329::AID-APP17>3.0.CO;2-0.
- [9] A. Bledzki, J. Gassan, Composites reinforced with cellulose based fibres, *Prog. Polym. Sci.* 24 (1999) 221–274. <http://www.sciencedirect.com/science/article/pii/S0079670098000185> (accessed November 29, 2012).
- [10] D.B. Dittenber, H.V.S. Gangarao, Critical review of recent publications on use of natural composites in infrastructure, *Compos. Part A Appl. Sci. Manuf.* 43 (2012) 1419–1429. doi:10.1016/j.compositesa.2011.11.019.
- [11] a. K. Mohanty, M. Misra, G. Hinrichsen, Biofibres, biodegradable polymers and biocomposites: An overview, *Macromol. Mater. Eng.* 276-277 (2000) 1–24. doi:10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W.
- [12] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, *Comprehensive Cellulose Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 1998. doi:10.1002/3527601929.
- [13] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Cellulose: Fascinating Biopolymer and Sustainable Raw Material, *Angew. Chemie Int. Ed.* 44 (2005) 3358–3393. doi:10.1002/anie.200460587.
- [14] H.A. Krässig, *Cellulose - Structure, Accessibility and Reactivity*. Polymer Monographs Vol 11, Gordon and Breach Science Publishers, Amsterdam, 1993.
- [15] C. Morvan, C. Andème-Onzighi, R. Girault, D.S. Himmelsbach, A. Driouich, D.E. Akin, Building flax fibres: more than one brick in the walls, *Plant Physiol. Biochem.* 41 (2003) 935–944. doi:10.1016/j.plaphy.2003.07.001.

- [16] G. Marques, J.C. del Río, A. Gutiérrez, Lipophilic extractives from several nonwoody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching., *Bioresour. Technol.* 101 (2010) 260–7. doi:10.1016/j.biortech.2009.08.036.
- [17] K. Lacasse, W. Baumann, *Textile Chemicals: Environmental Data and Facts*, Springer, 2004.
- [18] J. Müssig, M. Hughes, Reinforcements: fibres, in: *Flax Hemp Fibres a Nat. Solut. Compos. Ind.*, JEC Composites, Paris, 2012: pp. 39–60.
- [19] G. Coroller, A. Lefeuvre, A. Le Duigou, A. Bourmaud, G. Ausias, T. Gaudry, et al., Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional composite, *Compos. Part A Appl. Sci. Manuf.* 51 (2013) 62–70. doi:10.1016/j.compositesa.2013.03.018.
- [20] A. Bourmaud, C. Morvan, C. Baley, Importance of fiber preparation to optimize the surface and mechanical properties of unitary flax fiber, *Ind. Crops Prod.* 32 (2010) 662–667. doi:10.1016/j.indcrop.2010.08.002.
- [21] I. Van de Weyenberg, T. Chi Truong, B. Vangrimde, I. Verpoest, Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment, *Compos. Part A Appl. Sci. Manuf.* 37 (2006) 1368–1376. doi:10.1016/j.compositesa.2005.08.016.
- [22] L. Yan, N. Chouw, X. Yuan, Improving the mechanical properties of natural fibre fabric reinforced epoxy composites by alkali treatment, *J. Reinf. Plast. Compos.* 31 (2012) 425–437. doi:10.1177/0731684412439494.
- [23] P.J. Van Soest, J.B. Robertson, B.A. Lewis, Methods for Dietary Fiber, Neutral Detergent Fiber, and Nonstarch Polysaccharides in Relation to Animal Nutrition, *J. Dairy Sci.* 74 (1991) 3583–3597. doi:10.3168/jds.S0022-0302(91)78551-2.
- [24] L. Prosky, N.G. Asp, T.F. Schweizer, J.W. DeVries, I. Furda, Determination of insoluble, soluble, and total dietary fiber in foods and food products: interlaboratory study., *J. Assoc. Off. Anal. Chem.* 71 (1988) 1017–23. <http://europepmc.org/abstract/med/2853153> (accessed August 13, 2015).
- [25] R.R. Selvendran, A.V.F. V. Verne, The Chemistry and Properties of Plant Cell Walls and Dietary Fiber, in: D. Kritchevsky, C. Bonfield, J.W. Anderson (Eds.), *Diet. Fiber*, Springer US, Boston, MA, 1990: pp. 1–13. doi:10.1007/978-1-4613-0519-4.
- [26] R.D. Hatfield, H.-J.G. Junh, J. Ralph, D.R. Buxtond, P.J. Weimera, A Comparison of the Insoluble Residues Produced by the Klason Lignin and Acid Detergent Lignin Procedures, *J. Sci. Food Agric.* 65 (1994) 51–58. <http://naldc.nal.usda.gov/naldc/catalog.xhtml?id=26422> (accessed October 18, 2015).

- [27] I.M. De Rosa, C. Santulli, F. Sarasini, Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated Phormium tenax leaf fibers, *Mater. Des.* 31 (2010) 2397–2405. doi:10.1016/j.matdes.2009.11.059.
- [28] Wang Yueping, Wang Ge, Cheng Haitao, Tian Genlin, Liu Zheng, Xiao Qun Feng, et al., Structures of Bamboo Fiber for Textiles, *Text. Res. J.* 80 (2010) 334–343. doi:10.1177/0040517509337633.
- [29] L.Y. Mwaikambo, M.P. Ansell, Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization, *J. Appl. Polym. Sci.* 84 (2002) 2222–2234. doi:10.1002/app.10460.
- [30] T. Gorshkova, V. V Salnikov, N.M. Pogodina, S.B. Chemikosova, E. V. Yablokova, A. V. Ulanov, et al., Composition and Distribution of Cell Wall Phenolic Compounds in Flax (*Linum usitatissimum* L.) Stem Tissues, *Ann. Bot.* 85 (2000) 477–486. doi:10.1006/anbo.1999.1091.
- [31] X. Li, L.G. Tabil, S. Panigrahi, Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review, *J. Polym. Environ.* 15 (2007) 25–33. doi:10.1007/s10924-006-0042-3.
- [32] B. Vanleeuw, V. Carvelli, M. Barburski, S.V. Lomov, A.W. van Vuure, Quasi-unidirectional flax composite reinforcement: Deformability and complex shape forming, *Compos. Sci. Technol.* 110 (2015) 76–86. doi:10.1016/j.compscitech.2015.01.024.
- [33] M.J.A. Van Den Oever, H.L. Bos, M.J.J.M. Van Kemenade, Influence of the Physical Structure of Flax Fibres on the Mechanical Properties of Flax Fibre Reinforced Polypropylene Composites, *Appl. Compos. Mater.* 7 (2000) 387–402. doi:10.1023/A:1026594324947.
- [34] D. Gay, *Matériaux composites*, 1997.
- [35] AFNOR NF EN 2747, Série aérospatiale - Plastiques renforcés au verre textile - Essai de traction, (1998).
- [36] N. Le Moigne, M. Longerey, J.-M. Taulemesse, J.-C. Bénézet, A. Bergeret, Study of the interface in natural fibres reinforced poly(lactic acid) biocomposites modified by optimized organosilane treatments, *Ind. Crops Prod.* 52 (2014) 481–494. doi:10.1016/j.indcrop.2013.11.022.
- [37] Tappi T-264 cm-07, Preparation of wood for chemical analysis, 2007.
- [38] O. Theander, Chemical analysis of lignocellulose materials, *Anim. Feed Sci. Technol.* 32 (1991) 35–44. doi:10.1016/0377-8401(91)90007-F.

- [39] X. Li, L.G. Tabil, S. Panigrahi, Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review, *J. Polym. Environ.* 15 (2007) 25–33. doi:10.1007/s10924-006-0042-3.
- [40] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, California, 1991.
- [41] G. Ziegmann, A. Elsabbagh, Production techniques for natural fibre polymer composite, in: *Flax Hemp Fibres a Nat. Solut. Compos. Ind.*, JEC Composites, Paris, 2012: pp. 99 – 118.
- [42] B. Madsen, A. Thygesen, H. Lilholt, Plant fibre composites - porosity and volumetric interaction, *Compos. Sci. Technol.* 67 (2007) 1584–1600. doi:10.1016/j.compscitech.2006.07.009.
- [43] A. le Duigou, A. Bourmaud, E. Balnois, P. Davies, C. Baley, Improving the interfacial properties between flax fibres and PLLA by a water fibre treatment and drying cycle, *Ind. Crops Prod.* 39 (2012) 31–39. doi:10.1016/j.indcrop.2012.02.001.
- [44] K. Benzarti, L. Cangemi, F. Dal Maso, Transverse properties of unidirectional glass/epoxy composites: Influence of fibre surface treatments, *Compos. Part A Appl. Sci. Manuf.* 32 (2001) 197–206. doi:10.1016/S1359-835X(00)00136-6.
- [45] J.N. Reddy, *Mechanics of Laminated Composite Plates and Shells: Theory and Analysis*, Second Edi, CRC Press, 2003.
- [46] V. Joudon, G. Portemont, F. Lauro, B. Bennani, Experimental procedure to characterize the mode I dynamic fracture toughness of advanced epoxy resins, *Eng. Fract. Mech.* 126 (2014) 166–177. doi:10.1016/j.engfracmech.2014.05.010.
- [47] T. Mori, K. Tanaka, Average stress in matrix and average elastic energy of materials with misfitting inclusions, *Acta Metall.* 21 (1973) 571–574. doi:10.1016/0001-6160(73)90064-3.
- [48] C. Baley, Y. Perrot, F. Busnel, H. Guezenoc, P. Davies, Transverse tensile behaviour of unidirectional plies reinforced with flax fibres, *Mater. Lett.* 60 (2006) 2984–2987. doi:10.1016/j.matlet.2006.02.028.
- [49] N. Martin, N. Mouret, P. Davies, C. Baley, Influence of the degree of retting of flax fibers on the tensile properties of single fibers and short fiber/polypropylene composites, *Ind. Crops Prod.* 49 (2013) 755–767. doi:10.1016/j.indcrop.2013.06.012.
- [50] A. Lefeuvre, A. Le Duigou, A. Bourmaud, A. Kervoelen, C. Morvan, C. Baley, Analysis of the role of the main constitutive polysaccharides in the flax fibre mechanical behaviour, *Ind. Crops Prod.* 76 (2015) 1039–1048. doi:10.1016/j.indcrop.2015.07.062.

Chapter IV:
Chemical surface modification of flax
fibres to improve the fibre/matrix
interface in flax/epoxy composites

4.1.Introduction

From an environmental perspective, the replacement of fossil reinforcing elements in composite structures by those from natural origin as plant fibres, involves a reduction of CO₂ emissions into the atmosphere during fibre manufacturing and a transformation of emitted CO₂, into O₂ by the effect of photosynthesis [1].

Nevertheless incompatibilities between the plant fibres (in this study flax fibres) and the host matrix (in this study epoxy resin) usually result in a poor adhesion between the two materials. Consequently, the mechanical properties of the composite are lowered. Therefore, plant fibres are sometimes functionalized in order to improve the fibre/matrix interface, thereby improving the mechanical properties of the composite [2–4].

Currently, up until now, fibres were generally functionalized with solutions of non-bio-based molecules, e.g. with organosilanes or, with non-ecological methods. Therefore, the main objective of this work is, as it will be presented in this chapter, the application of different functionalization molecules on flax fibres using clean methods. Non-bio-based molecules, such as an aminosilane and an epoxysilane, were used, as well as bio-based molecules such as an amino acid and a polysaccharide.

This chapter will first present the state of the art concerning the above molecules. Then specifications of each material as well as the preparation of functionalization solutions and the experimental techniques used for the different characterizations will be exposed. Finally the molecules grafting efficiency onto flax fabrics was evaluated by FT-IR and the influence of this grafting on fabrics properties (dimension, areal density), on composite microstructure (SEM, AFM) and mechanical properties (DMTA, tensile test) were studied.

4.2. State of the art on the molecules used for the chemical modification of flax fibres

Composite mechanical properties depend on fibre, matrix and interface properties. Improvement of agro-composites properties can be obtained either by plant breeding or by the use of high performances resins, a better fibre/fibre interface and improving the adhesion between the fibre and the matrix using coupling agents [5]. One of the most common coupling agents used for glass fibre manufacture is organosilanes. In the case of epoxy-based composites, aminosilane and epoxysilane are commonly used as organosilanes, due to the good chemical interactions with fibre and with matrix. In this way, two bio-based molecules with good reactional groups with the matrix (amines and epoxy) and with the fibre (acids and alcohols) were also used, i.e. an amino acid (gamma-aminobutyric acid called afterwards GABA) and a polysaccharide (chitosan). A schema of the reactional groups is shown in Fig. IV - 1

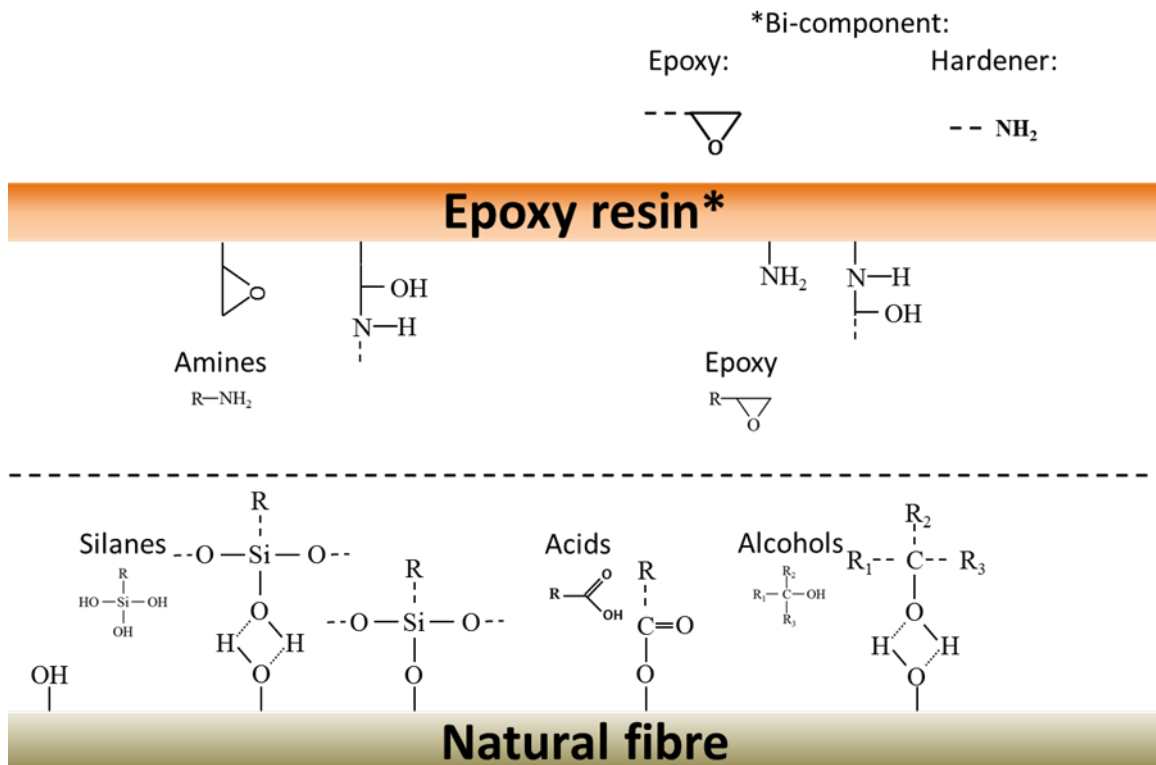


Fig. IV - 1 Schema of the reactional groups between the epoxy resin, the natural fibres and the functional groups of coupling molecules

4.2.1. Organosilanes

Organosilanes are organic compounds containing Si – C covalent bonds. It is well known, that this kind of molecules have been used in the functionalization of glass fibre and its effects have been largely investigated [6,7]. Organosilanes can also be used on the functionalization of natural fibres. Xie et al. [2] reported that different silanes can be used with natural fibres, depending on the targeted matrices. For this study, two organosilanes, commonly used in the compatibility with epoxy resins, have been selected: 3-aminopropyltriethoxysilane (called APS) (Fig. IV - 2a)) and 3-glycidoxypropyltrimethoxysilane (called GPS) (Fig. IV - 2b)),



Fig. IV - 2 3-aminopropyltriethoxysilane (APS) and b) 3-glycidoxypropyltrimethoxysilane

Functionalization of flax fibre with APS in the elaboration of epoxy based composites was previously investigated by Van de Weyenberg et al. [8]. Authors observed an improvement on transverse (in strength about 115% and in modulus about 400%) and longitudinal properties (in strength about 4% and in modulus about 45%) in three points bending test.

Other natural fibres have been also functionalised with APS [3,9,10] and GPS treatments [10,11]. An extended description of organosilane functionalized natural fibres/epoxy composites studies were described in chapter 1.

4.2.2. GABA

Gamma-aminobutyric acid (GABA) is an amino acid, which is the major inhibitory neurotransmitter in mammalian brain (about 1mg/g) [12,13]. GABA can also be found in tissues like the lymph nodes, the islets of Langerhans and in a high enough concentration in blood to activate, for example, GABA-A channels. GABA is biosynthesized by decarboxylation of the amino acid glutamate by the enzyme glutamic acid decarboxylase (GAD) (Fig. IV - 3) [13,14].

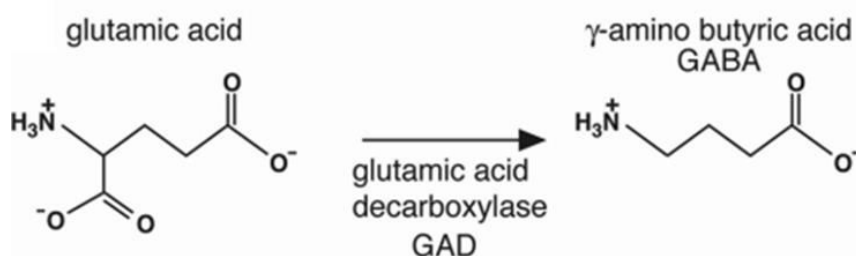


Fig. IV - 3 GABA biosynthesis from glutamate [13]

GABA molecule structure is composed of a linear chain with an amino group and a carboxylic acid group on each side of the chain. In the solid state, GABA exists as zwitterion (Fig. IV - 4b)) [15,16]. The pKa of GABA is of 4.03 [16].

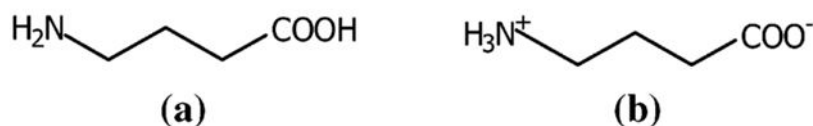


Fig. IV - 4 Schematic representation of neutral (a) and zwitterionic (b) structures of GABA [15]

Up to our knowledge, GABA has not been used before as a coupling agent to improve the fibre/matrix interface in composite systems.

However other amino acids have been used for cellulose modification. For instance, Kalaskar et al. [17] have modified cellulose with three different amino acids: Glycine (Gly), Leucine (Leu) and Phenylalanine (Phe). In this work, amino acids have been protected using fluorenylmethoxycarbonyl (Fmoc). After the reaction between cellulose OH groups and acids groups of amino acids, Fmoc were removed as described on Fig. IV - 5

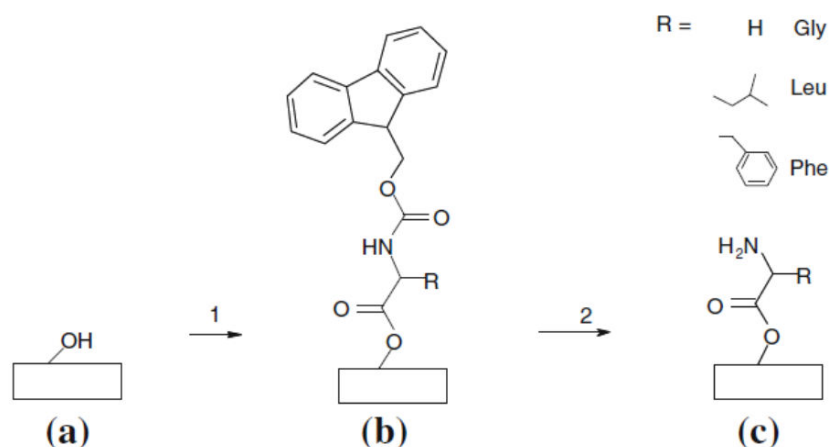


Fig. IV - 5 Chemical steps in solid-phase peptide synthesis of cellulose using amino acids. Showing unmodified cellulose (a), Fmoc-amino acid modified cellulose (b) and amino acid modified cellulose after de-protection (c) [17]

Amino acids functions were also involved in some polymer matrix in composite materials. For instance, Behera et al. [18] developed a biodegradable composite using jute fibre and soy protein modified glyoxal as matrix. Soy protein is composed of a short amino acid linkage of Phenylalanine (Phe), Valine (Val), Arginine (Arg) and Lysine (Lys). The soy resin preparation has been carried out mixing and stirring for 20 min a solution of 10 wt% glyoxal, 10 wt% glycerol and soymilk. Jute has been impregnated with the resin and dried in an oven at 60°C for 45 min. The partially dried soy resin impregnated jute has been then compressed using a hydraulic press at 125°C and at a pressure of 8 tons for 25 min to obtain composites. The potential crosslinking between soy protein and glyoxal with cellulose is represented in Fig. IV - 6.

Up to our knowledge, chitosan has not been used as a coupling agent between plant fibres and epoxy matrix.

However it has been often used as a treatment for vegetable fibres. Liu et al. [20] conducted a study on the physical properties of cotton modified with chitosan. In a first step, cotton was subjected to a cellulose oxidation treatment using $K^+IO_3^-$ (Fig. IV - 8a). The oxidation of cellulose allows the apparition of aldehyde groups on the surface (cellulose di-aldehyde). Then chitosan treatment was performed by immersing the cotton in a solution of chitosan (Fig. IV - 8b). Amine groups present in chitosan, form bonds with the aldehyde groups. The efficiency of the grafting of chitosan on the fibres was studied by fluorescence microscopy. Zhang et al. [21] have studied the improvement of the dyeing properties and softness of hemp fabrics. In this study, the authors treated tissue with a mixture of a chitosan solution and an epoxy-functionalized silicone oil. The results showed that the addition of chitosan increases the efficiency of the dye by improving the adsorption of the dye molecules on the fabric and thus reducing the non-absorbed amount lost. Bhuiyan et al. [22] used chitosan to enhance the absorption properties of jute fibres. They showed that the absorption of the dye by the chitosan treated fibre is significantly higher than in the case of the untreated fibre.

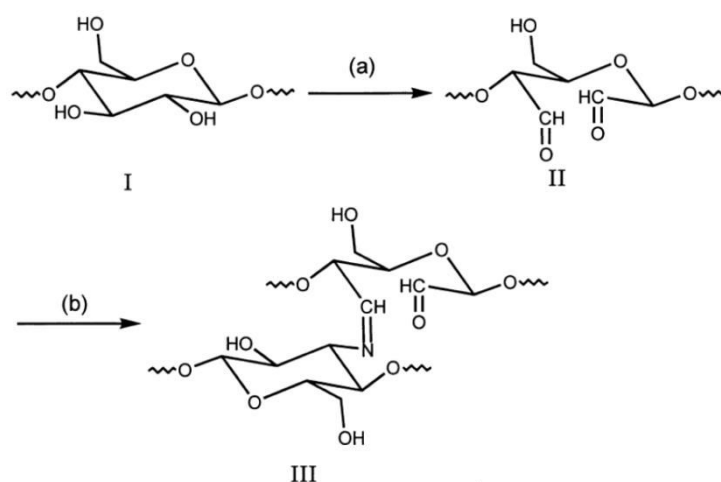


Fig. IV - 8 Schema of cellulose – chitosan reaction: a) cellulose oxidation, b) application and reaction with chitosan [20]

Nevertheless chitin and chitosan were used as coupling agents in wood-flour/PVC composites by Shah et al. [23] making the wood surface more hydrophobic. The authors

also note the presence of acid-base interactions at the wood-flour/PVC interface. Flexural properties were investigated and showed an increase of the maximum stress and the flexural modulus of the composite after the functionalization of the wood-flour with chitin and chitosan (Table IV - 1).

Table IV - 1 Flexion mechanical properties of PVC, Wood-flour/PVC and Wood-flour/PVC modified with chitin and chitosan [23]

	PVC	Wood-flour/PVC	Wood-flour + chitin 6.6%/PVC	Wood-flour + chitosan 0.5%/PVC
Ultimate strength	57 MPa	45 MPa	54 MPa	53 MPa
Young's modulus	2.2 GPa	3.2 GPa	3.7 GPa	3.5 GPa

4.3. Materials and experimental methods

After a presentation of materials used in this study, the experimental procedures carried on for the flax fabrics functionalization are exposed. Composite manufacturing conditions are then detailed. Finally all technics used for the characterization of the grafting efficiency, the physicochemical properties of yarns, fabrics and composites and the mechanical properties of composites are presented.

4.3.1. Materials

UD flax yarns woven fabric (UD19), provided by Fibre Recherche Développement (FRD, France), was used for this study. The transformation process to obtain flax yarns and woven fabrics was the standard process, including the mixing and washing of fibres.

Resoltech® 1800 epoxy resin and Resoltech® 1805 aliphatic amine hardener were purchased from Resoltech (France). Epoxy resin and hardener were mixed in a ratio 100/17 w/w.

3-aminopropyltriethoxysilane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) were purchased from Sigma Aldrich. Acetic acid was supplied from Analytic lab (France). Demineralised water was used in organosilane hydrolysis. Gamma-aminobutyric acid (GABA) was purchased from Sigma Aldrich and chitosan was

supplied by France Chitine. Acetic acid was supplied from Analytic lab (France). Demineralised water was used in GABA solution and regular water in chitosan solution.

4.3.2. Preparation of functionalization solutions

4.3.2.1. Silanes

3-aminopropyltriethoxysilane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) solutions were carried out by hydrolysis process. Demineralized water was mixed with ethanol in a proportion 60/40 w/w in order to prepare 300 ml of solution for each treatment. The pH of the solution was regularized at pH 5 using acetic acid. Several organosilane solutions for both molecules were prepared at 1 wt% and 5 wt%. The organosilanes were added to the mixture and pH was regularized again at pH 5. Solutions were stirring 1 h at room temperature. A schematic representation of silane hydrolysis is shown in Fig. IV - 9a).

4.3.2.2. GABA

Three different concentrations (1%, 5% and 10%) of GABA were diluted in demineralized water. GABA is found as a zwitterion in neutral pH, with the carboxylic acid group deprotonated. Therefore in order to graft GABA onto flax fibres, GABA must be modified to allow the zwitterion formation as shown on Fig. IV - 10a). Thus, the GABA solution was acidified over the pKa (4.03) at pH 4 with acetic acid. For the purpose of GABA zwitterion formation, FT-IR analysis was carried out. Corresponding FT-IR results are presented in section 4.4.2.1.

4.3.2.3. Chitosan

Chitosan powder was diluted in regular water at 0.5%, 1%, 2% and 5% concentrations and stirred with a magnetic mixer. Once powder was completely diluted, acetic acid in the same percentage than chitosan was added and stirred until completely homogenization. Fig. IV - 11a) shows a schematic representation of chitosan diluted in water/acetic acid.

4.3.3. Chemical modification of flax woven fabrics

UD flax woven fabrics were cut with a dimension of 200 x 300 mm² (approx. 11 g). A pad machine was used to apply the different solutions onto the woven fabrics. Rolls velocity was established at 6 m/min and the pressure between rolls was adjusted in order to double the wet fabric mass (fabric weigh approx. 22 g). Then fabrics were dried at 60°C for 24h.

4.3.3.1. Organosilanes

The reaction between organosilanes and natural fibres occurs in three steps (Fig. IV - 9): hydrolysis of organosilanes, adsorption of molecules by the fibre and condensation or grafting. The kinetics of self-condensation (Fig. IV - 9b) during the silane hydrolysis is very fast. In order to reduce this kinetics of self-condensation and to increase the rate of hydrolysed silanes, the solution must be acidified [24]. The application of the silane solution must be done just after hydrolysis. The chemical grafting between fibres and silane happens by condensation of hydrogen bonds at high temperature during dried step, forming Si-O-C bonds.

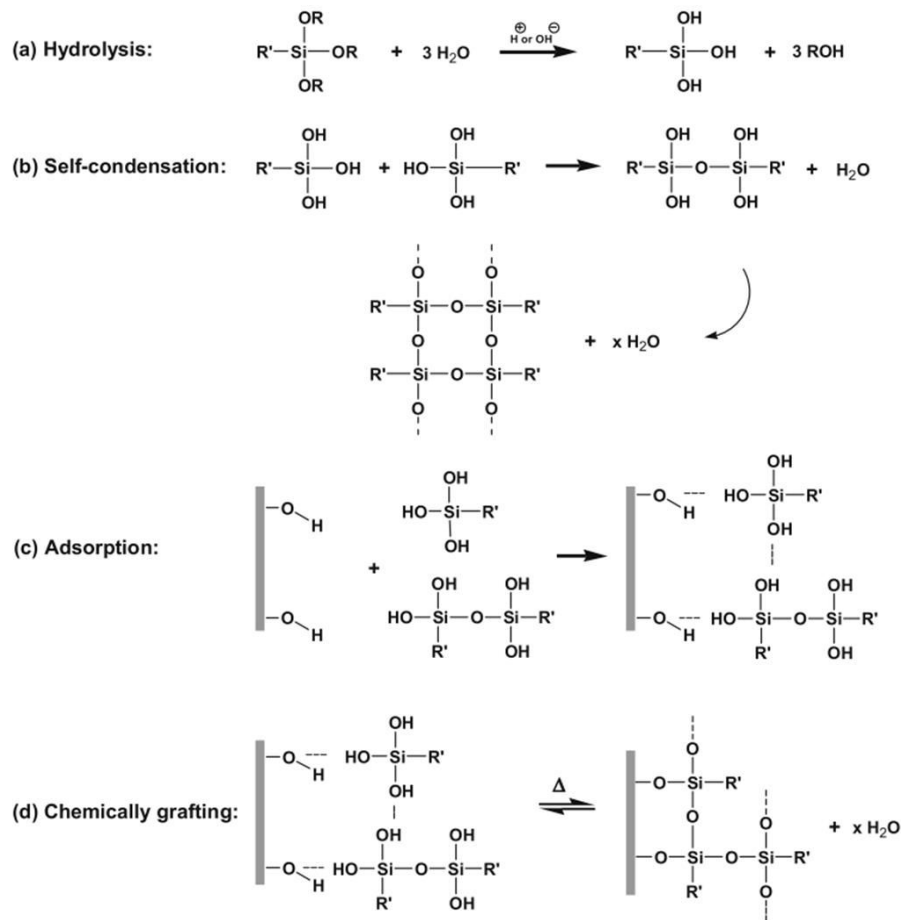


Fig. IV - 9 Interaction of silane with natural fibres by hydrolysis process [2]

4.3.3.2. GABA

The grafting reaction of GABA onto the flax fibre surface corresponds to an esterification reaction between OH groups of flax fibre and acid groups of GABA molecule. Esterification is a complex process used for example in acetylation of cellulose. Chemically, acetylation is normally carried out using solvents as, for example, dichloromethane [25]. As one of the main objectives of this study is the application of molecules without solvent, water was used as a vector in order to disperse GABA onto flax fibres. Flax fibres were impregnated with the solution and then esterification was carried out during drying. Fig. IV - 10b) shows a schematic representation of the probable esterification between flax fibres and GABA. Chemical modification of flax fibres with GABA was verified by FT-IR analysis and results are presented in section 4.4.2.2.

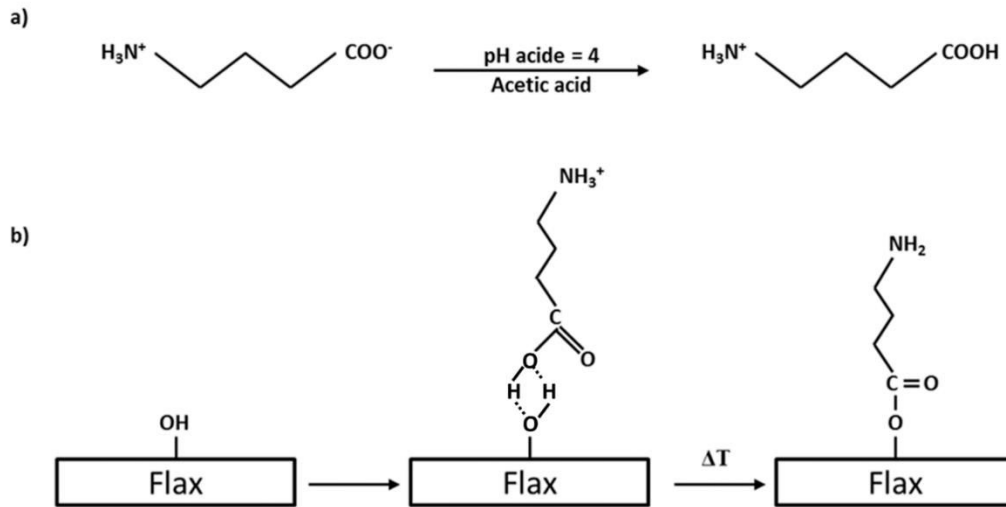


Fig. IV - 10 Schematic representation of probable a) GABA zwitterion modified with acetic acid and b) crosslinking between flax fibre and GABA

4.3.3.3. Chitosan

The reaction between chitosan and flax fibres occurs through by hydrogen bondings between cellulosic chains. Fibres were impregnated with chitosan solution in order to disperse chitosan around the surface of the fibres. Then, chitosan modified fibres were dried in order to extract the water and the acetic acid. Fig. IV - 11b) shows a schematic representation of a possible reaction between flax fibres and chitosan.

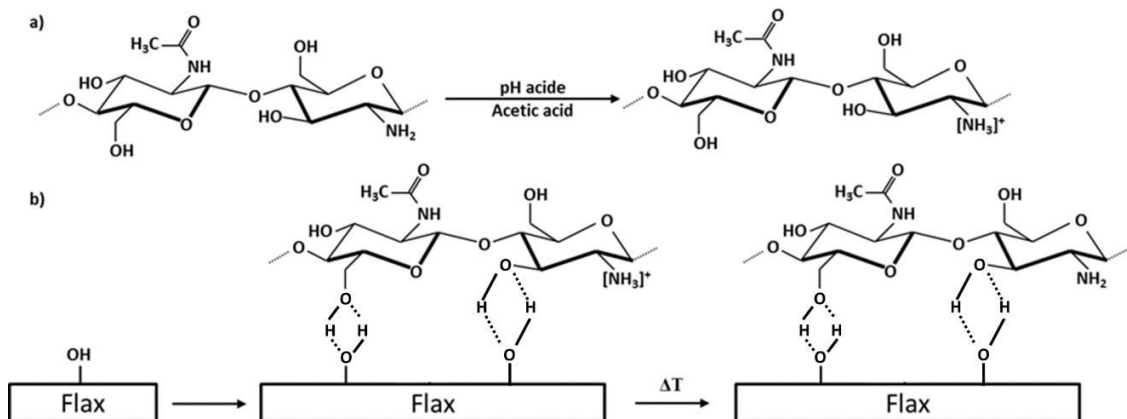


Fig. IV - 11 Schematic representation of probable a) Chitosan diluted in water/acetic acid and b) crosslinking between flax fibre and chitosan

Chemical modification of flax fibres with chitosan molecules was verified by FT-IR analysis and results are presented in section 4.4.2.3.

4.3.4. Manufacturing of flax-epoxy composite plates

Untreated and treated UD woven fabrics were dried at 60°C for 24 h to minimize the moisture content. A hand lay-up technic was used to impregnate the UD flax fabrics with a mixture of Resoltech® 1800 epoxy resin and Resoltech® 1805 aliphatic amine hardener (100/17 w/w). Ten impregnated layers were stacked retaining a 0° orientation. Reticulation of composite was carried out using a Daragon thermo-compression press at a thickness of 3 mm under a constant pressure of 50 Bars during 21h at 60°C.

4.3.5. Determination of physicochemical properties of flax yarns and fabrics and of composites

As concerns the physicochemical properties, FTIR experiments were carried out to evaluate the efficiency of molecules grafting onto flax fabrics. Dimension and density (linear and areal density) of flax yarns and fabrics were measured after each treatment as well as the reinforcing and porosity rates of composites.

4.3.5.1. FT-IR analysis

FT-IR spectra were recorded with a Bruker IFS66 spectrometer in attenuated total reflectance (ATR) mode with a resolution of 2 cm⁻¹ and 32 scans in the range 4000-400 cm⁻¹.

4.3.5.2. Dimension and density of flax yarns and fabrics

Flax fabrics and yarns shrinkage may occur after washing, surface treatment or drying operations. In flax woven fabrics, this shrinkage was 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, respectively. The ratio of shrinkage was determined by the increased number of ends and picks per cm compared with the initial fabric. Linear density (g/Km or TEX) and areal density (g/m²) were measured for yarns and woven fabrics respectively. The measurement of the linear density consisted in the extraction of ten yarns of the fabric that are cut at 10 cm. Then the yarn weight was measured using an IR-balance (Precisa XM66) at 105°C in order to evaluate the weight without moisture. This analysis was carried out in the weft direction and in the warp

direction three times. For the areal density of fabrics, three discs of 25 mm diameter were cut and the weight was measured using the same IR-balance. Three measurements were performed for each flax fabric sample.

4.3.5.3. Reinforcing rate and degree of porosity of composites

In order to obtain the composite reinforcing rate ($\%_v$), areal density of fabrics and of composites were determined as well as the density of the fabric, the resin and the composite.

The areal density measurement of fabrics was explained in section 4.3.5.1.

Areal density of composites was carried out on discs of 40 mm diameter cut with a hole saw. Then the areal density (g/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 10 layers of UD flax woven fabric in the dried state.

The bulk densities of flax fibre fabrics (ρ_f), epoxy resin (ρ_m) and composite plates (ρ_c) were obtained on dried materials using a gas pycnometer (Micromeritics AccuPyc 1330) in helium atmosphere.

Based on these measurements, the fibre ($\%_{vf}$), matrix ($\%_{vm}$) and porosity ($\%_{vp}$) volume fractions were calculated using Eq. 1, Eq. 2 and Eq. 3 [26]:

$$\%_{vf} = \%_{mf} \cdot \frac{\rho_c}{\rho_f} \quad (\text{Eq. 1})$$

$$\%_{vm} = \%_{mm} \cdot \frac{\rho_c}{\rho_m} \quad (\text{Eq. 2})$$

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

4.3.6. Microstructure analysis

As concerns the microstructure analysis, it was carried on through SEM and AFM observations performed on composites.

4.3.6.1. SEM observations

The effect of organosilanes, GABA and chitosan treatments 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 the 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).

4.3.6.2. AFM observations

Atomic force microscopic test was carried out at SeaTech Engineering School (Université de Toulon et du Var, France) in MAPIEM (Matériaux Polymères Interfaces Environnement Marin) laboratory by Thaïs Armagnat and Léa Distaso supervised by Lenaïk Belec (Associate Professor).

AFM observations were conducted using multimode Nanoscope V from Bruker AXS with a scanner type 8610 JVLR. The transverse cross-sections of flax fabric composite were polished with sandpaper then diamond paste in dried conditions to avoid any fibre modifications. Images were obtained at 0.5 and 1Hz of velocity and with a peak force set-point between 20 and 30 nN.

In a first time, AFM was used to obtain a topographic image of the transverse cross-section of the composite. The topographic image allows detecting the holes produced at the interface zone due to the non-adhesion of the fibre and the matrix.

The application of a contact force to the surface using a module PeakForce allows obtaining a topographic image of the deformation along of the surface measured. The

high deformation at the interface can be considered as de-cohesion between the fibre and the matrix. Young's modulus and adhesion force were calculated using the DMT model (Derjaguin-Mulle-Toporov) [27] (Eq. 4). Young's modulus was used to observe the effect of treatments on the crosslinking of the matrix close to the interface zone. A comparison with T_g was carried out.

	DMT		
$a = \sqrt[3]{\frac{R}{E_{tot}} (F + 2\pi RW)}$		- R: tip radius	
		- a: diameter of the contact zone	
$\delta = \frac{a^2}{R} = \frac{(F + 2\pi RW)^{2/3}}{\sqrt[3]{RE_{tot}^2}}$		- δ : Indentation	(Eq. 4)
		- E_{tot} : modulus of sample + tip	
$F_{ad} = 2\pi RW$		- W: adhesion force	

4.3.7. Mechanical characterizations

The mechanical performances of composites were analysed through both dynamic mechanical and static tensile tests.

4.3.7.1. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal measurements were investigated using a VA 815 Metravib RDS in the dual cantilever bending mode in transverse direction for composites. In the case of epoxy resin, test was carried out firstly in dual cantilever bending mode and then in traction compression due to an important deformation of the sample around T_g , which produced micro-ruptures at the grips zone. Rectangular samples of 80 mm x 10 mm x 3 mm were cut from untreated and treated composites. First, a linearity test was carried out on untreated flax/epoxy composite, where different displacement amplitudes were tested for constant frequency and temperature, in order to determine the displacement for which the material is in its linear domain. The optimal dynamic displacement amplitude was found to be around 10 μm . Based on this linearity result, samples were heated from 25°C to 150°C with a heating rate of 3°C/min at a frequency of 5 Hz and fixed displacement of 10 μm . The storage modulus (E'), the loss

modulus (E''), the loss factor ($\tan \delta$) and the temperature of the loss factor peak T_{α} , were recorded.

4.3.7.2. Static tensile mechanical properties

Tensile mechanical properties were investigated in the transverse direction, i.e. perpendicular to fibre direction and in longitudinal direction, so as to determine the effect of organosilanes, GABA and chitosan treatments 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 [28], composite plates were cut to obtain specimens of 3 mm x 10 mm x 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. For each composite 5 samples were tested in transverse direction and 3 in longitudinal direction.

4.4. Evaluation of the molecules grafting efficiency onto flax fibre fabrics

Chemical surface modifications of flax fibre fabrics with non-bio-based solutions (APS and GPS) and bio-based solutions (GABA and chitosan) were investigated in this part. The chemical bonds produced by the functionalisation of the different molecules on the flax fibre fabric surface was characterised by FT-IR analysis. A comparison between organosilane and biopolymer grafting is therefore presented.

4.4.1. Characterization of the grafting of organosilanes (APS, GPS) onto flax fibres

4.4.1.1. Characterization of APS grafting onto flax fabrics

FT-IR analysis was carried out on untreated and APS (1% and 5%) treated flax fabrics in order to determine the presence of amino groups on flax fibre surface (Fig. IV - 12). All the spectra were normalized according to the band located at 1202 cm^{-1} ,

corresponding to OH in plane bending vibrations of cellulose component [29]. The band used to determine amino groups is located around 1564 cm^{-1} , corresponding to NH_2 bending vibrations [30]. For a detailed analysis, the ratio between bands at 1564 cm^{-1} and 1202 cm^{-1} was analysed using three different scans performed on untreated and treated flax fibres (Fig. IV - 13). The presence of amino groups on flax fibre surface was confirmed by an increase of this ratio.

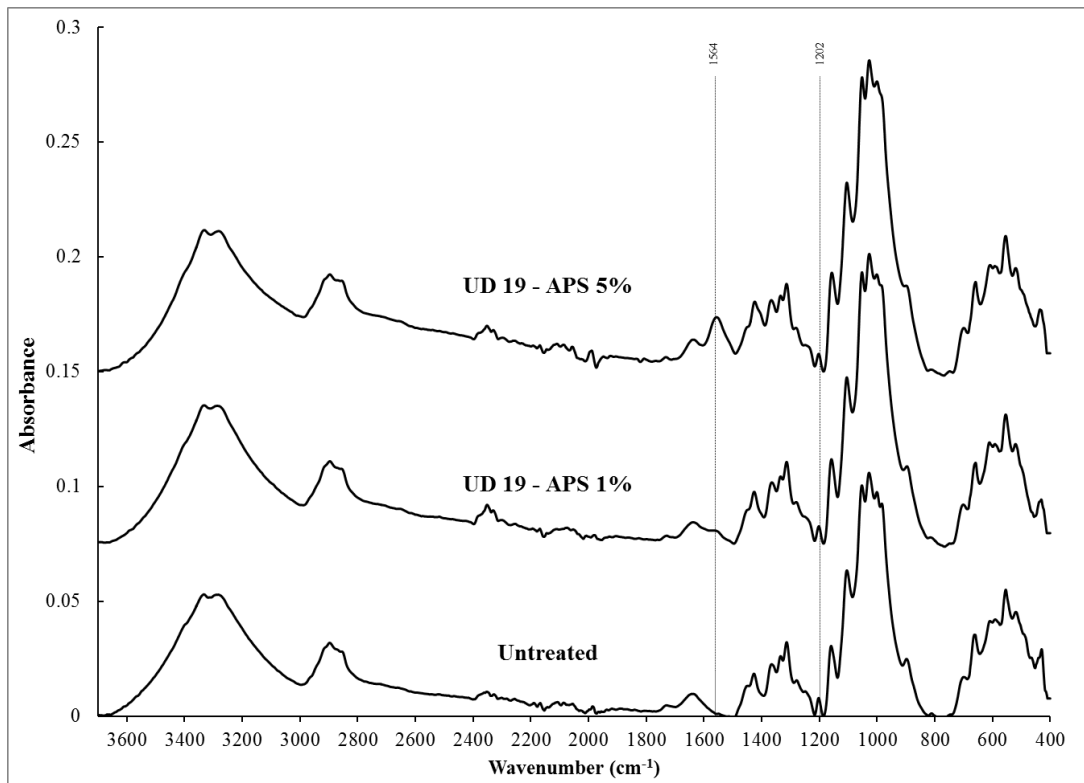


Fig. IV - 12 Spectra of untreated and APS (1% and 5%) treated flax fibres

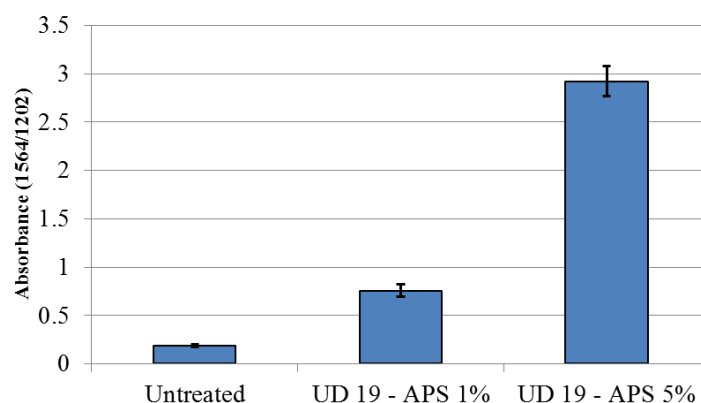


Fig. IV - 13 Ratio between the intensity of FT-IR peaks located at 1564 cm^{-1} and 1202 cm^{-1} of untreated and APS (1% and 5%) treated flax fabrics

To complete the study of the APS grafting, IPC measurements were carried on. As shown on Table IV - 2, the presence of silanes groups on flax fibre fabrics was confirmed also by silicium and silice composition using IPC analysis.

Table IV - 2 Silicium and silice composition of APS treated flax fabrics (5%)

	APS 5%
Silicium (wt%)	1.7
Silice (in SiO_2) (wt%)	3.6

4.4.1.1. Characterization of GPS grafting onto flax fabrics

GPS treatments were also analysed by FT-IR. In Fig. IV - 14, the spectra of untreated and GPS treated (1% and 5%) flax fibres are shown. As for APS treatments analysis, untreated and treated spectra were normalized according to the band at 1202 cm^{-1} . Bands corresponding to epoxy groups were not perceptible due to the moisture presence (H_2O). Nevertheless a band located at 1727 cm^{-1} can be observed for all spectra. Its intensity increased for GPS treated flax fibre at 5% (Fig. IV - 15). This band may correspond to saturated aliphatic and aromatic ester $\text{C}=\text{O}$ stretching [31] from lignin in flax fibre (Chapter 3). The increment of the intensity of this peak may be due to an increase of ester groups produced by secondary reactions especially for high GPS concentration (5%).

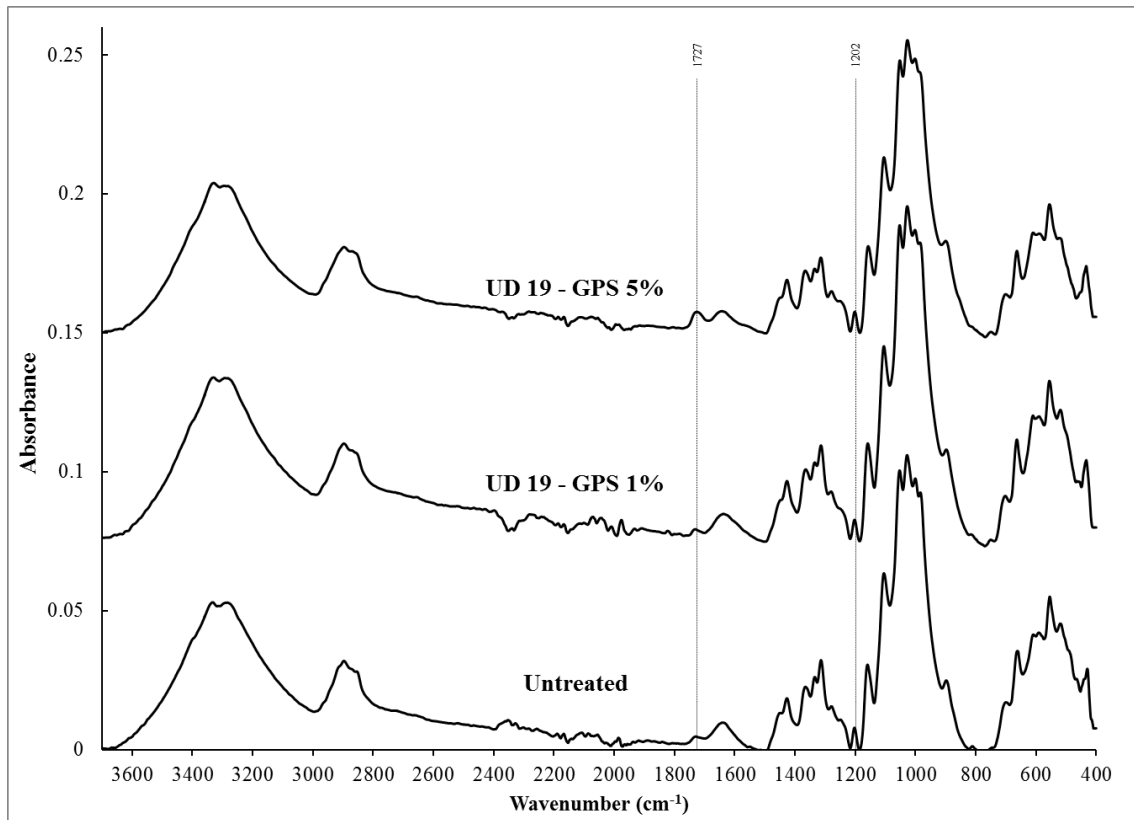


Fig. IV - 14 Spectra of untreated and GPS (1% and 5%) treated flax fibres

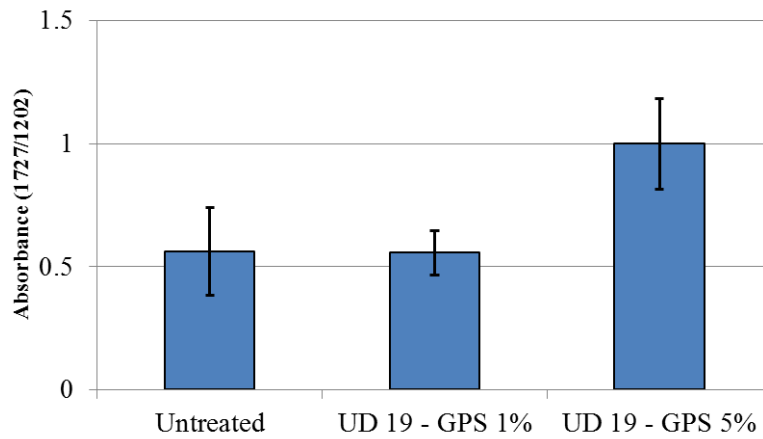


Fig. IV - 15 Ratio between the intensity of FT-IR peaks located at 1727 cm^{-1} and 1202 cm^{-1} of untreated and GPS (1% and 5%) treated flax fabrics

These reactions occur between acetic acid used for pH control and epoxy groups from GPS during hydrolysis process as already shown in literature [32] (Fig. IV - 16). It

could be expected that this ester formation would decrease the adhesion between fibre and matrix, due to the reduction of the number of reactive functions towards the matrix.

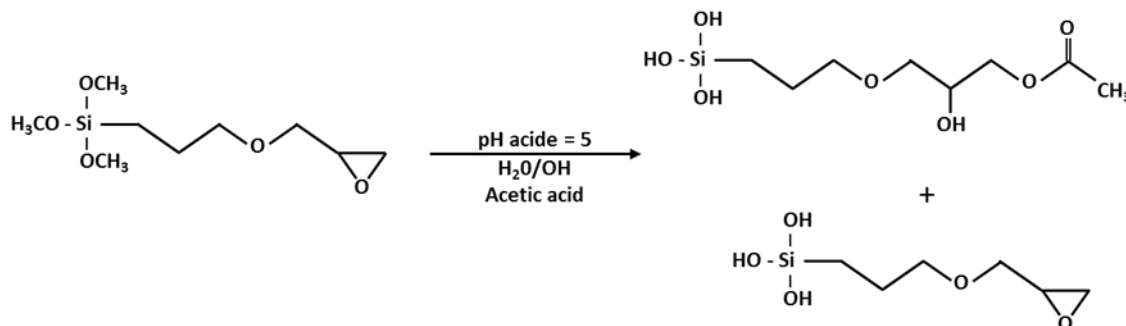


Fig. IV - 16 Possible secondary reactions occurring during GPS hydrolysis (for high GSP concentration, 5%)

To complete the study of the GPS grafting, inverse phase chromatography (IPC) measurements were carried on by SGD Multilab Rouen. As shown on Table IV - 3, the presence of silane groups on flax fibre fabrics was confirmed also by the presence of silicium and silice

Table IV - 3 Silicium and silice compositions of GPS treated flax fabrics (5%)

	GPS 5%
Silicium (wt%)	0.9
Silice (in SiO ₂) (wt%)	1.9

4.4.2. Characterization of the grafting of biopolymers (GABA, chitosan) onto flax fibres

In this part, chemical modification of fibres was carried out using new bio-based molecules (GABA and chitosan) in order to improve the interface adhesion between flax fibre and epoxy resin. To our knowledge, these molecules have not been used previously as functionalisation agents in natural fibres/epoxy composites.

4.4.2.1. Characterization of individual components before grafting

A FT-IR analysis of GABA, chitosan and untreated flax fabric was performed in order to determine the characteristic bands for each component. The spectrum of each component is shown in Fig. IV - 17.

Untreated flax fibre and chitosan presented FT-IR spectra very similar. The high content of cellulose on flax fibre and the similitude between both polysaccharides induce the apparition of similar peaks. The main difference between their spectra is the apparition of bands at 1585cm^{-1} corresponding to N-H bonds in primary amines [31]. At the same time, the absence of aliphatic groups in chitosan, produce a decreasing of the bands intensity observed between 2800 and 3000 cm^{-1} , corresponding to CH_2 and CH_3 stretching

In the case of GABA molecule, a characteristic band appears around 2180 cm^{-1} . This band combined with the band at 1575 cm^{-1} corresponds to symmetric and antisymmetric deformation of NH_3^+ bonds respectively. The band at 1575 cm^{-1} (displaced to 1585 cm^{-1} in the case of chitosan), corresponds to N-H bonds in primary amines. All the spectra were normalized according to the band at 1202 cm^{-1} , corresponding to OH in plane bending vibrations of cellulose component [29].

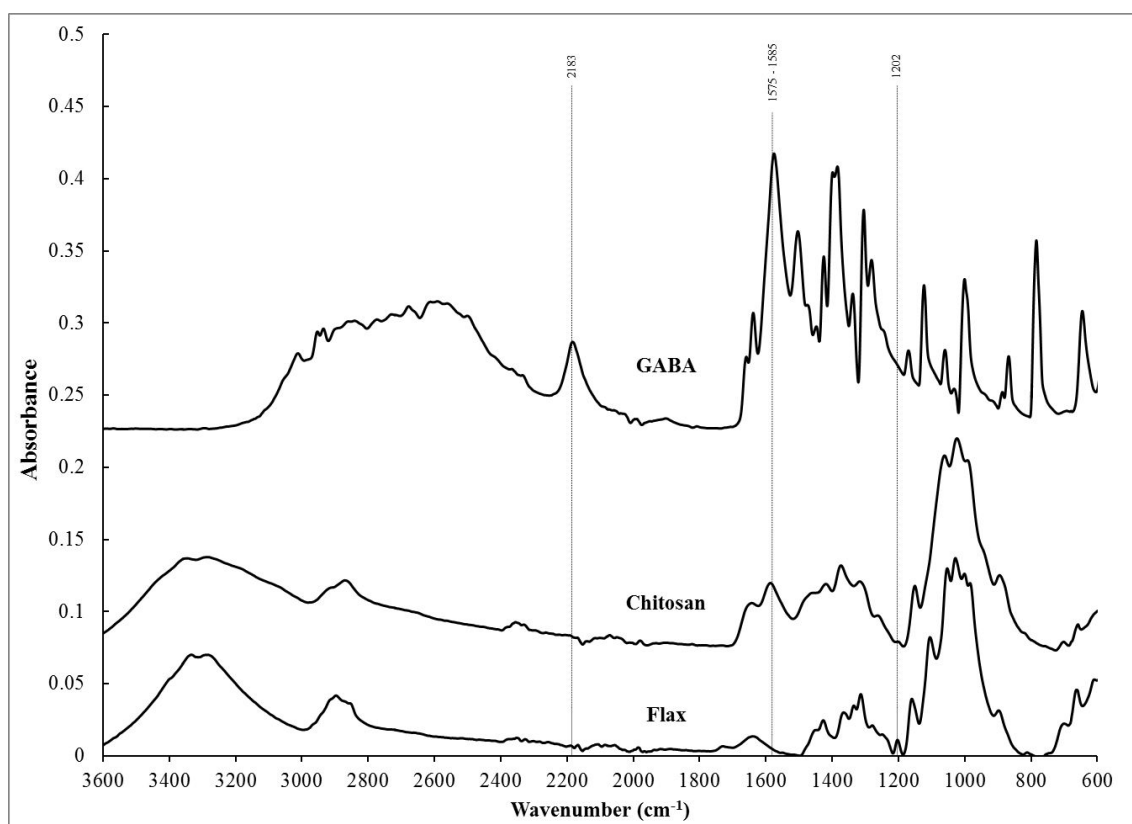


Fig. IV - 17 FT-IR Spectra of GABA and chitosan molecules and flax fabric

To determine GABA zwitterion formation (see section 4.3.2.2), GABA was diluted in demineralized water at 5% and then, solution was acidified with acetic acid taking samples at different pHs between 4 and 6.3. At the same time, acid solutions without GABA but with the same quantities of acetic acid were prepared as references. CO₂ and H₂O bands were removed from the spectra. The zwitterion formation was verified using FT-IR analysis as shown in Fig. IV - 18. There are two strong bands common to all spectra. The first one, detected about 1553 cm⁻¹, corresponds to NH₃⁺ antisymmetric deformation bonds. The second one, located at about 1411 cm⁻¹ for pH 6.3, corresponds to antisymmetric CO⁻ stretching vibration and is shifted to 1416 cm⁻¹ for pH 4, corresponding to OH bending vibrations in acids. When pH is decreased, a characteristic band appears at 1345 cm⁻¹, corresponding to OH deformation and C-O stretching modes. A ratio between the intensities of the peaks located at 1345 cm⁻¹ and 1551 cm⁻¹ was carried out (Fig. IV - 19). Until pH 4.8 a decrease in the intensity ratio is observed. This phenomenon can be produced by secondary reactions with acetic acid. An increase is observed from pH 4.7 to pH 4.2 with a stabilization of the intensity after pH 4.2.

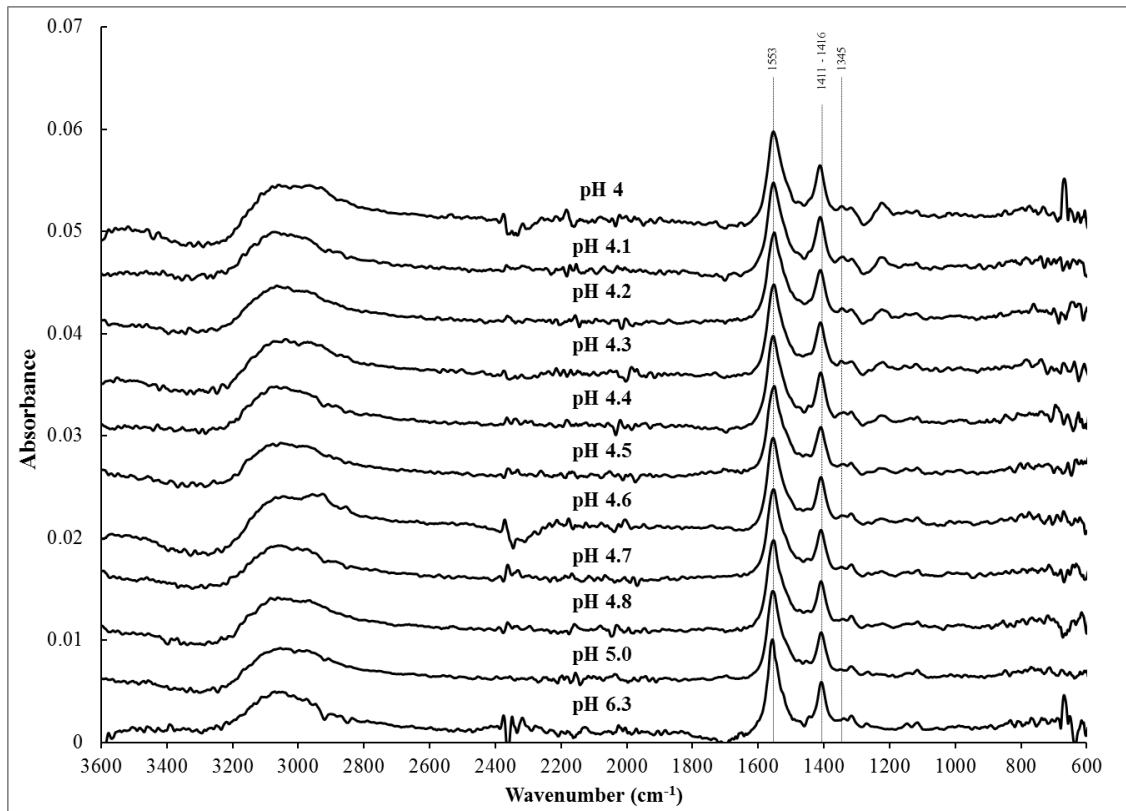


Fig. IV - 18 FT-IR spectra of GABA solutions at different pHs

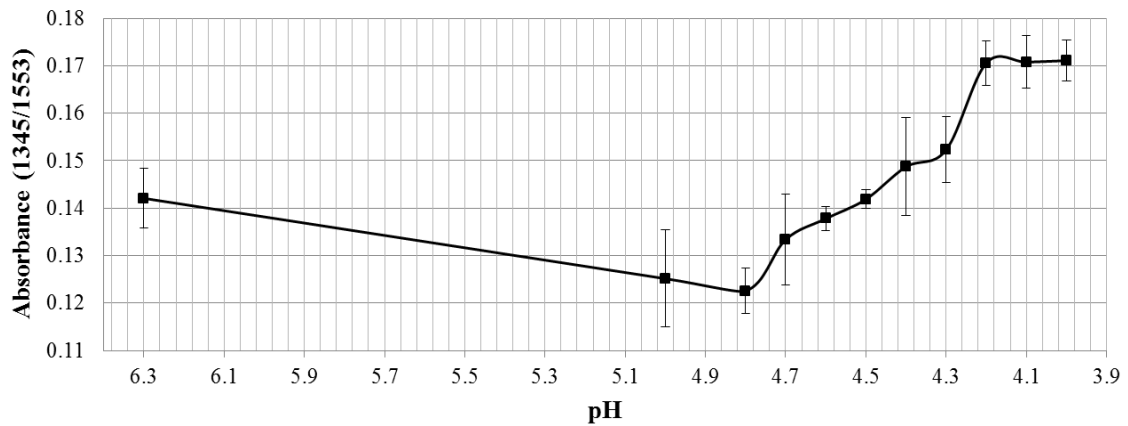


Fig. IV - 19 Ratio between the intensity of 1345 cm⁻¹ and 1553 cm⁻¹ peaks of GABA in solution at different pHs

4.4.2.2. Characterization of GABA grafting onto flax fabrics

Untreated and GABA treated (1, 5 and 10%) FT-IR spectra were performed and normalized according to the band at 1202 cm⁻¹, corresponding to OH in plane bending vibrations of cellulose component [29]. As it is shown in Fig. IV - 17, this band is

mainly attributed to the flax fibre. The band used to determine GABA amino groups is located around 1564 cm^{-1} , corresponding to N-H bonds.

Fig. IV - 20 shows the spectra of untreated and treated fabrics with GABA at concentrations of 1, 5 and 10%. An increase of the amino band at 1564 cm^{-1} is easily observed with the increase of GABA concentration. In the Fig. IV - 21, the ratio between amino group band (1564 cm^{-1}) and the reference band (1202 cm^{-1}) is shown. The increase in the amine content with the GABA concentration is confirmed. No esterification reaction was detected (apparition of an ester bond around 1740 cm^{-1}), may be because of the low reactivity. In turn, no bands corresponding to GABA zwitterion formation are observed, suggesting that the grafting between flax fibre surface and GABA molecules may occur through hydrogen bonds.

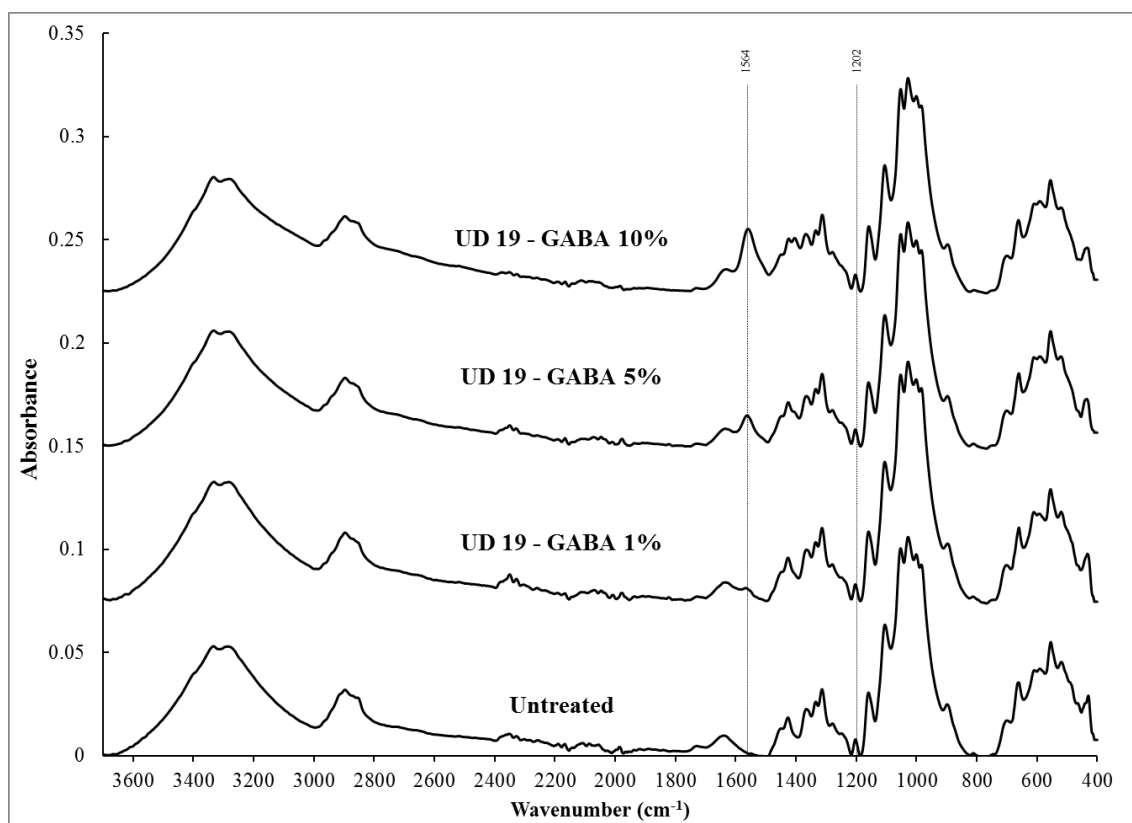


Fig. IV - 20 FT-IR Spectra of untreated and treated flax fibre with GABA solutions at 1, 5 and 10%

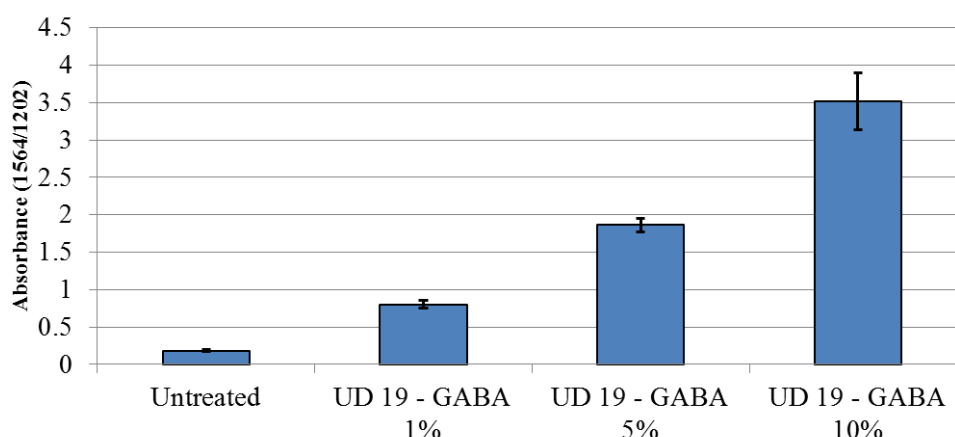


Fig. IV - 21 Ratio between the intensity of 1564 cm⁻¹ and 1202 cm⁻¹ peaks of untreated and treated flax fabric with GABA at different concentrations

4.4.2.3. Characterization of chitosan grafting onto flax fabrics

Fig. IV - 22 shows the infrared spectra of untreated and chitosan treated (0.5, 1, 2, 5%) flax fibre woven fabrics. Bands at 1564 cm⁻¹, corresponding to N-H bonds, are observed on treated fabrics. Increasing chitosan concentration increases the intensity of this band. The ratio between the intensity of the N-H peak at 1564 cm⁻¹ and a reference peak at 1202 cm⁻¹ was also carried out for each treatment (Fig. IV - 23). As might be expected, the ratio is higher when concentration of chitosan is increased. Nevertheless, bands referring to a possible chemical interaction between cellulose and chitosan were not clearly observed on these FT-IR spectra. These latter bonds cannot be easily identified due to the presence, at the same wavelength range, of hydrogen groups of moisture (between 3000 and 3600 cm⁻¹) contained in flax fibres.

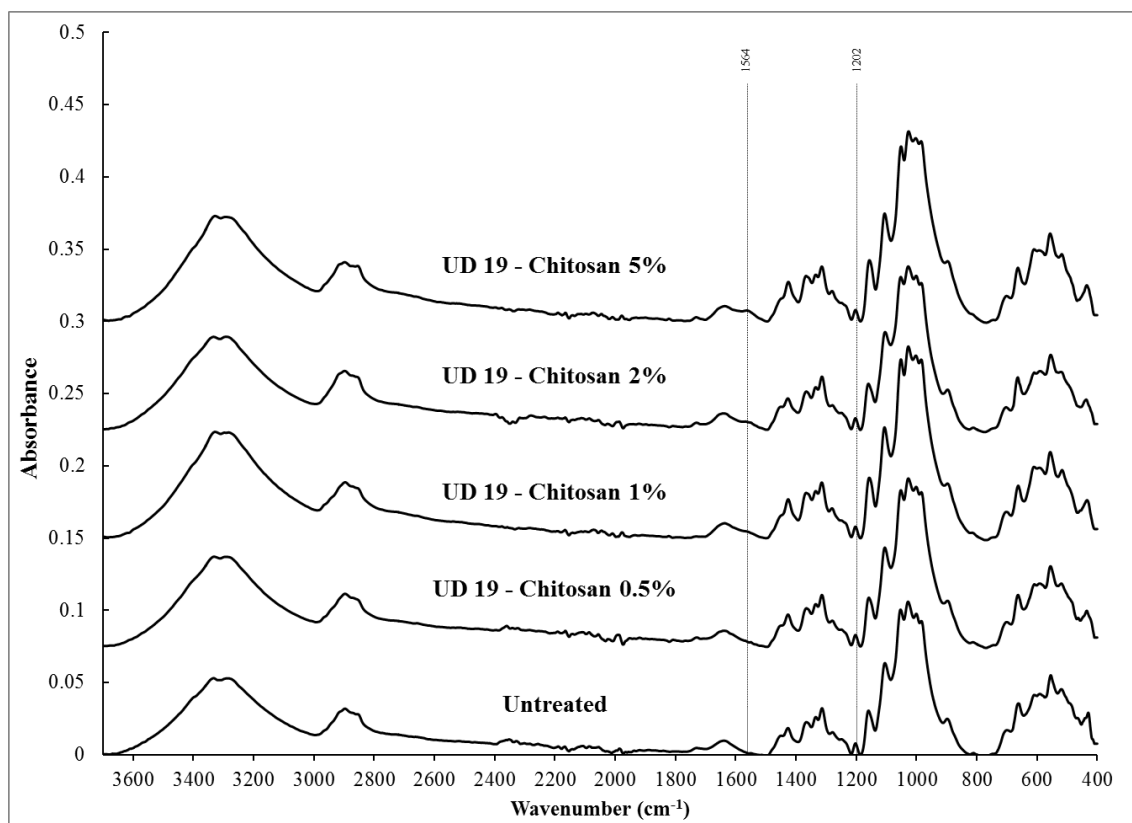


Fig. IV - 22 FT-IR spectra of untreated and chitosan treated (0.2, 1, 2 and 5%) flax fibre woven fabrics

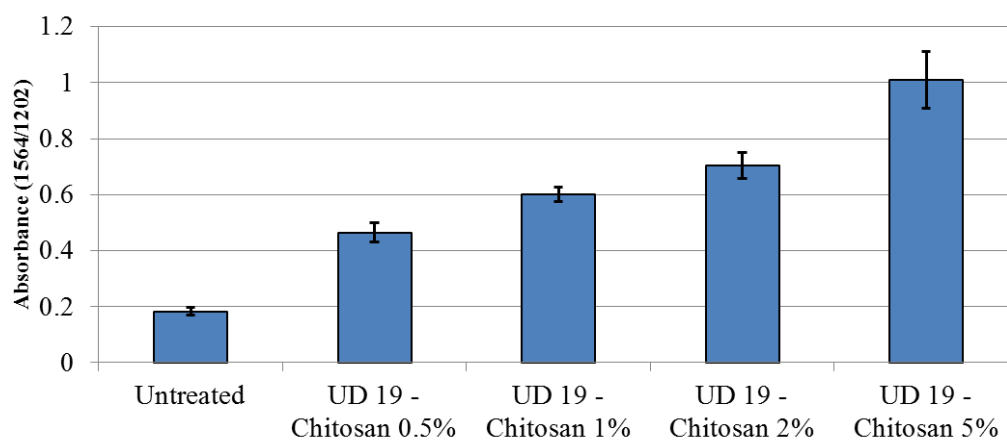


Fig. IV - 23 Ratio between the intensity of 1564 cm^{-1} and 1202 cm^{-1} peaks of untreated and of chitosan treated flax fibre woven fabrics

4.4.3. Comparison between organosilane and biopolymer presence onto flax fabrics

One scientific strategy of this study for improving the adhesion between flax fibres and epoxy matrix was the formation of NH_2 groups on the surface of flax fibres using on one hand a non-bio-based molecule, i.e. an aminosilane (APS) and on the other hand, bio-based molecules, i.e. an amino acid (GABA) and chitosan. The intensity ratio between 1564 cm^{-1} and 1202 cm^{-1} corresponding to N-H bonds in APS, GABA and chitosan treatments at 1 and 5% was compared in Fig. IV - 24. For a concentration of 1%, almost similar intensity ratios are obtained for GABA and APS treatments and a lower intensity for chitosan treatment. For a concentration of 5%, APS and GABA intensity ratios are around 3 times and twice respectively higher than those of chitosan.

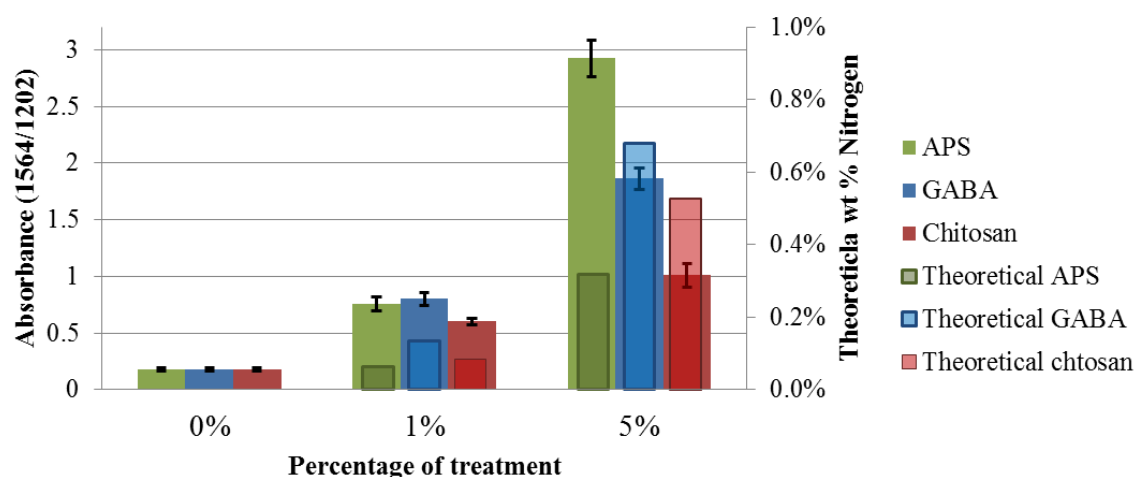


Fig. IV - 24 Comparison between intensity ratios of peaks located at 1564 cm^{-1} and 1202 cm^{-1} for APS, GABA and chitosan treatments at 1 and 5% and theoretical wt % nitrogen added to flax fabric for each treatment

Theoretical weight percentage of nitrogen added through each treatment can be calculated knowing the molecular weights of each molecule (or of each repetitive unit). These later are 221 g/mol , 103 g/mol and 164 g/mol for APS, GABA and chitosan respectively. For chitosan a 90% de-acetylation is considered. A molecular weight of 191 g/mol corresponds therefore to an acetylated chitosan repetitive unit and 161 g/mol to de-acetylated chitosan repetitive unit. Results are shown in Fig. IV - 24.

It can be observed that it is difficult to make simple correlations with FT-IR results. Only the fibre extreme surfaces are analysed through FT-IR, so that FT-IR results strongly depend on the diffusion of the grafted molecules in the core of the flax fibres. In the case of GABA treatment, GABA molecules are small, very soluble in water and cannot be self-condensed, so that a diffusion through the core of the fibre is possible, reducing the quantity of NH_2 groups analysed by FT-IR at the fibre surface. In the case of APS treatment, APS molecules have a higher steric volume than GABA molecules and silane self-condensation could occur so that APS molecule diffusion through the core of the fibre is more limited and the quantity of NH_2 groups at the surface is higher. . In the case of chitosan treatment, another parameter should be considered that is viscosity. This later increased considerably with concentration. A chitosan layer around fibres can be formed so that elementary fibres can be agglomerated especially at high chitosan concentration (5%), as it will be shown in 4.6.1.2. In this case, the thickness of layer can be responsible of the decrease of NH_2 detected at the fibre surface by FT-IR.

4.5.Changes in the dimension and areal density of flax yarns and fabrics after chemical surface modification

The dimensions and density of flax fibre fabrics after each treatment were then studied in this section.

4.5.1. Organosilane (APS, GPS) treatments

The hydration and dehydration of plant fibres produce an effect on shrinkage of fibres. As it was shown in chapter 3, the shrinkage also depends on the nature of solvent as well on the temperature of treatment during the time of washing. In this chapter, fabrics were not immersed in a solvent. The application of treatments was carried out by padding application at room temperature, minimizing the quantity of solvent and the time of application. The dry linear and areal mass density of flax yarns and woven fabrics, and the dimensional density of untreated and treated woven fabrics are shown in Table IV - 4. In warp direction, a low variation of ends/cm was observed for treated fabrics, producing a minimal contraction for treatments at 1% (about 0.05 ends/cm for APS 1% and 0.15 ends/cm for GPS 1%) and a minimal dilatation of the fabrics for treatments at 5% (about 0.05 ends/cm the APS 5% and about 0.1 end/cm the GPS 5%).

These modifications of the fabrics can be produced by the stretching effect of padding and as a consequence of shrinkage in weft direction. The number of picks/cm in weft direction was increased with treatment application, producing a shrinkage of the fabric of about 1.8% for APS and GPS at 1%, 3.2% for APS at 5% and 3.9% for GPS at 5%. A tendency between concentration of molecules and shrinkage was observed, but significantly, this shrinkage (only produced in weft direction) was low. Due to the shrinkage and the addition of molecules, the dry mass areal density was increased. APS 1% and 5% treatments increased the mass in 3.9 and 14.5 g/cm² respectively and GPS 1% and 5% in 7.5 and 15.4 g/cm² respectively. Low variations were observed in the linear mass density. The loss of molecules at the fibre surface during the yarn extraction from the fabric, as well as the irregularity of the yarns or the low errors in the manipulation and measurements could be responsible of these low differences. During the padding process, the local concentration of functionalizing molecules in the vicinity of the flax fabrics was higher than in the rest of the functionalizing solution, possibly due to their good interactions with the fabrics. As a consequence, the real molecules rate over the fabric (calculated in Table IV - 4) was higher than the expected percentage of molecule added.

Table IV - 4 Dimensional and mass density of untreated and organosilane (APS, GPS) treated (1%, 5%) flax fibre yarns and fabrics

	Calculated molecules rate (%)	Insertion density		Dry linear mass density		Dry mass areal density Fabric (g/m ²)
		Warp (ends/cm)	Weft (picks/cm)	Warp (TEX)	Weft (TEX)	
UD 19	0	12.85 ± 0.05	13.6 ± 0	22.8 ± 1.0	99.7 ± 8.0	161.84 ± 2.70
APS 1%	2.3	12.9 ± 0	13.85 ± 0.05	23.3 ± 0.7	86.3 ± 7.5	165.69 ± 0.77
APS 5%	8.2	12.8 ± 0	14.05 ± 0.05	22.8 ± 0.3	98.7 ± 4.7	176.33 ± 0.44
GPS 1%	4.4	13 ± 0	13.85 ± 0.05	23.8 ± 0.3	98.7 ± 2.8	169.31 ± 4.23
GPS 5%	8.7	12.75 ± 0.05	14.15 ± 0.15	23.2 ± 0.3	102 ± 6.9	177.24 ± 1.33

The density of untreated and silane treated fabrics is shown in Table IV - 5 Untreated flax fibre density is around 1.52 g/cm³, very similar to results obtained by other authors (1.4 – 1.5 g/cm³) [33–35]. A low modification of density was observed for treated fabrics with APS 1% and GPS 1% in relation with the untreated fabric. However, a

reduction of density was produced when concentration was increased (APS 5% and GPS 5%). This reduction could be probably produced mainly by the closed porosity formed between fibre and molecules, as it is represented in Fig. IV - 25.

Table IV - 5 Density of untreated and silane (APS, GPS) treated (1%, 5%) flax fibre fabrics

	Untreated	APS 1%	APS 5%	GPS 1%	GPS 5%
Density (g/cm ³)	1.514 ± 0.002	1.517 ± 0.002	1.499 ± 0.001	1.517 ± 0.001	1.496 ± 0.001

Fig. IV - 25 Schematic representation of a) open porosity in fibre and b) possible effect of closing porosity by treatment effect

4.5.2. Biopolymers (GABA, chitosan) treatments

The dry linear and areal mass density of flax yarns and woven fabric, and the dimensional density of untreated and treated woven fabrics are shown in Table IV - 6. The variation of ends/cm in the warp direction was not very important. In this case, a variation between 0.05 and 0.1 ends/cm was observed for GABA treatments and between -0.5 and 0.15 ends/cm for chitosan treatments. As it was observed for silane treatments, an effect of shrinkage was also produced for GABA and chitosan treatments. Due to this shrinkage and the addition of molecules, the dry mass areal density was increased more considerably than for organosilane treatments. In this case, GABA 1%, 5% and 10% treatments increased the areal mass of 10.9, 24.5 and 22.6 g/cm² respectively, and chitosan 0.5%, 1%, 2% and 5% of 10, 11.3, 15 and 19.7 g/cm² respectively, with respect to the untreated fabric. Low variation was observed in the linear mass density for GABA and chitosan treatments too. The loss of treatments during the yarn extraction from the fabric, as well as the irregularity of the yarns or the low errors in the manipulation and measurements could be also responsible of these low differences as for organosilane based treatments. As it was shown for APS and GPS

treatments, the real molecules rate over the fabric was higher than the expected percentage of molecule added.

Table IV - 6 Dimensional and mass density of untreated and GABA (1, 5, 10%) and chitosan (0.5, 1, 2, 10%) treated flax fibre yarns and fabrics

	Calculated molecules rate (%)	Insertion density		Dry linear mass density		Dry mass areal density Fabric (g/m ²)
		Warp (ends/cm)	Weft (picks/cm)	Warp (TEX)	Weft (TEX)	
UD 19	0	12.85 ± 0.05	13.60 ± 0	22.8 ± 1.0	99.7 ± 8.0	161.84 ± 2.7
GABA 1%	6.3	12.95 ± 0.05	14.05 ± 0.05	22.7 ± 0.7	92.7 ± 7.7	172.71 ± 1.17
GABA 5%	13.1	12.95 ± 0.05	14.15 ± 0.05	24.5 ± 2.9	99.0 ± 3.9	186.29 ± 1.18
GABA 10%	12.3	12.90 ± 0	13.95 ± 0.05	24.3 ± 0.0	101 ± 7.9	184.48 ± 0.44
Chitosan 0.5%	5.8	13 ± 0	14.25 ± 0.05	22.8 ± 0.3	100.7 ± 4.3	171.80 ± 3.35
Chitosan 1%	6.4	12.95 ± 0.05	14.1 ± 0	23.2 ± 0.3	96.3 ± 5.6	172.94 ± 1.17
Chitosan 2%	8.5	12.8 ± 0	14.25 ± 0.1	24.2 ± 0.3	101 ± 6.3	176.78 ± 3.94
Chitosan 5%	10.9	12.8 ± 0.1	14.1 ± 0.1	25.3 ± 0.7	95.3 ± 2.8	181.54 ± 5.12

Density of untreated and treated fabrics is shown in Table IV - 7. In the case of GABA treatments, density did not significantly change after the treatment application. Little changes could be produced due to a slight degradation of flax components because of acid GABA solution (pH 4). In the case of chitosan treatments, density was significantly reduced depending on chitosan concentration from 1.52 to 1.47 g/cm³. The main difference between chitosan and the other treatments used in this study was the higher viscosity of chitosan, which increased with the concentration of the molecule in the solution. The higher viscosity of chitosan is produced as a consequence of long chain of polymers in chitosan solution. The application of a viscous solution on flax fibre makes more difficult the impregnation of solution through the porosity of fibres. In this case, the chitosan treatment could be considered as a coating and the other treatments as an impregnation. The effect of coating could be responsible of an increase of closed porosity in comparison with the impregnation.

Table IV - 7 Density of untreated and GABA (1, 5, 10%) and chitosan (0.5, 1, 2, 10%) treated flax fibre fabrics

	Untreated	GABA 1%	GABA 5%	GABA 10%	Chitosan 0.5%	Chitosan 1%	Chitosan 2%	Chitosan 5%
Density (g/cm³)	1.541 ± 0.002	1.528 ± 0.001	1.504 ± 0.001	1.515 ± 0	1.511 ± 0.003	1.506 ± 0.001	1.494 ± 0.002	1.472 ± 0.005

4.6. Influence of chemical surface modification on flax fabrics/epoxy composite microstructure

The analysis of the micro-structure was carried out at two different levels. In a first approach, SEM observations of flax/epoxy composites cross-sections were performed in order to evaluate the bundles dispersion as well as the porosity presence. Then this method was completed by an AFM analysis (roughness, deformation, Young's modulus) in the fibre/matrix interface zone.

4.6.1. SEM observations

4.6.1.1. Organosilane (APS, GPS) treatments

SEM transverse cross sections images of untreated, APS 5% and GPS 5% treated flax fibre/epoxy composites at 100x and 2000x magnifications are presented in Fig. IV - 26 and Fig. IV - 27 respectively.

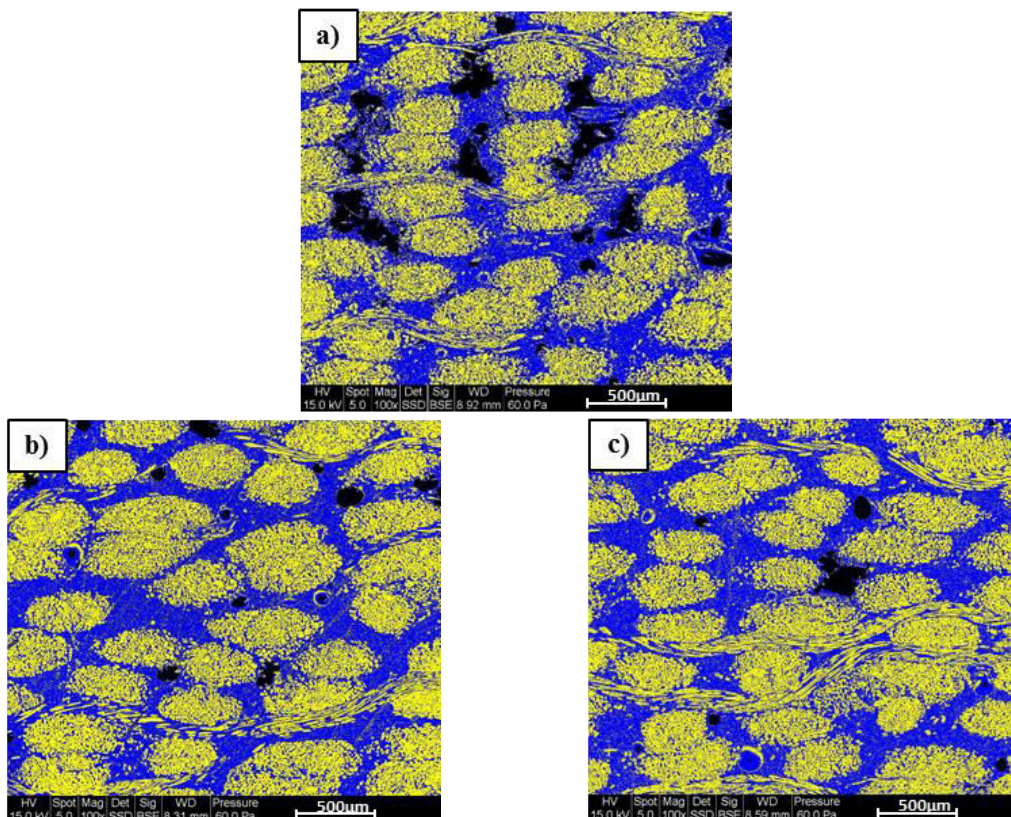


Fig. IV - 26 SEM cross sections at magnification 100x of a) Untreated flax fabric/epoxy composite, b) APS 5% treated flax fabric/epoxy composite and c) GPS 5% treated flax fabric/epoxy composite (fibre in yellow, epoxy in blue and porosity in black)

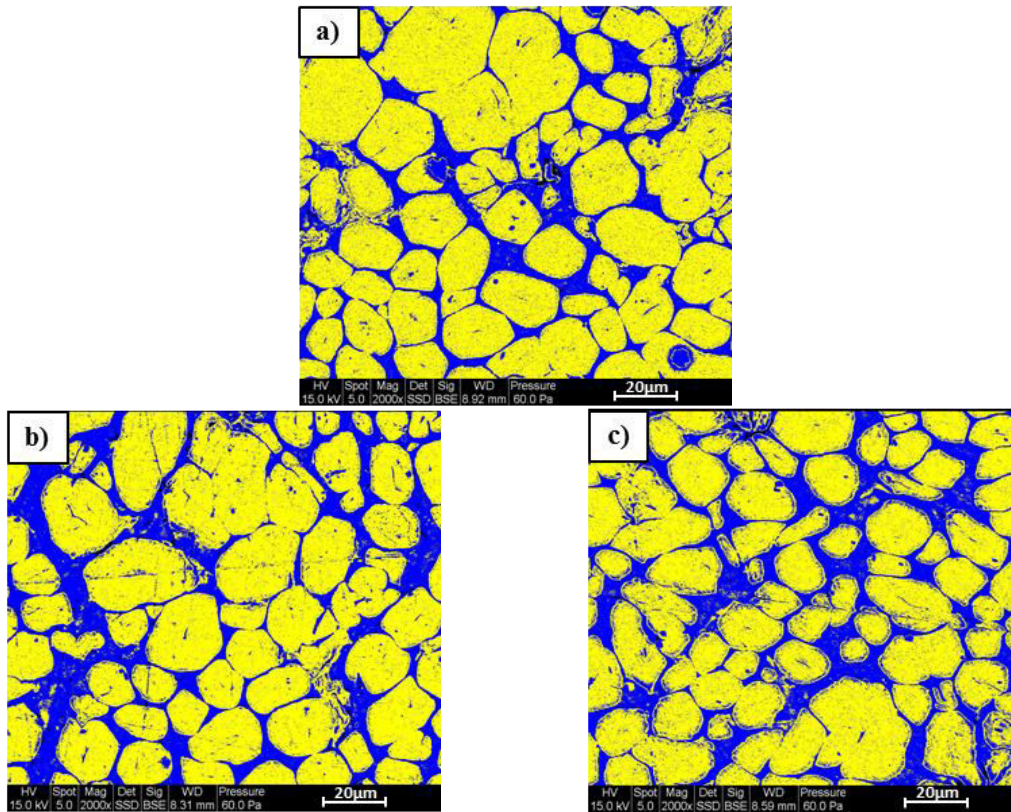


Fig. IV - 27 SEM cross section at magnification 2000x of a) Untreated flax fabric/epoxy composite, b) APS 5% treated flax fabric/epoxy composite and c) GPS 5% treated flax fabric/epoxy composite (fibre in yellow, epoxy in blue and porosity in black)

Based on a qualitative visual observation, a reduction of matrix porosity in treated composites with respect to untreated sample was observed. This phenomenon was observed previously in chapter 3 in the case of washing treatments of flax fibres. Nevertheless no change in the fibre dispersion is given in evidence after silane treatment contrarily to the case of washing treatments where a better dispersion of unitary fibres was observed. The quick application of solution at room temperature and the fact that fibres were not immersed in a bath (as it was the case in chapter 3 for washing treatments), could be responsible of the unchanging dispersion of bundles.

4.6.1.2. Biopolymers (GABA, chitosan) treatments

SEM cross section images of untreated flax fabric/epoxy composite and of GABA treated flax fabric/epoxy composite at 5 and 10% and of chitosan treated flax fabric/epoxy composites at 0.5, 1, 2 and 5% are observed at 100x (Fig. IV - 28) and 2000x (Fig. IV - 29) magnifications.

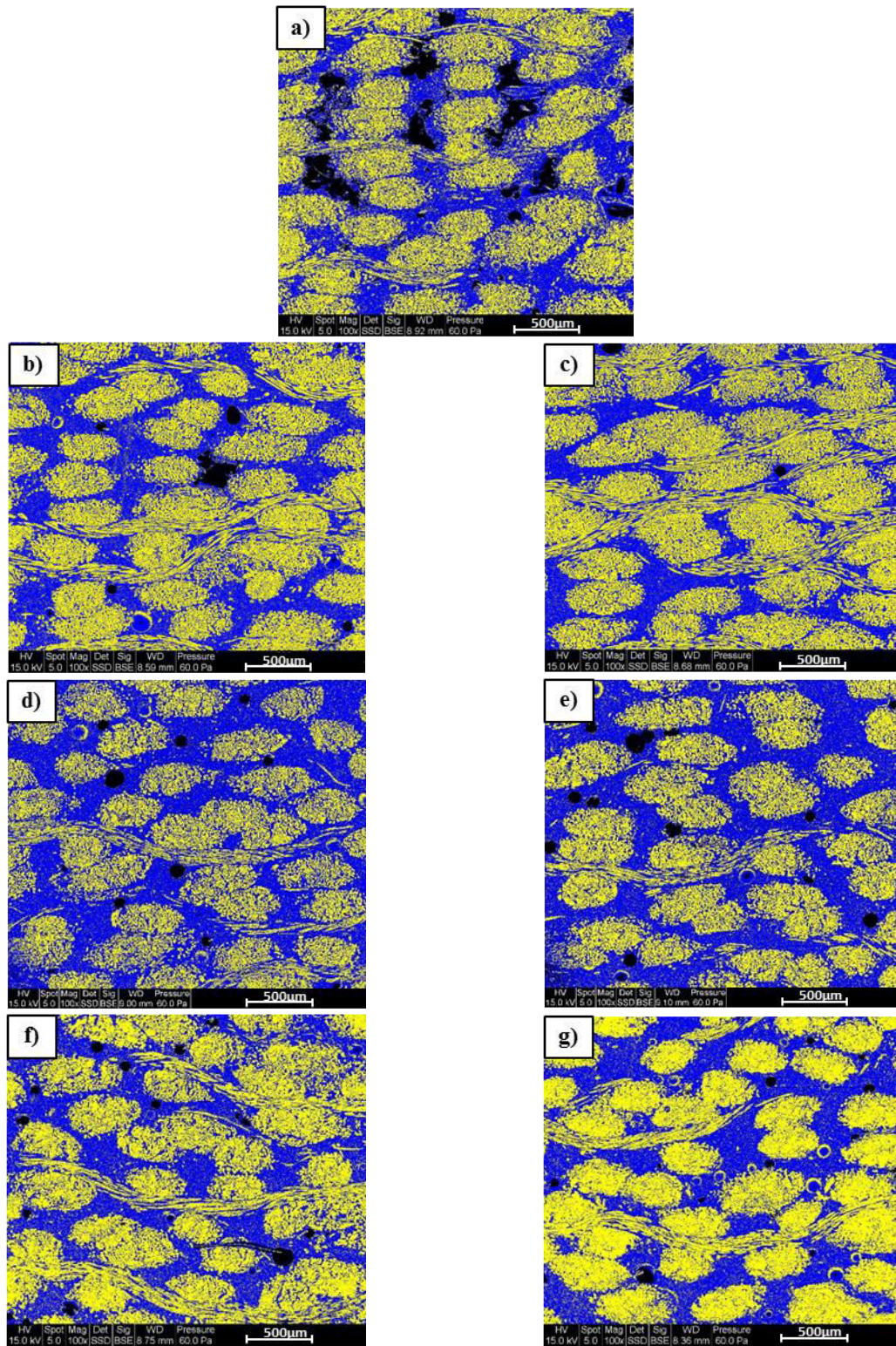


Fig. IV - 28 SEM cross section at magnification 100x of a) Untreated flax fabric/epoxy composite, b) GABA 5% treated flax fabric/epoxy composite and c) GABA 10% treated flax fabric/epoxy composite d) chitosan 0.5% treated flax fabric/epoxy composite, e) chitosan 1% treated flax fabric/epoxy composite, f) chitosan 2% treated flax fabric/epoxy composite and g) chitosan 5% treated flax fabric/epoxy composite (fibre in yellow, epoxy in blue and porosity in black) (fibre in yellow, epoxy in blue and porosity in black)

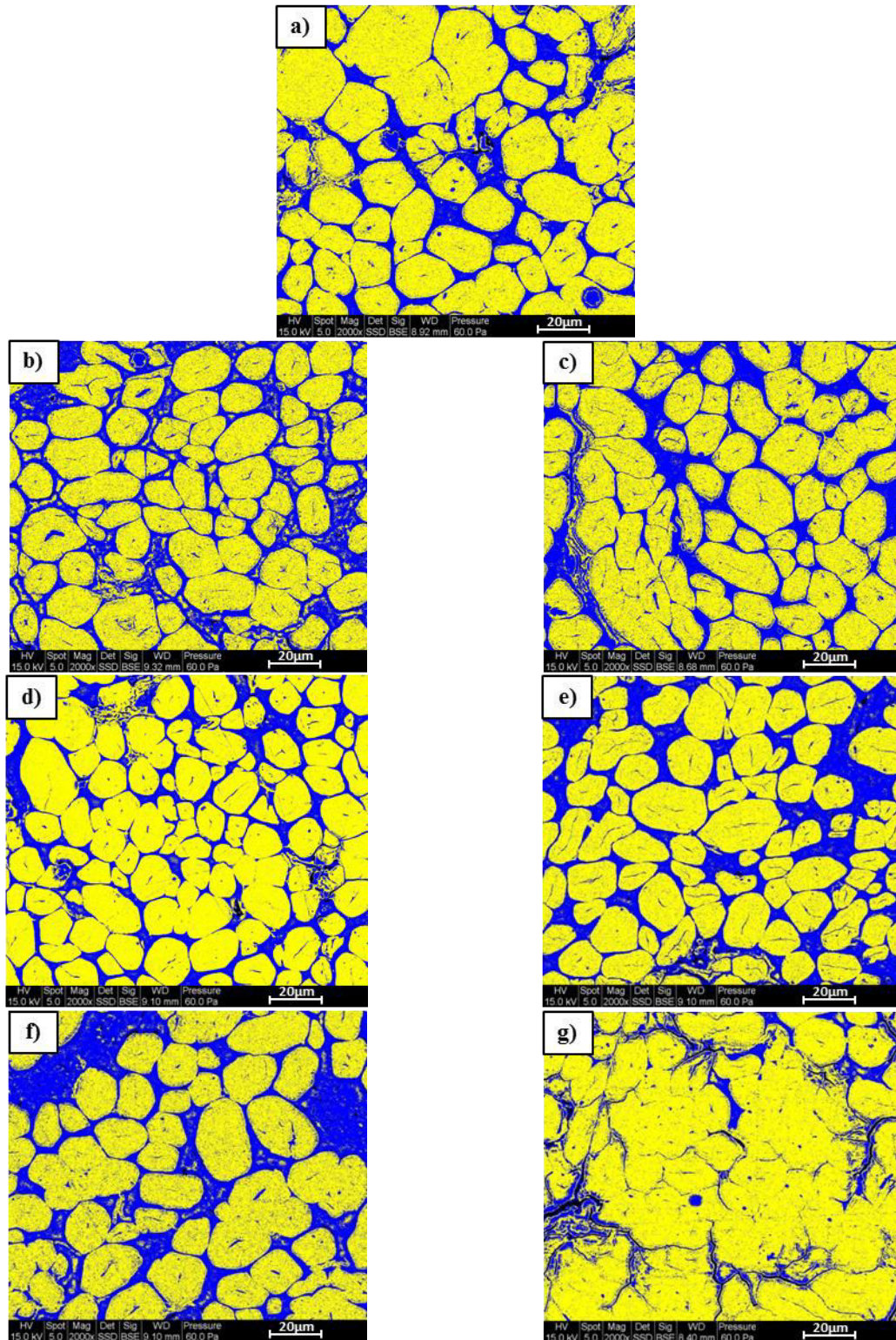


Fig. IV - 29 SEM cross section at magnification 2000x of a) Untreated flax fabric/epoxy composite, b) GABA 5% treated flax fabric/epoxy composite and c) GABA 10% treated flax fabric/epoxy composite d) chitosan 5% treated flax fabric/epoxy composite, e) chitosan 1% treated flax fabric/epoxy composite, f) chitosan 2% treated flax fabric/epoxy composite and g) chitosan 5% treated flax fabric/epoxy composite (fibre in yellow, epoxy in blue and porosity in black)

It can be observed a decrease in porosity when flax fabrics are treated whatever the biopolymer used (GABA or chitosan). No changes were observed on fibre dispersion in matrix, neither in fibre defibrillation in the case of GABA treatment whatever the concentration. At high concentration, chitosan involve in a sticking of flax fibres.

4.6.2. AFM observations

4.6.2.1. Organosilane (APS, GPS) treatments

The first step of the AFM study was to produce 3D topographic images. Fig. IV - 30 depicted the AFM topographic image of untreated flax fibre/epoxy composite at the fibre/matrix interface. A gap could be easily observed between fibres and matrix that illustrates a bad interface between these two materials.

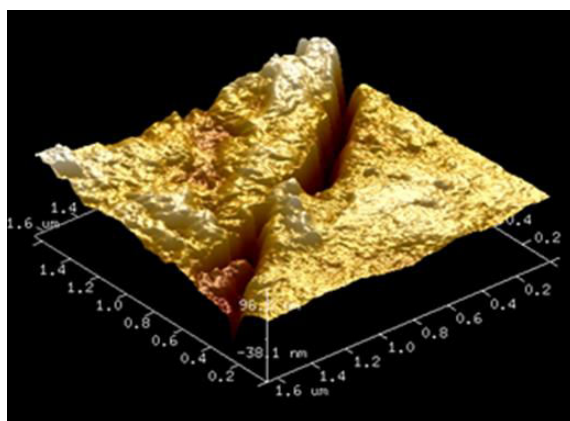


Fig. IV - 30 3D AFM topographic image of untreated flax fibre/epoxy composite interface (fibre at left and matrix at right)

The second step consisted in the analysis of the composite deformation in the interfacial zone. Fig. IV - 31 shows the strain of untreated, APS 5% and GPS 5% treated flax fibre/epoxy composites cross sections. In Fig. IV - 31a), a homogenous deformation was observed at the matrix zone (left), being a little bit higher closer to the interface. The deformation produced at the interface of untreated composite was around 60 nm respect to the low deformation on matrix region, which can be considered as a hole, corresponding to de-cohesion of the interface. When fibres were treated (Fig. IV - 31b) and c)), the deformation at interface zone was much lower (around 3 nm for APS 5% and 1.5 nm for GPS 5%), which can be explained as an improvement of the interfacial adhesion.

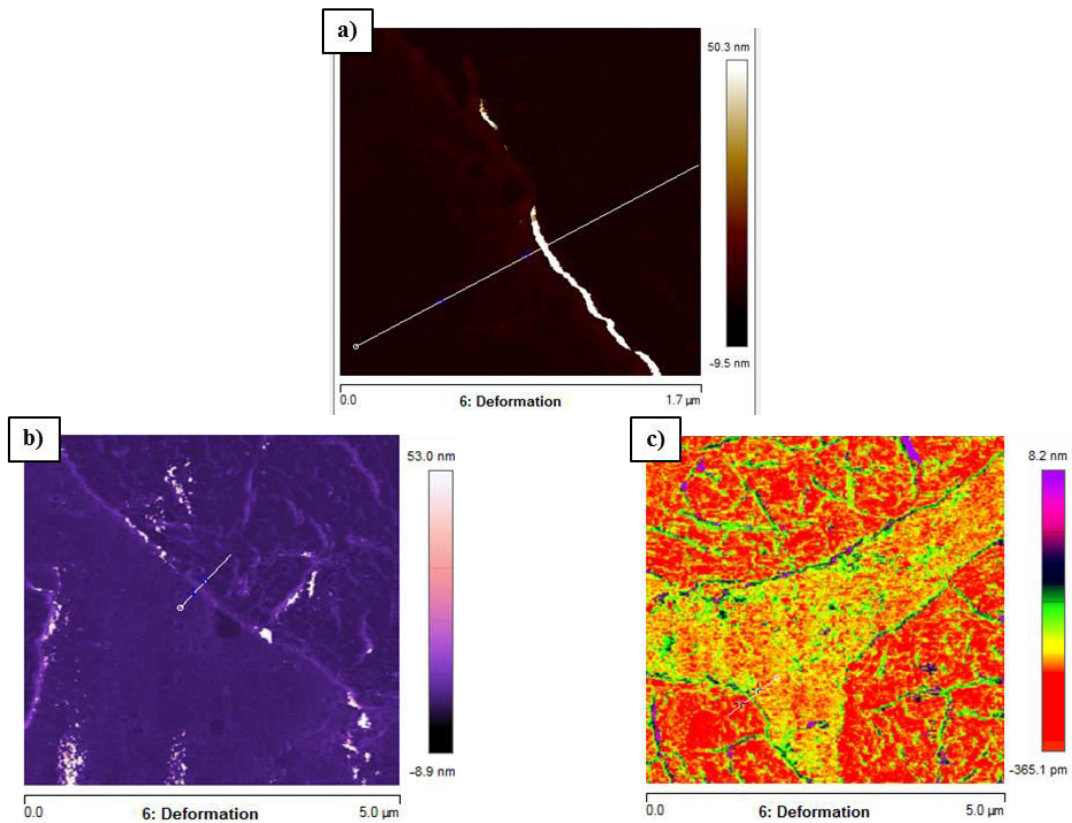


Fig. IV - 31 Strain across the flax fibre/epoxy interface zone: a) untreated, b) APS 5% and c) GPS 5%

Finally the third step was focused on the study of the Young's modulus cartography in the interfacial zone. Fig. IV - 32 shows the topography of Young's modulus at composite cross-section surface of untreated and of silane treated flax/epoxy composites. Values are presented in Table IV - 8 as well as T_g values measured by DSC and reinforcing rates.

The average Young's modulus of the matrix (far from the interphase) was around 2.6 GPa, 2.7 GPa and 2.6 GPa for untreated, APS 5% and GPS 5% treated composites respectively. The Young's modulus was increased on the interphase zone for untreated and GPS 5% treated composites in about 0.9 GPa (3.5 GPa) and 0.4 GPa (3 GPa) respectively. It is decreased for APS 5% treated composites in about 0.3 GPa (2.4 GPa). The glass temperatures (T_g) were $79.9 \pm 1.5^\circ\text{C}$, $80.4 \pm 2.2^\circ\text{C}$ and $81.3 \pm 1.3^\circ\text{C}$ for untreated, APS 5% and GPS 5% treated flax/epoxy composites respectively. These temperatures showed a similar crosslinking between composites. Moreover reinforcing rates were also almost similar for the three composites (about $43.8 \pm 0.8\%$, $43.1 \pm 0.1\%$ and

44.2±0.4% in volume for untreated, APS 5% and GPS 5% treated flax/epoxy composite respectively)

It can be noticed that in some cases, the techniques of characterisation can show an apparent Young's modulus stronger at the interphase due to boundary effects produced by the high indentation depth and the lateral resolution of the probe close to the fibre surface [36]. But this hypothesis contrasts with the low depth produced by AFM method.

In the case of untreated flax reinforced composite, it can be assumed that the presence of the flax fibres with a very low thermal conductivity (about 0.055 W/m/K [37]) may change the diffusion kinetics of the composite, as it can be observed in the decrease of the T_g respecting the bulk resin (93.6±0.9°C). In this way, some studies using microthermal analysis combined with AFM microscopy with glass fibre or beads/epoxy composites were carried out [36,38]. In these studies, thermal conductivity of glass was higher than those of the matrix and a low crosslink was observed around the fibre. In the case of flax fibre, the conductivity is much lower (0.055 W/m/K) than glass fibre (E-glass fibre: 1 W/m/K, R-glass fibre: 1 W/m/K and D-glass fibre: 0.8 W/m/K [39]). This phenomenon could be produced by the residual thermal zones after post-curing around the fibres, increasing the cross-linking and thus the higher stiffness in the interphase zone (+0.9 GPa) for untreated flax reinforced composite. Another effect that should produce an increment of Young's modulus at the interphase zone is the migration of amine groups to the fibre surface during the curing process [40]. In the case of GPS 5% treated flax reinforced composite, the good adhesion between matrix and fibre, that is improved further by heating, may hinder the crosslinking and the increase in Young's modulus close to the interfacial zone is of a lower amplitude (0.4 GPa). For APS treatment, another phenomenon should occur as a decrease of Young's modulus around 0.3 GPa (2.4 GPa) was observed at the interphase zone. Some authors related this effect when using silanes sizing [36,41,42]. This plasticizing could be produced by the formation of three dimensionally crosslinked siloxane polymer [43]. The lower concentration of Silicium observed by IPC technique on GPS treatment (Table IV - 3) in comparison with APS treatment (Table IV - 2) could be responsible of the formation

of a lower three dimensionally crosslinked network for this polymer, which present an increasing in the Young's modulus at the interphase zone.

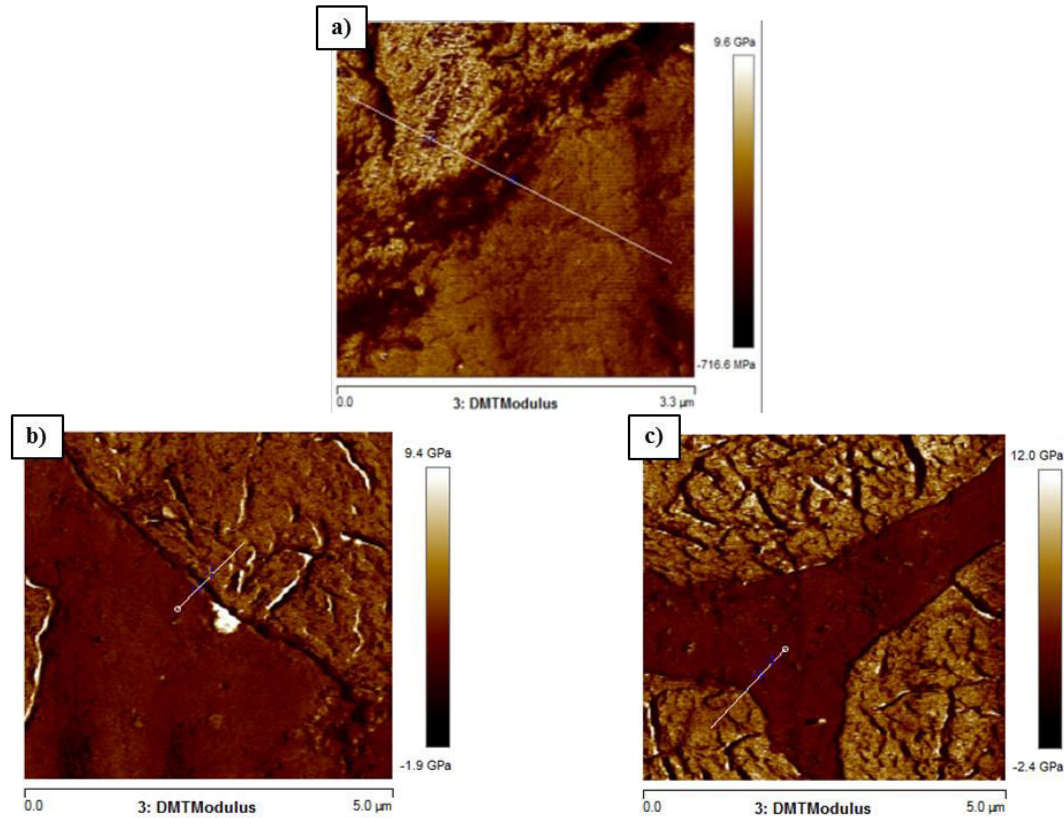


Fig. IV - 32 Young's modulus across the flax fibre/epoxy interface zone: a) untreated, b) APS 5% and c) GPS 5%

Table IV - 8 T_g (DSC) and Young's modulus (AFM) close to the matrix and in the interfacial zone for untreated, silane (APS, GPS) flax/epoxy treated composites

	Epoxy	Untreated	APS 5%	GPS 5%
Fibre rate (%v)	-	43.8 ± 1.8	43.1 ± 0.1	42.2 ± 0.4
T_g (°C)	93.6 ± 0.9	79.9 ± 1.5	80.4 ± 2.2	81.3 ± 1.3
Young's modulus (GPa) in the matrix	-	2.6	2.7	2.6
Young's modulus (GPa) in the interphase zone	-	3.5	2.4	3.0

4.6.2.2. Biopolymers (GABA, chitosan) treatments

The same analysis was carried on for GABA and chitosan treated flax/epoxy composites.

In Fig. IV - 33 the strain of untreated flax fibre/epoxy composite, GABA 5% treated flax fibre/epoxy composite and chitosan 5% treated flax fibre/epoxy composite is

presented. As well as for silane treated flax/epoxy composites, deformation observed at the matrix zone was homogeneous, being higher around the interface zone. With regards to untreated composites, as for silane treatments, deformation at interface was much lower (around 7 nm for GABA (Fig. IV - 33b) and 2.5 nm for chitosan (Fig. IV - 33c)), which can be related to an improvement of the interfacial adhesion. It can be noticed that the deformation is slightly higher for bio-based treatments in comparison with organosilane based treatments.

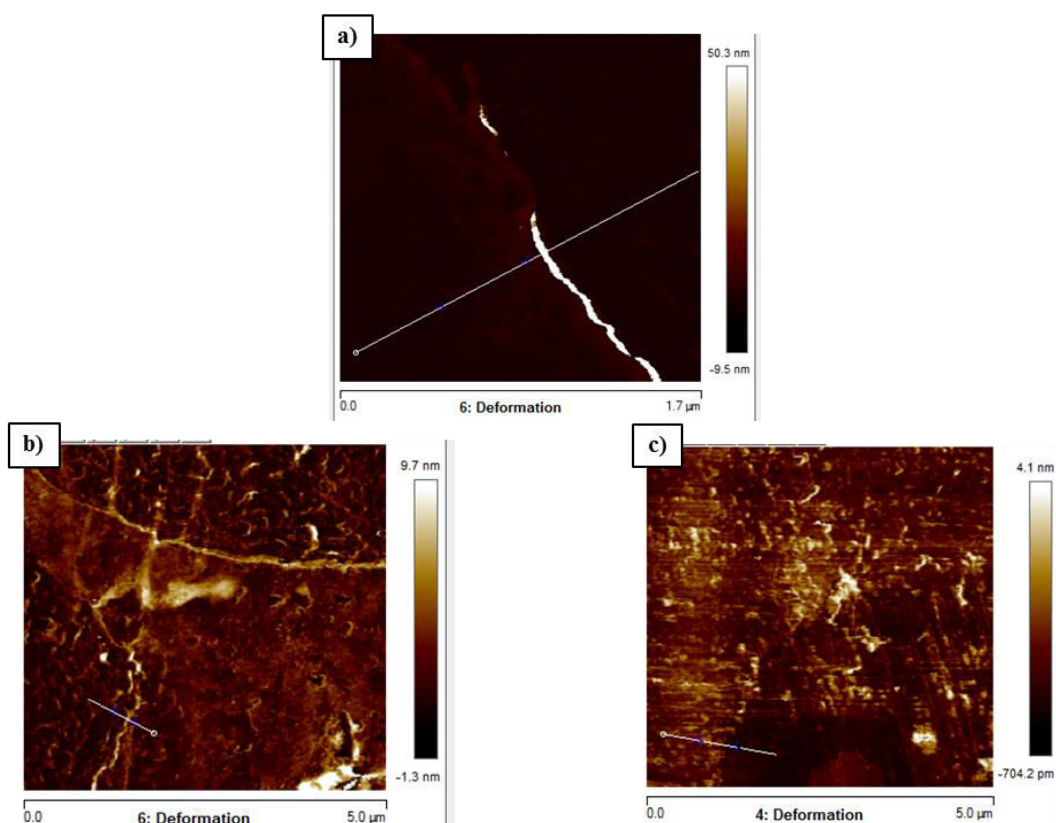


Fig. IV - 33 Strain across the flax fibre/epoxy interface zone: a) untreated, b) GABA 5% and c) chitosan 5%

Fig. IV - 34 shows the AFM topography of Young's modulus of the matrix and in the interphase zone for untreated, GABA 5% and chitosan 5% treated flax/epoxy composites. Values are presented in Table IV - 9 as well as T_g measured by DSC.

The average Young's modulus of the matrix (far from the interphase zone) of GABA 5% and chitosan 5% treated flax reinforced composites were respectively around 1.9 GPa and 2.5 GPa. For all reinforced composites in comparison with the bulk resin were observed a reduction in the cross-linking and as consequence, a reduction in the

Young's modulus of the matrix. This effect was more pronounced in the case of GABA treated fibre which presented a higher reinforcing rate. This can be explained by the steric hindrance provoked by the presence of fibres, which disturbs the structural mobility of epoxy chains to reticulate and hence lowers the crosslinking rate.

When Young's modulus was analysed at the interphase zone, an increment was observed of about 0.7 GPa (2.6 GPa) and 0.9 GPa (3.4 GPa) for GABA 5% and chitosan 5% treated flax reinforced composites respectively. This phenomenon, similar that in untreated and GPS 5% treated flax reinforced composite, was probably produced by residual thermal zones around the fibre, due to their low thermal conductivity or by migration of amine groups to the fibre surface, as it was explained in 4.6.2.1. Like silane treatments, the glass temperatures (T_g) obtained by DSC analyses for GABA 5% ($82.0 \pm 2.8^\circ\text{C}$) and chitosan 5% ($79.4 \pm 0.6^\circ\text{C}$) treated flax reinforced composites were very close to the untreated composite (about $79.9 \pm 1.5^\circ\text{C}$), even though the difference observed for GABA treatment. The incoherence on T_g of GABA treated flax reinforced composite, a little bit higher than the other composites, could be produced by the size of the composite analysed by DSC, as well as the diminution of the matrix zones far of the interphases.

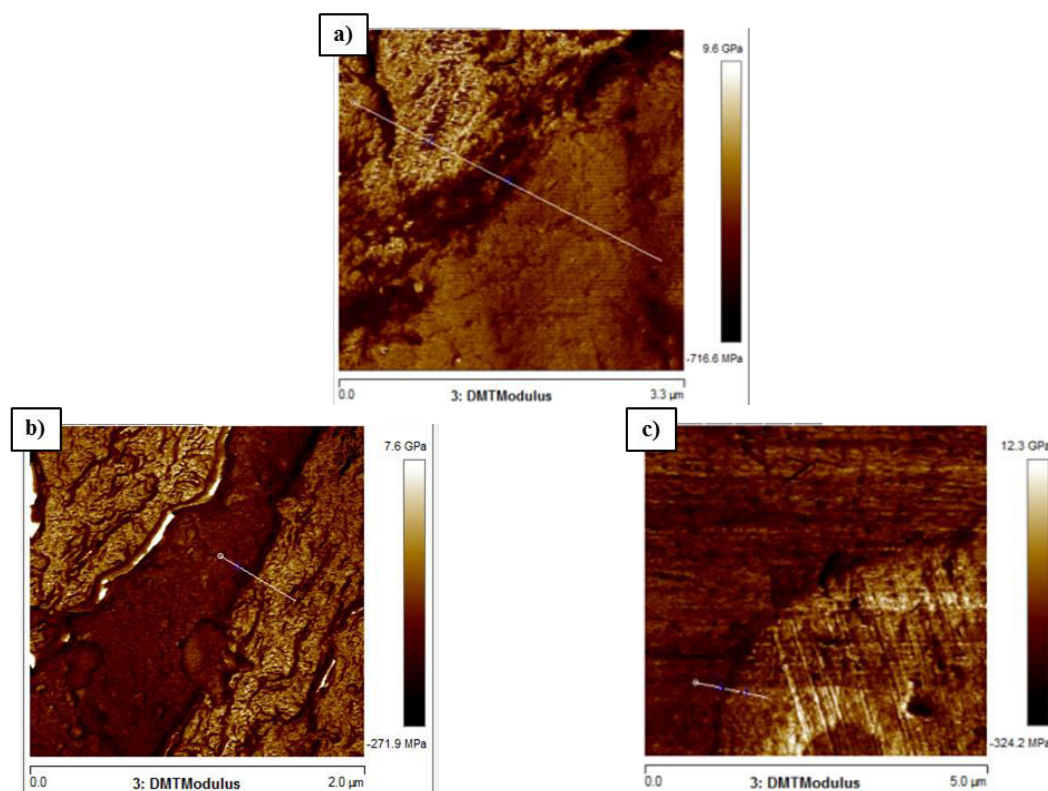


Fig. IV - 34 Young's modulus of flax fibre/epoxy composite at interface zone flax fibre treated with: a) untreated, b) GABA at 5% and c) chitosan at 5%

Table IV - 9 T_g (DSC) and Young's modulus (AFM) close to the matrix and in the interfacial zone for untreated, silane (APS, GPS), GABA and chitosan treated flax/epoxycomposites

	Epoxy	Untreated	GABA 5%	Chitosan 5%
Fibre rate (%v)	-	43.8 ± 1.8	46.3 ± 0.9	43.8 ± 1.1
T_g (°C)	93.6 ± 0.9	79.9 ± 1.5	82.0 ± 2.8	79.4 ± 0.6
Young's modulus (GPa)	On the matrix	-	2.6	1.9
	On the interphase zone	-	3.5	2.6

4.7. Influence of chemical surface modification on the interfacial properties in flax fabrics/epoxy composite

In this study, the interfacial mechanical properties of flax/epoxy composites were investigated by indirect methods. In a first time, viscoelastic properties of untreated, APS 5%, GPS 5%, GABA 5% and chitosan 5% treated flax /epoxy composites were investigated by dynamic mechanical thermal analysis (DMTA) in dual cantilever transverse bending mode. The flexural deformation produces a high load at interface, providing a sensitive detection of the mechanical properties in this region [44–47]. Static mechanical properties were afterwards investigated by tensile test in transverse

and longitudinal direction. The transverse tensile strength is mainly influenced by the quality of the fibre/matrix interface, the matrix failure strain, the fibre content, the fibre distribution, the fibre diameter and the residual stresses [6,48–51]. Finally, the longitudinal tensile strength allows evaluating the mechanical properties of the composites.

4.7.1. Dynamic tensile properties

Samples of epoxy resin, untreated and all treated flax/epoxy composites were tested two consecutive times (noted as 1st and 2nd cycles) in dual cantilever bending in transverse direction. Bending test in transverse direction allows a better visualizing of the interface behaviour due to a greater load applied to the interface. Table IV - 10 describes all characteristics obtained through this test.

4.7.1.1. Case of epoxy resin

In the case of the pure epoxy resin without fibres (Fig. IV - 35), an important deformation of the sample around T_g was observed, resulting in micro-ruptures at the grips zone. Consequently, a drastic decrease in the storage modulus E' is obtained, thereby preventing the measurement of the temperature of the maximum damping factor ($\tan \delta$). For this reason, a comparison between dual cantilever bending tests and tensile-compression tests was carried out. Results show that storage modulus E' and loss modulus E'' curves are identical until the break zone. However, an inflexion point was observed on $\tan \delta$ curve of dual cantilever bending test but corresponds perfectly to the peak of $\tan \delta$ (T_α) obtained during tensile-compression test. Therefore DMTA experiments for epoxy resin were afterwards carried out using tensile compression mode.

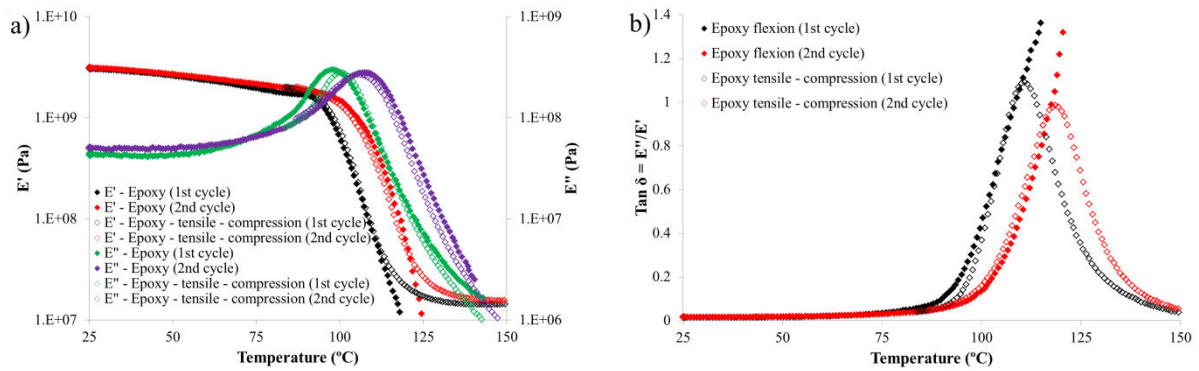


Fig. IV - 35 Comparison between E' , E'' and $\tan \delta$ from 25°C to 150°C of epoxy cured resin carried out (a) through dual cantilever bending test and (b) through traction-compression test

4.7.1.2. Comparison between 1st and 2nd temperature increase (or cycle)

Damping factor curves of both cycles for each sample are shown in Fig. IV - 36. In the case of composites, $\tan \delta$ analysis can be used to evaluate interface bonding, being highly affected by the molecular motions of macromolecular chains within the core matrix but at the fibre/matrix interface [44,47].

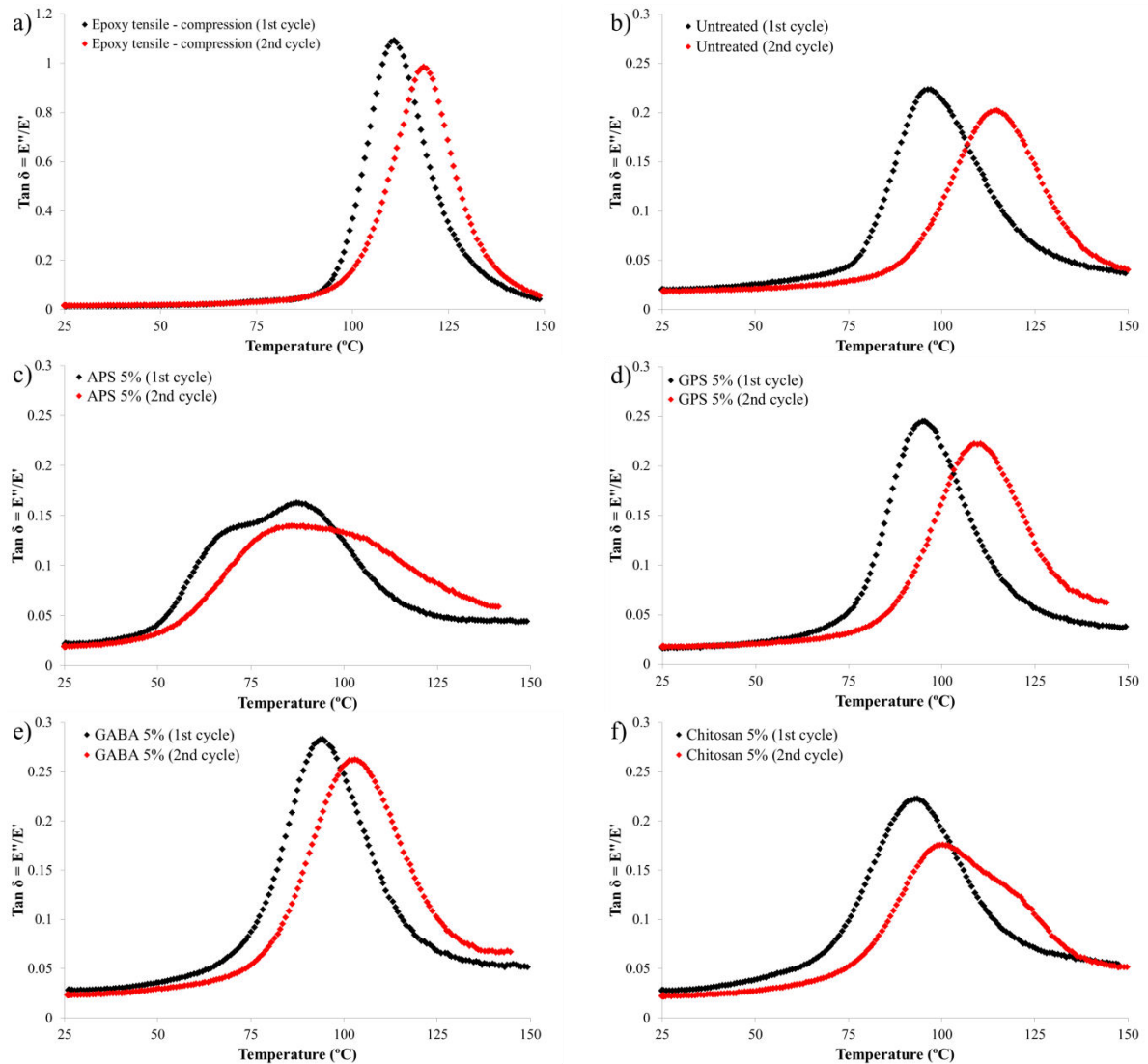


Fig. IV - 36 Damping factor at α transition from 25°C to 150°C for (a) epoxy resin, (b) untreated, (c) APS 5% and (d) GPS 5%, and (e) GABA 5% and (f) chitosan 5% treated flax fibre/epoxy composites

It can be first observed that, except for APS 5% treated flax/epoxy composite for both cycles and for chitosan 5% treated flax/epoxy composite for the second cycle, a single relaxation peak was observed for all materials. The presence of two relaxation peaks around the glass transition could be explained by the presence of different crosslinking rates within epoxy resin [36] and/or the formation of an interphase with a different chemical structure than the epoxy resin[43]. In the case of APS, AFM results previously showed that a polysiloxane network could be created to the fibre surface, making a plasticized interphase (see section 4.6.2.1), so that two relaxation peaks could be involved. In the case of chitosan, as it was observed in the SEM observations (see

section 4.6.1.2), the thickness of this treatment was very important in comparison with the other treatments, which probably produces a thicker interphase in the composite. As it was shown for APS, a double relaxation peak, produced by the plasticized interphase in that case, can be observed for chitosan in the second cycle. J. Mano et al [52] investigated the viscoelastic properties of chitosan at different hydration degrees. Authors observed that an increment on the hydration of composite increased the viscous properties decreasing the elastic properties. At the same time, they observed in chitosan conditioned at environmental humidity an increment in the storage modulus between 30°C to 65°C probably due to the loss of moisture. In our case, the apparition of a second relaxation peak in the second cycle could be produced by the dehydration of the samples produced in the first cycle and, in consequence the formation of a stronger interphase, which cannot be appreciated at the first cycle.

Whatever the material, a shift of T_{α} to higher temperatures for the second cycle compared to the first one was observed: 8.4°C for epoxy resin, 17.7°C for untreated flax fibre/epoxy composite and 15.9°C for GPS 5%. 10.3°C for GABA 5% and 4°C for chitosan 5% treated flax/epoxy composites. As concerns APS 5% treated flax/epoxy composite for which two relaxation peaks were obtained, an equivalent shift was observed. Indeed during the first cycle, the peaks were observed at 72.5 ± 1.1 °C and 87.4 ± 0.3 °C while during the second cycle, they were at 86.4 ± 0.5 °C and 103.8 ± 2.9 °C. This shift can be explained by a non-optimal or insufficient post-curing process during the elaboration of the composites. This phenomenon can be corroborated with the decrease in $\tan \delta$ peak magnitude. This result is related to a reduction of the macromolecular chain molecular motions, or in other terms, is related to resin crosslinking.

The evolution of storage modulus (E') and loss modulus (E'') from 25°C to 150°C for cycles 1 and 2 is shown in Fig. IV - 37.

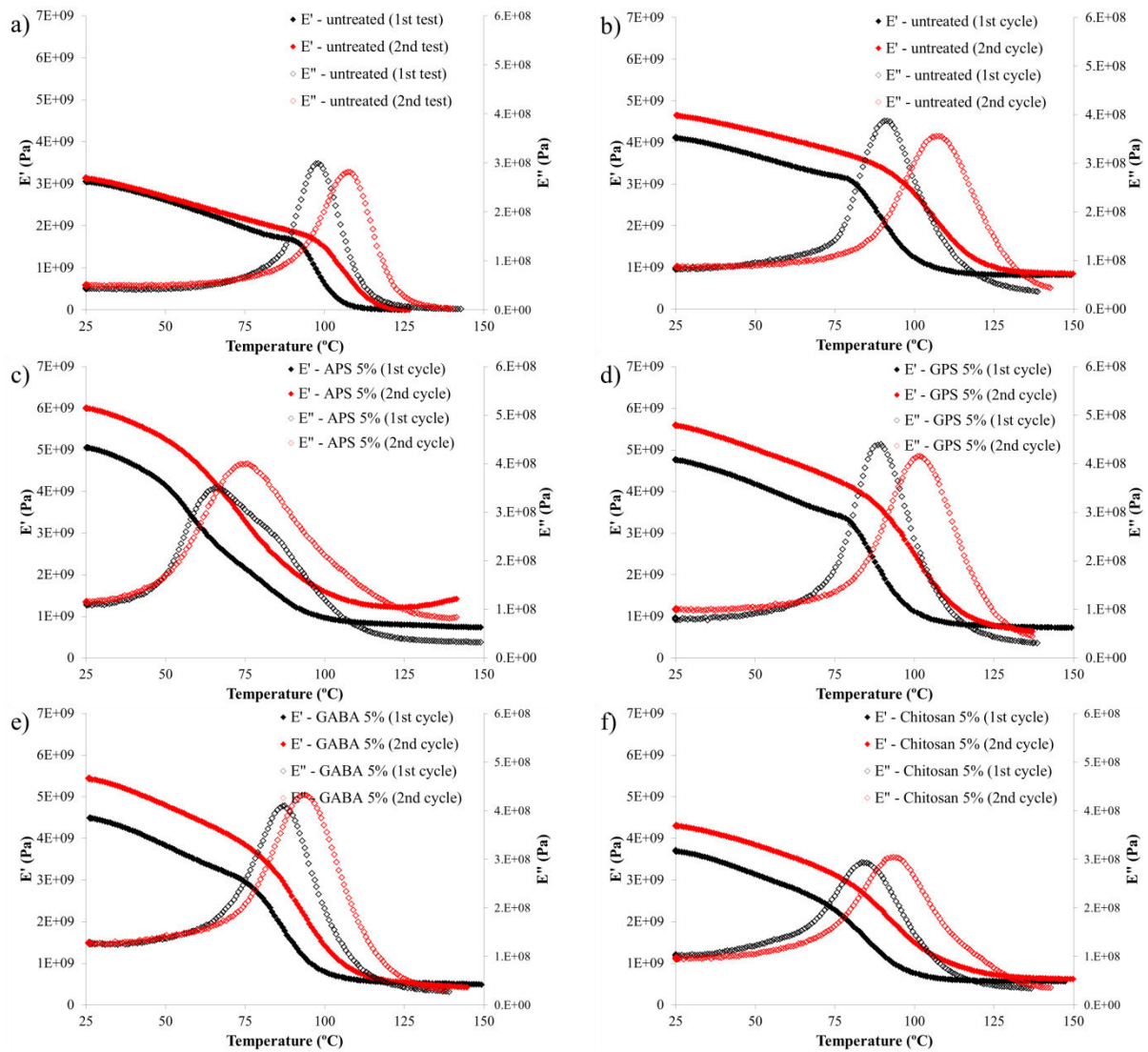


Fig. IV - 37 Evolution of storage modulus (E') and loss modulus (E'') from 25°C to 150°C for (a) epoxy resin, (b) untreated, (c) APS 5%, (d)GPS 5%(e) GABA 5% and (f) chitosan 5% treated flax fibre/epoxy composites

The incomplete post-curing can also be observed in the increasing of storage modulus E' from the first to the second cycle. At 30°C, whatever the materials, the increase of E' was significantly different between pure epoxy resin and epoxy resin reinforced with flax fibres. As concerns the epoxy resin, E' increased from 2.89 to 2.94 (about 2%) while for untreated flax fibre/epoxy composite E' increased from 4.21 to 4.69 GPa (about 11%), from 5.06 to 5.57 GPa (about 10%) for GPS 5% treatment, from 3.76 to 4.18 GPa (about 11%) for chitosan treatment, from 4.91 to 5.73 GPa (about 17%) for APS 5% treatment and from 4.45 to 5.36 GPa (about 20%) for GABA treatment. The low increase obtained for pure epoxy resin is evidence of a good post-curing unlike

composites. This phenomenon can be explained by a steric hindrance due to the presence of fibres that disturbs the chains mobility and their ability to crosslink easily. This complementary crosslinking for composites is also related to the fibre reinforcing rate. As the fibre reinforcing rate of untreated flax/epoxy composites, of GPS and chitosan treated ones was around 43% and the increase of E' was around 10%. For GABA treated flax/epoxy composites, the reinforcing rate was higher (around 46%) inducing a higher increase of E' around 20%.

As concerns E'' curves, epoxy resin and all composites showed a shift of the peak to higher temperature between the first and the second cycles. Thomason et al. [53] defined the glass transition temperature (afterwards called T_g') as being the temperature of the maximum of loss modulus peak. Based on this definition, the heating cycles induced an increase of T_g' which corroborates with lower chain mobility due to crosslinking by a complementary curing process during the analysis.

4.7.1.3. Influence of the chemical surface modification on dynamic mechanical thermal behaviour

Damping factors at α transition of epoxy resin and all composites in the 2nd cycle are shown in Fig. IV - 38.

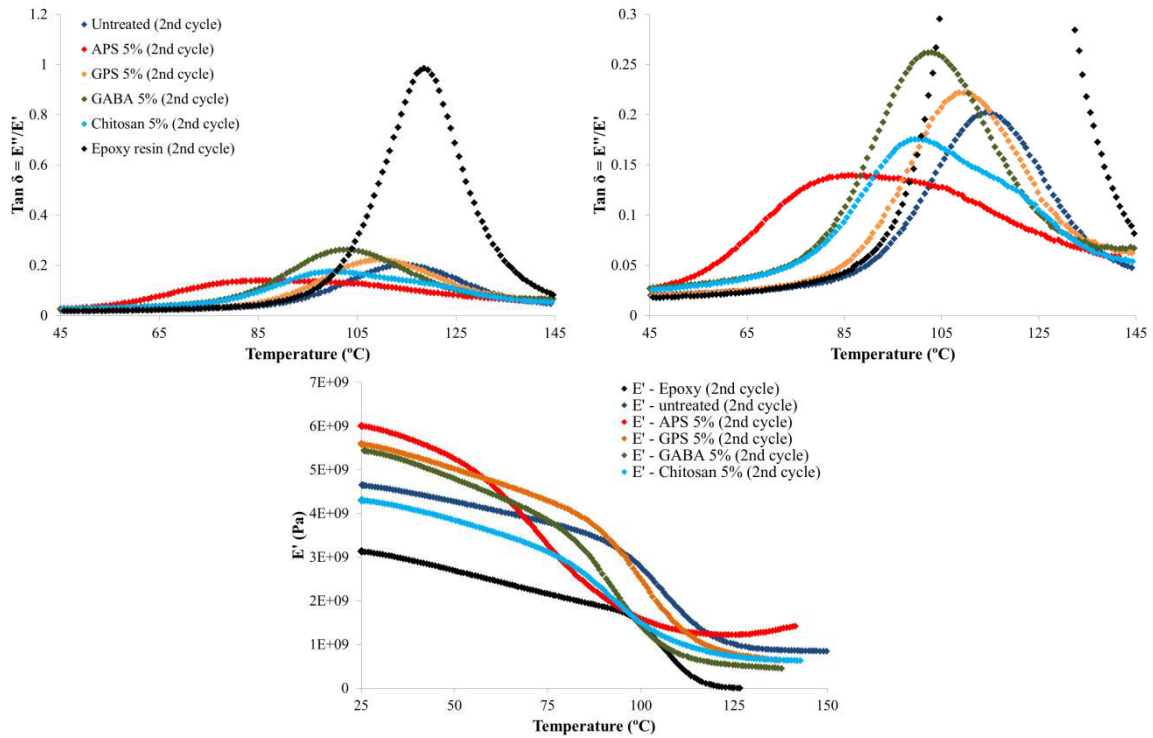


Fig. IV - 38 Damping factor and storage modulus at α transition from 45°C to 145°C of epoxy resin, untreated and treated flax fibre/epoxy composites (2nd cycle)

Tan δ curves during the 2nd cycle showed a high intensity peak (~ 0.99) for epoxy resin at around 120°C while it was shifted to lower temperatures in the presence of fibres with an intensity not exceeding 0.28. This significant decrease of the peak intensity can be explained by the presence of fibres so that a reduction in amorphous phase quantity occurs.

If we compare only the peak intensities of flax fibres/epoxy composites, GABA treated flax/epoxy composites presented the higher damping factor peak which is a surprising result regarding the fact that the higher fibre reinforcing rate is obtained for that composite. Nevertheless AFM results (Table IV - 9) showed a lower Young's modulus of the matrix for GABA 5% treatments, which implies the lower cross-linking degree and in consequence the increasing of the amorphous phase.

Untreated and GPS treated flax/epoxy composites showed close peak intensities with a slightly higher damping for GPS. In the case that this difference is considered as significant, it can be explained by the presence of epoxy groups in GPS that may react

with the amine hardener used to crosslink the epoxy resin, so that a reduction in the crosslinking rate inducing higher epoxy chains mobility can be observed.

Chitosan and APS treated flax/epoxy composites showed the lower damping implying very low chain mobility, with a slightly lower value for APS. This low mobility can be due to the presence of amino groups either in chitosan or APS molecules that are both highly reactive towards epoxy groups of the resin. This may hinder the epoxy network and chain mobility.

Table IV - 10 Main results obtained by DMTA (double cantilever transverse bending) and DSC of epoxy resin, untreated and silane (APS and GPS) treated flax fibre/epoxy composites – T_g' correspond to E'' maximum

	Fibre rate (%v)	DSC T_g (°C)	DMTA measures					
			Cycle	E' @ 30°C (GPa)	E'' @ 30°C (MPa)	T_α magnitude	T_α (°C)	T_g' (°C)
Epoxy	0	93.6 ± 0.9	1 st	2.89 ± 0.23	42.7 ± 2.8	1.09 ± 0.01	110.7 ± 0.4	97.5 ± 1.2
			2 nd	2.94 ± 0.26	46.4 ± 4.1	0.99 ± 0.01	119.1 ± 1	104.5 ± 8.6
Untreated	43.8 ± 1.8	79.9 ± 1.5	1 st	4.21 ± 0.30	81.1 ± 7.2	0.23 ± 0.02	96.9 ± 0.4	90.7 ± 1.6
			2 nd	4.69 ± 0.19	85.8 ± 2.7	0.21 ± 0.01	114.6 ± 0.4	108.2 ± 0.5
APS 5%	43.1 ± 0.1	80.4 ± 2.2	1 st	4.91 ± 0.12	112 ± 3.9	0.15 ± 0.02	72.5 ± 1.1	66.9 ± 2.5
			2 nd	5.76 ± 0.36	118 ± 2.0	0.16 ± 0.04	86.4 ± 0.5	76 ± 0.1
GPS 5%	44.2 ± 0.4	81.3 ± 1.3	1 st	5.06 ± 0.72	90.2 ± 16.6	0.23 ± 0.03	93.5 ± 2.7	88.2 ± 2.8
			2 nd	5.57 ± 0.12	106 ± 9.8	0.21 ± 0.02	109.4 ± 2.0	101 ± 1.8
GABA 5%	46.3 ± 0.9	82 ± 2.8	1 st	4.45 ± 0.04	128 ± 7.8	0.28 ± 0.01	93.3 ± 2.2	86.3 ± 2.3
			2 nd	5.36 ± 0.00	126.5 ± 1.0	0.28 ± 0.04	103.6 ± 1.0	92.4 ± 2.7
Chitosan 5%	43.8 ± 1.1	79.4 ± 0.6	1 st	3.76 ± 0.25	105 ± 2.0	0.22 ± 0.00	90.4 ± 6.2	81.5 ± 4.0
			2 nd	4.18 ± 0.15	105.1 ± 19.4	0.19 ± 0.02	94.4 ± 7.6	89.1 ± 8.7

4.7.2. Static mechanical properties

4.7.2.1. Transverse tensile properties

As it was shown in the microstructural analysis, functionalizing molecules seems to improve the interfacial adhesion between the matrix and the fibres. De Kok et al. [50] investigated the influence of the adhesion between the fibre and the matrix on the transverse properties of unidirectional composites. The authors demonstrated that in transverse mode, composite fracture depends on the critical stress produced by the matrix failure or interface failure. As the matrix properties are constants, transverse failure depends on interfacial strength and fibre volume fraction. Others parameters such as porosity also play a role in the mechanical behaviour.

Median stress-strain curves of transverse tensile test of epoxy resin, of untreated, APS 5%, GPS 5%, GABA 5% and chitosan 5% treated flax fibres/epoxy composites are shown in Fig. IV - 39. Transverse tensile properties are detailed in Table IV - 11.

In contrast with composites analysed in Chapter 3, which presented a large yield plateau corresponding to plastic deformation, these composites presented a limited plastic zone without yield plateau. The transition between the elastic zone and the plastic zone was determined by the offset yield point ($R_{P0,2\%}$). Young's modulus and stress and strain at break were also analysed in order to compare the transverse mechanical properties related to the interface properties.

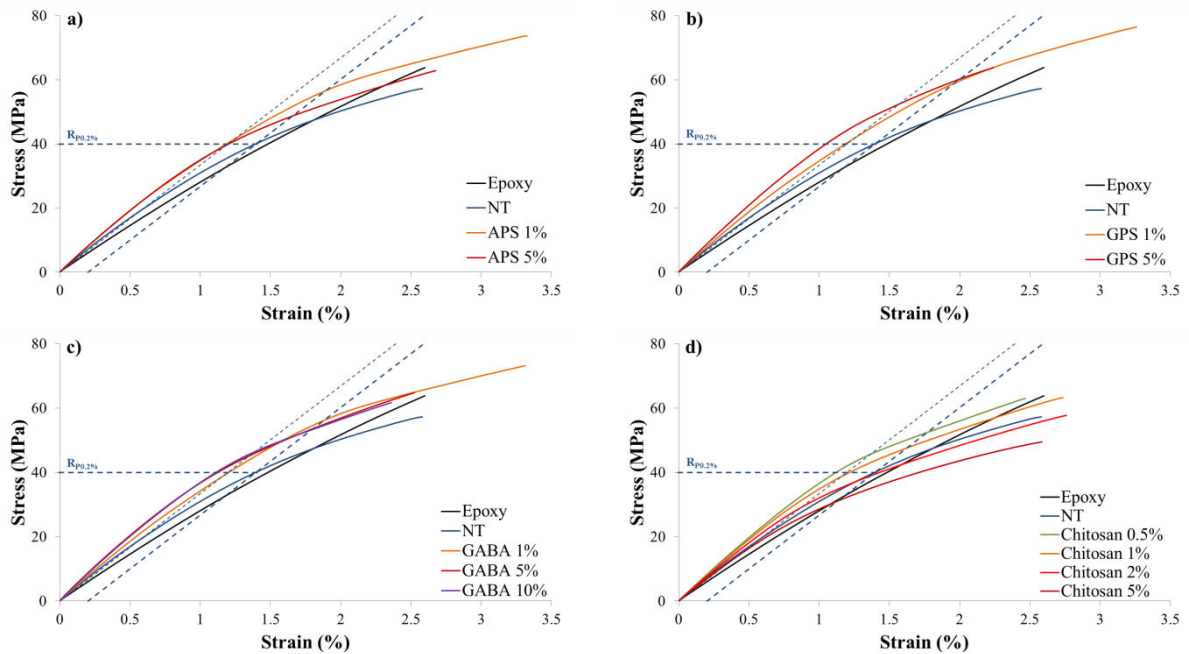


Fig. IV - 39 Median strain/stress curves of transverse tensile test measured at 2 mm/min without extensometer for epoxy resin, untreated a) APS 1% and 5% treated, b) GPS 1% and 5% treated, c) GABA 1%, 5% and 10% treated and d) chitosan 0.5%, 1%, 5% and 10% treated flax fibres/epoxy composites

The application of treatments onto flax woven fabrics modified the fabric dimension, and in consequence the areal density, increased by the effect of shrinkage and the added mass of molecules. Small variations in reinforcing rates were observed between untreated and treated flax fibres/epoxy composites, as a consequence of the low shrinkage of fabrics and low quantity of treatments applied. Molecules, especially chitosan, made a coating layer around the fibres and yarns, changing some surface

properties as roughness or porosity. The functionalization of amine or epoxy groups on the fibre surface, by the application of the different treatments, modified the interfacial adhesion. The variation of the reinforcing rate, along with differences on the interfacial adhesion produced by the functionalisation of amine or epoxy groups, possibly modified the resin crosslinking in the vicinity of the interface zone, as it was shown in section 4.6.2 (Table IV - 8 and Table IV - 9) by the variation of the glass temperature (T_g) and the modulus of the matrix. However, the T_g s were rather similar for all the composites, suggesting that the resin curing and crosslinking were also comparable.

The porosity rate was also modified by the application of functionalization solutions. In the untreated flax fibre/epoxy composite, porosity rate was around 1.8% increasing until 8.9% for chitosan 5% treatment. This modification could be produced by variations in impregnation quality and closing of open porosity of the fibre, as it was shown in sections 4.5.1 and 4.5.2. Variations in porosity rate was less important for GABA and organosilane treatments, with porosity rate of around 2.3 – 2.5% for GABA treatments, 2.7 - 3.2% for APS treatments and 2.3 - 3.4 % in GPS treatments.

An increment of the Young's modulus was observed for all treated fibre composites, except for chitosan 5% treatment. As discussed above, the treatments applied had an effect on the reinforcing rate and porosity, influencing in turns the mechanical behaviour of the composite. However, the interfacial adhesion is also assumed to be responsible for the variations in transverse mechanical properties. Young's modulus was increased by 14.5% and 19% for APS treatment at 1% and 5% respectively, around 17% for GPS treatments whatever the concentration (1% or 5%), around 25%, 12% and 11.5% for GABA treatments at 1%, 5% and 10% respectively and around 13%, 10% and 10% for chitosan treatments at 0.5%, 1% and 2%, respectively, as compared to untreated fabric reinforced composite. On the other hand, a decrease of Young's modulus of about 10% was noticed for chitosan treatment at 5%. In the case of chitosan 5% treatment, the excess of molecules produced a thick coating layer of chitosan, with lower mechanical properties [54], reducing the efficiency of the treatment and decreasing the mechanical properties of the composite.

The non-treated composite presents maximum strength at break of 57 MPa which is lower than the one of the neat matrix, suggesting an adhesive interfacial failure. For treated composites, maximum strength at break was increased to a maximum of 74.7 MPa (31% increase) for GPS 1% and APS 1% treatments and 72.7 MPa (27 % increase) for GABA 1% bio-based treatment, attesting for the creation of a strong interphase zone able to sustain higher mechanical stresses and a more cohesive interfacial failure. No increase was observed with chitosan treatments. Besides, increasing amounts of molecules resulted in a significant decrease of the stress at break whatever the functionalizing molecules.

Table IV - 11 Experimental properties of unidirectional composites in transverse tensile test

	Reinforcing rate (Vol. %)		Porosity rate (Vol. %)	Transverse Young's mod. (GPa)	Offset yield point $R_{p0.2\%}$ (MPa)	Stress at break (MPa)	Strain at break (%)
	Warp	Weft					
Epoxy	-	-	-	3.14 ± 0.06	-	62.6 ± 3.5	2.73 ± 0.26
UD 19	7.8 ± 0.4	36.0 ± 2.94	1.8 ± 2.8	5.12 ± 0.18	38.9 ± 0.6	57.12 ± 0.9	2.66 ± 0.09
APS 1%	8.4 ± 0.23	33.3 ± 2.64	2.7 ± 1.2	5.87 ± 0.38	44.4 ± 2.4	74.70 ± 2.3	3.35 ± 0.19
APS 5%	7.5 ± 0.08	35.6 ± 1.5	3.2 ± 0.2	6.10 ± 0.16	44.3 ± 0.9	62.90 ± 2.5	2.65 ± 0.10
GPS 1%	7.7 ± 0.19	34.1 ± 1.17	3.4 ± 1.6	5.99 ± 0.13	45.2 ± 1.9	74.77 ± 2.2	3.43 ± 0.16
GPS 5%	7.5 ± 0.11	36.7 ± 2.22	2.3 ± 0.7	5.98 ± 0.33	45.7 ± 1.5	63.04 ± 2.7	2.35 ± 0.17
GABA 1%	7.6 ± 0.18	33.5 ± 2.49	2.4 ± 0.7	6.40 ± 0.33	48.1 ± 1.5	72.73 ± 1.6	3.37 ± 0.10
GABA 5%	8.5 ± 0.76	37.7 ± 1.52	2.3 ± 1.5	5.74 ± 0.25	45.5 ± 0.7	65.80 ± 2.3	2.62 ± 0.13
GABA 10%	8.5 ± 0.16	38.3 ± 2.75	2.5 ± 1.4	5.71 ± 0.22	50.2 ± 1.0	61.64 ± 1.8	2.37 ± 0.16
Chitosan 0.5%	7.3 ± 0.15	35.2 ± 1.47	2.9 ± 1.3	5.80 ± 0.15	47.7 ± 0.7	62.92 ± 1.6	2.48 ± 0.08
Chitosan 1%	7.6 ± 0.09	34.6 ± 1.79	3.5 ± 0.5	5.63 ± 0.15	42.9 ± 0.8	63.29 ± 2.1	2.83 ± 0.06
Chitosan 2%	7.7 ± 0.17	35.6 ± 2.09	5.8 ± 1.4	5.62 ± 0.06	37.6 ± 0.4	57.33 ± 1.6	2.67 ± 0.06
Chitosan 5%	8.5 ± 0.27	35.3 ± 1.29	8.9 ± 1.7	4.60 ± 0.14	36.1 ± 1.2	48.87 ± 2.2	2.56 ± 0.13

4.7.2.1. Longitudinal tensile properties

In order to analyse the influence of mechanical properties of composites in longitudinal direction, a longitudinal tensile test was carried out. Median stress-strain curves of longitudinal tensile test of epoxy resin, untreated, APS, GPS, GABA and chitosan treated flax fibres/epoxy composites are shown in Fig. IV - 40. Young's modulus, stress at break and strain at break of untreated and treated flax fibre/epoxy composite in longitudinal direction are given in Table IV - 12.

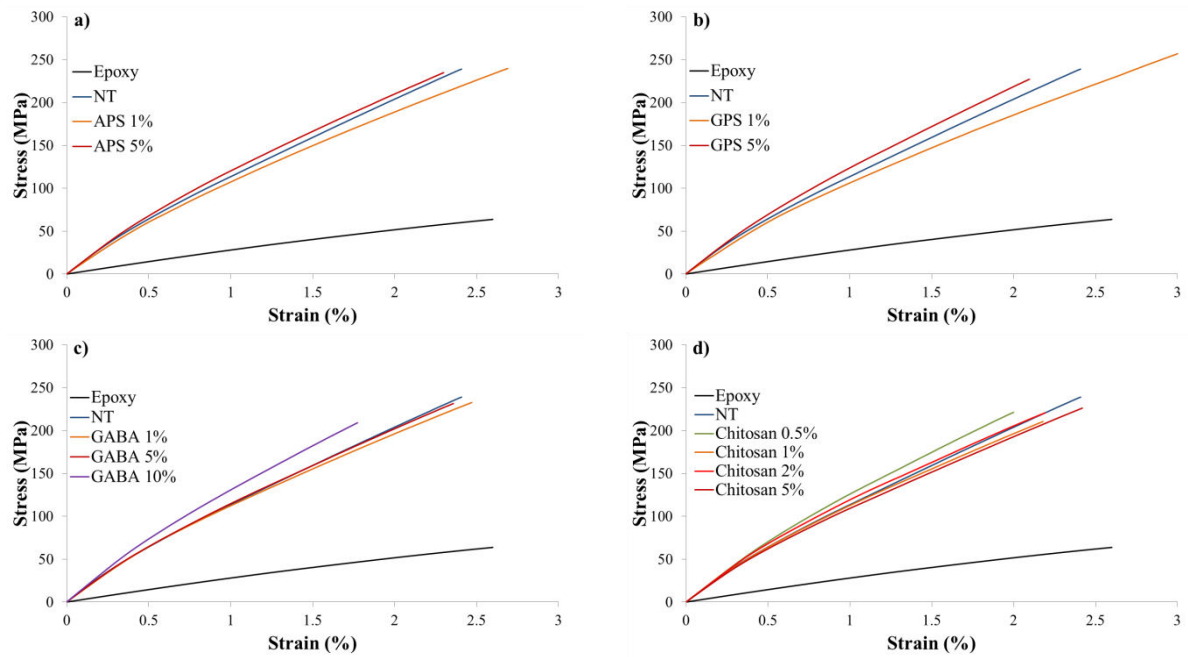


Fig. IV - 40 Median strain/stress curves of longitudinal tensile test measured at 2 mm/min without extensometer for epoxy resin, untreated a) APS 1% and 5% treated, b) GPS 1% and 5% treatments, c) GABA 1%, 5% and 10% treated and d) chitosan 0.5%, 1%, 2% and 5% treated fibres/epoxy composites

As for the mechanical behaviour analysed in transverse direction, mechanical properties of composites in longitudinal direction depend on several factors such as the reinforcing rate, porosity or the resin crosslinking, as well as the adhesion between the fibres and the matrix. As discussed above, even if variation in T_g was more important in localized zones or at the interphase, as it was observed using AFM and DTMA techniques, the global crosslinking can be considered similar for all composites.

Table IV - 12 Longitudinal mechanical properties of unidirectional composites

	Young's mod. (GPa)	Stress at break (MPa)	Strain at break (%)
Epoxy	3.14 ± 0.06	62.6 ± 3.5	2.73 ± 0.26
UD 19	13.52 ± 0.77	242.0 ± 6.0	2.51 ± 0.10
APS 1%	18.53 ± 0.80	239.0 ± 14.2	2.83 ± 0.36
APS 5%	14.54 ± 0.53	233.0 ± 7.4	2.26 ± 0.04
GPS 1%	18.09 ± 0.36	261.0 ± 9.3	2.97 ± 0.07
GPS 5%	14.69 ± 0.37	230.0 ± 6.7	2.11 ± 0.05
GABA 1%	19.23 ± 0.36	231.3 ± 7.5	2.57 ± 0.24
GABA 5%	14.28 ± 0.35	238.0 ± 13.0	2.38 ± 0.11
GABA 10%	15.20 ± 0.29	208.5 ± 3	1.80 ± 0.05
Chitosan 0.5%	14.88 ± 0.13	217.5 ± 7.5	1.96 ± 0.07
Chitosan 1%	13.73 ± 0.07	219.0 ± 9.0	2.29 ± 0.11
Chitosan 2%	14.17 ± 0.29	217.0 ± 8.0	2.17 ± 0.07
Chitosan 5%	13.18 ± 0.29	226.0 ± 2.0	2.50 ± 0.09

Using mixture rules (Eq. 5 and Eq. 6), Coroller et al. [55] have compared the longitudinal mechanical properties of unidirectional epoxy composites reinforced with three different varieties of flax fibres.

$$E_{L,UD} = k \cdot (E_{L,f} \cdot V_f) + (1 - V_f) \cdot E_m \quad (\text{Eq. 5})$$

$$\sigma_{L,UD} = k \cdot V_f \cdot \sigma_{L,f} + (1 - V_f) \cdot \sigma_{L,f} \cdot \frac{E_m}{E_{lf}} \quad (\text{Eq. 6})$$

where $E_{L,UD}$, $\sigma_{L,UD}$ and E_f , σ_f are respectively the Young's modulus and the tensile strength of the composite and the fibre in longitudinal direction; and k represent the efficiency load transfer factor. As previously discussed, the load transfer from the matrix to the fibres is related to the quality of the fibre/matrix interface, that is governed by the chemical interactions and mechanical interlocking and the quantity of interface developed. Coroller et al. [55] found that the rule of mixture with a k value of 1 (Eq. 4.5) allows to obtain theoretical composites Young moduli $E_{L,UD}$ in good agreement with experimental ones for all fibre types and fibre volume fractions tested. In contrast, the authors noticed that the experimental tensile strengths were significantly lower than the theoretical ones obtained with the rule of mixture if $k = 1$ (Eq. 4.6). The calculated efficiency factors k varied between 0.54 and 0.72 depending on fibre type and fibre volume fraction. This result was attributed to the dispersion state of elementary fibres within the matrix. The better the dispersion state, the highest was the k value, supporting that the dispersion state plays a key role for an optimal load transfer. In this regard, it was shown in Chapter 3 that the ethanol treatment applied on flax tow fabrics enhanced the elementary fibres dispersion within the matrix, and possibly improved the interfacial adhesion, leading to higher transverse tensile strength.

Based on these results and observations, same approach was conducted for the untreated and treated fibres reinforced composites. Table IV - 13 shows the efficiency load transfer factors k_E and k_σ calculated based on the longitudinal tensile moduli and strengths of the composites, respectively, as a function of treatment types and taking into account the weft fibre volume fraction. The small amount of fibres in the warp direction (around 7.9 Vol. % versus 35.5 Vol. % in weft direction) is indeed not

considered to have a strong influence in the longitudinal mechanical response of the composites. Since the tensile properties of flax fibres used in this work were not measured experimentally, the calculations were based on the properties of Hermes flax fibres measured by Coroller et al. [55], i.e. Young modulus 48.9 ± 12.0 GPa and strength at break 1066 ± 342 MPa. The results show that non-treated flax fabrics does not provide an efficient load transfer with efficiency factors k_E and k_σ of 0.65 and 0.52, respectively. Interestingly, APS, GPS and GABA treatments at 1% increase markedly the efficiency factors up to 1 for k_E and 0.6 for k_σ , attesting for a significant improvement of the fibre/ matrix load transfer through enhanced chemical interactions brought by functionalizing molecules. As previously observed for the transverse mechanical behaviour of the composites, chitosan treatments were not so efficient to improve the fibre/ matrix load transfer with k_E and k_σ factors that did not exceed 0.75 and 0.49, respectively. Besides, whatever the functionalizing molecule, increasing amounts of molecules also resulted in a significant decrease of efficiency load transfer factors, even lower than for untreated flax fabrics.

All of these results demonstrate that, beyond microstructural variations in terms of porosity and reinforcing rate, the treatments applied on flax fabrics had a great influence on the interfacial adhesion, and accordingly on transverse and longitudinal mechanical properties of the composites. Furthermore, it is worth noting that the concentration of functionalizing molecules should be controlled with care. Indeed, lowest concentration has a much more positive effect on load transfer and reinforcement. This suggests that the creation of a coating layer of functionalizing molecules on flax fibres and fabrics may not be a relevant strategy to enhance the mechanical performances of the composites through the modification of the interfacial adhesion.

Table IV - 13 Efficiency load transfer factors k_E and k_σ calculated based on the longitudinal tensile moduli and strengths of the composites, respectively, and as a function of treatment types

	Efficiency factors k_E	Efficiency factors k_σ
UD 19	0.65	0.52
APS 1%	1.01	0.55
APS 5%	0.72	0.51
GPS 1%	0.96	0.60
GPS 5%	0.71	0.49
GABA 1%	1.05	0.53
GABA 5%	0.67	0.49
GABA 10%	0.71	0.41
Chitosan 0.5%	0.75	0.47
Chitosan 1%	0.69	0.48
Chitosan 2%	0.70	0.46
Chitosan 5%	0.65	0.49

4.8. Conclusions

Four different molecules at different concentrations were used in this study: two organosilanes (APS, GPS) as non-bio-based molecules and GABA and chitosan as bio-based molecules. Results show that adhesion mechanisms of these molecules onto flax fibres are different. The main differences are: (i) the viscosity, much more higher for chitosan solution; (ii) the pH of the solution, more acid for GABA (pH 4); (iii) the concentration of free amino groups, higher in the case of GABA and APS; (iv) the functionalizing epoxy groups of GPS; and (v) finally the application on the surface: in the case of APS, GPS and GABA, an impregnation is produced and in the case of chitosan, a coating layer is produced.

The presence of molecules on flax fibre surfaces were confirmed by FT-IR spectra analysis. The N-H bands, corresponding to free amines used for coupling with epoxy resin, were detected for APS, GABA and chitosan treatments. The grafting of GABA in flax fibre was not possible to identify by the ester formation between acid and alcohol groups of cellulose, because of the low reactivity between both molecules and, evenly, the low concentration of molecules added to the fabric. Likewise, epoxy groups beared by GPS grafting were not identified due to the superposition with H₂O bands. A chitosan coating layer could be observed on flax surface using SEM. The concentration of chitosan molecules has a direct impact on the thickness of the coating layer. This effect could be produced by the high molecular weight of chitosan and the increased viscosity of concentrated solutions.

Results show that the padding process did not modify the macrostructure or microstructure of flax fibres. Dimensional analysis showed very low shrinkage for treated fabrics in both warp and weft directions. As it was shown in SEM images, defibrillation of flax fibres and yarns was not produced.

Compatibility between epoxy and flax fibres was analysed by AFM. The incompatibilities that produce decohesion seen in untreated flax fibre/epoxy composite were satisfactorily resolved using organosilanes and bio-based molecules, as it was seen on the AFM images and on deformation analysis. A decrease in epoxy crosslinking was

observed in the presence of flax fibres, which disturbs the structural mobility of epoxy chains to reticulate and hence lowers the crosslinking rate. Otherwise, cross-linking for untreated, GPS, GABA and chitosan treatments was higher at the interphase zone than in the bulk of the matrix. This effect could be produced by low thermal diffusion at the interphase zone due to the low thermal conductivity of flax fibre or by a migration of amine groups from the hardener to the fibre surface. Besides, comparing the Young's modulus at the interphase zone for the treated composites with the untreated one, a reduction of the stiffness was observed, suggesting a modification of the chemical networks at the fibre/matrix interface, hence of crosslinking of the matrix. A peculiar behaviour was observed with the APS treatment, for which a decrease of the Young's modulus at the interphase zone was lower than Young's modulus in the bulk of the matrix. This effect could be explained by the formation of siloxane network at the interphase region, which was not observed for GPS treatment maybe, due to the lower amounts of GPS molecules present on the fibres as revealed by the lower silicium concentration measured by IPC analysis.

Viscoelastic behaviour of epoxy resin and composites was investigated by DTMA analysis. As the interface fibre/matrix behaviour is better detected in transverse flexural deformation, the analysis of composites was carried out in dual cantilever transverse bending. Experimental difficulties were encountered with epoxy resin in dual cantilever bending test, due to the apparition of micro-failure at the grips zone. A comparison between traction-compression and dual cantilever bending of the epoxy presented similar results until breakage. Consequently, the traction-compression curves were used as reference in the analysis of composites viscoelastic behaviour. Making two consecutive cycles of temperature, differences in the T_{α} and in the Young's modulus at 30 °C in cycle 1 and 2 were observed, probably due to a non-optimal post-curing in composites. This difference was less important for the epoxy resin. For APS treatment, two relaxation peaks were observed especially in the 1st cycle, produced probably by the plasticized interphase made of siloxane network [43].

The effectiveness of treatments was finally determined by static mechanical tensile tests in transverse and longitudinal directions. An increment of Young's modulus and stress

at break was observed for all treated composites with the exception of chitosan 5% treated flax fibre/epoxy composites. The best tensile properties were obtained with low treatment concentrations. Efficiency of treatments was also investigated by measuring longitudinal Young's modulus and stress at break and by determining efficiency load transfer factors for longitudinal Young's modulus (k_E) and stress at break (k_σ) using mixture rules. Higher efficiency factors were observed for APS, GPS and GABA at 1% for Young's modulus (up to 1) and for stress at break (up to 0.6). These results show the efficiency of treatments on flax fibre/epoxy composites especially for treatments at low concentrations.

4.9. References

- [1] Van Dam JEG. Environmental benefits of natural fibre production and use. Proc Symp Nat Fibres 2009.
- [2] Xie Y, Hill C a. S, Xiao Z, Militz H, Mai C. Silane coupling agents used for natural fiber/polymer composites: A review. Compos Part A Appl Sci Manuf 2010;41:806–19.
- [3] Bisanda E, Ansell M. The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. Compos Sci Technol 1991;41:165–78.
- [4] Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ. Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. Compos Part B Eng 1999;30:309–20.
- [5] Cooper G, Kelly A. Role of the interface in the fracture of fiber-composite materials. Interfaces Compos 1969.
- [6] Keusch S, Haessler R. Influence of surface treatment of glass fibres on the dynamic mechanical properties of epoxy resin composites. 2. Influence of fibre–matrix adhesion. Compos Part A Appl Sci Manuf 1999;30:997–1002.
- [7] Liu X, Thomason JL, Jones FR. XPS and AFM Study of Interaction of Organosilane and Sizing with E-Glass Fibre Surface. J Adhes 2008;84:322–38.
- [8] Van de Weyenberg I, Ivens J, De Coster A, Kino B, Baetens E, Verpoest I. Influence of processing and chemical treatment of flax fibres on their composites. Compos Sci Technol 2003;63:1241–6.

- [9] Doan T-T-L, Brodowsky H, Mäder E. Jute fibre/epoxy composites: Surface properties and interfacial adhesion. *Compos Sci Technol* 2012;72:1160–6.
- [10] Lu J, Askeland P, Drzal LT. Surface modification of microfibrillated cellulose for epoxy composite applications. *Polymer (Guildf)* 2008;49:1285–96.
- [11] Sgriccia N, Hawley MC, Misra M. Characterization of natural fiber surfaces and natural fiber composites. *Compos Part A Appl Sci Manuf* 2008;39:1632–7.
- [12] Harris R a, Allan a M. Functional coupling of gamma-aminobutyric acid receptors to chloride channels in brain membranes. *Science* 1985;228:1108–10.
- [13] Jorgensen EM. GABA. *WormBook* 2005;1:1–13.
- [14] Jin Z, Mendu SK, Birnir B. GABA is an effective immunomodulatory molecule. *Amino Acids* 2013;45:87–94.
- [15] Crittenden DL, Chebib M, Jordan MJT. Stabilization of Zwitterions in Solution: γ -Aminobutyric Acid (GABA). *J Phys Chem A* 2004;108:203–11.
- [16] Shelp B, Bown AW, McLean MD. Metabolism and functions of gamma-aminobutyric acid. *Trends Plant Sci* 1999;4:446–52.
- [17] Kalaskar DM, Ulijn R V., Gough JE, Alexander MR, Scurr DJ, Sampson WW, et al. Characterisation of amino acid modified cellulose surfaces using ToF-SIMS and XPS. *Cellulose* 2010;17:747–56.
- [18] Behera AK, Avancha S, Basak RK, Sen R, Adhikari B. Fabrication and characterizations of biodegradable jute reinforced soy based green composites. *Carbohydr Polym* 2012;88:329–35.
- [19] Ravi Kumar MN. A review of chitin and chitosan applications. *React Funct Polym* 2000;46:1–27.
- [20] Liu X, Nishi N, Tokura S, Sakairi N. Chitosan coated cotton fiber: preparation and physical properties. *Carbohydr Polym* 2001;44:1–6.
- [21] Zhang H, Zhang LM. Improving the dyeing properties and softness of hemp fabric using chitosan and epoxy modified silicone oil. *J Text Inst* 2010;101:849–57.
- [22] Bhuiyan M, Shaid A, Bashar M. A Novel Approach of Dyeing Jute Fiber with Reactive Dye after Treating with Chitosan. *Open J Org ...* 2013;2013:87–91.
- [23] Shah BL, Matuana LM, Heiden P a. Novel coupling agents for PVC/wood-flour composites. *J Vinyl Addit Technol* 2005;11:160–5.

- [24] Brochier Salon M-C, Bayle P-A, Abdelmouleh M, Boufi S, Belgacem MN. Kinetics of hydrolysis and self condensation reactions of silanes by NMR spectroscopy. *Colloids Surfaces A Physicochem Eng Asp* 2008;312:83–91.
- [25] Fan G, Wang M, Liao C, Fang T, Li J, Zhou R. Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid. *Carbohydr Polym* 2013;94:71–6.
- [26] Gay D. *Matériaux composites*. 1997.
- [27] Derjaguin B., Muller V., Toporov Y. Effect of contact deformations on the adhesion of particles. *J Colloid Interface Sci* 1975;53:314–26.
- [28] AFNOR NF EN 2746. Série aéronautique - Plastiques renforcés au verre textile - Essai de flexion. Méthode des trois pannes 1998.
- [29] Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W. *Comprehensive Cellulose Chemistry: Volume I: Fundamentals and analytical Methods*. 1998.
- [30] Shanmugaraj AM, Rhee KY, Ryu SH. Influence of dispersing medium on grafting of aminopropyltriethoxysilane in swelling clay materials. *J Colloid Interface Sci* 2006;298:854–9.
- [31] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. *The handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. California: Academic Press; 1991.
- [32] Bergeret A, Bozec MP, Quantin JC, Crespy A, Gasca JP, Arpin M. Study of interphase in glass fiber–reinforced poly(butylene terephthalate) composites. *Polym Compos* 2004;25:12–25.
- [33] Li X, Tabil LG, Panigrahi S. Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *J Polym Environ* 2007;15:25–33.
- [34] Van Den Oever MJA, Bos HL, Van Kemenade MJJM. Influence of the Physical Structure of Flax Fibres on the Mechanical Properties of Flax Fibre Reinforced Polypropylene Composites. *Appl Compos Mater* 2000;7:387–402.
- [35] Vanleeuw B, Carvelli V, Barburski M, Lomov SV, van Vuure AW. Quasi-unidirectional flax composite reinforcement: Deformability and complex shape forming. *Compos Sci Technol* 2015;110:76–86.
- [36] Joliff Y, Rekik W, Belec L, Chailan JF. Study of the moisture/stress effects on glass fibre/epoxy composite and the impact of the interphase area. *Compos Struct* 2014;108:876–85.

- [37] Gupta KM. Starch Based Composites for Packaging Applications. In: Pilla S, editor. *Handb. Bioplastics Biocomposites Eng. Appl.*, John Wiley & Sons; 2011, p. 189–243.
- [38] Van Assche G, Van Mele B. Interphase formation in model composites studied by micro-thermal analysis. *Polymer (Guildf)* 2002;43:4605–10.
- [39] Saint-Gobain Vetrotex. Technical datasheet of E, R and D Glass Fibre Properties 2002.
- [40] Drzal L. The interphase in epoxy composites. *Epoxy Resins Compos II* 1986:1–32.
- [41] Tillman MS, Hayes BS, Seferis JC. Examination of interphase thermal property variance in glass fiber composites. *Thermochim Acta* 2002;392-393:299–302.
- [42] Mallarino S, Chailan JF, Vernet JL. Interphase investigation in glass fibre composites by micro-thermal analysis. *Compos Part A Appl Sci Manuf* 2005;36:1300–6.
- [43] Jones FR. Interphase Formation and Control in Fibre Composite Materials. *Key Eng Mater* 1996;116-117:41–60.
- [44] Dong S, Gauvin R. Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials. *Polym Compos* 1993;14:414–20.
- [45] Gerard JF, Andrews SJ, Macosko CW. Dynamic mechanical measurements: Comparison between bending and torsion methods on a graphite-reinforced and a rubber-modified epoxy. *Polym Compos* 1990;11:90–7.
- [46] Reed KE. Dynamic mechanical analysis of fiber reinforced composites. *Polym Compos* 1980;1:44–9.
- [47] Le Moigne N, Longerey M, Taulemesse J-M, Bénézet J-C, Bergeret A. Study of the interface in natural fibres reinforced poly(lactic acid) biocomposites modified by optimized organosilane treatments. *Ind Crops Prod* 2014;52:481–94.
- [48] Baley C, Perrot Y, Busnel F, Guezenoc H, Davies P. Transverse tensile behaviour of unidirectional plies reinforced with flax fibres. *Mater Lett* 2006;60:2984–7.
- [49] Benzarti K, Cangemi L, Dal Maso F. Transverse properties of unidirectional glass/epoxy composites: Influence of fibre surface treatments. *Compos Part A Appl Sci Manuf* 2001;32:197–206.

- [50] de Kok JMM, Peijs T. Deformation, yield and fracture of unidirectional composites in transverse loading. 2. Influence of fibre-matrix adhesion. *Compos Part A Appl Sci Manuf* 1999;30:917–32.
- [51] de Kok JMM, Meijer HEH. Deformation, yield and fracture of unidirectional composites in transverse loading. 1. Influence of fibre volume fraction and test-temperature. *Compos Part A Appl Sci Manuf* 1999;30:905–16.
- [52] Mano JF. Viscoelastic Properties of Chitosan with Different Hydration Degrees as Studied by Dynamic Mechanical Analysis. *Macromol Biosci* 2008;8:69–76.
- [53] Thomason JL. Investigation of composite interphase using dynamic mechanical analysis: Artifacts and reality. *Polym Compos* 1990;11:105–13.
- [54] Bégin A, Van Calsteren M-R. Antimicrobial films produced from chitosan. *Int J Biol Macromol* 1999;26:63–7.
- [55] Coroller G, Lefeuvre A, Le Duigou A, Bourmaud A, Ausias G, Gaudry T, et al. Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional composite. *Compos Part A Appl Sci Manuf* 2013;51:62–70.

Conclusions

This PhD subject is born from the common goal of involved partners (FRD Company/Fibre Recherche Développement (Troyes), ADEME/French Environment and Energy Management Agency (Angers), Centre des Matériaux des Mines d'Alès/C2MA (Alès)) of replacing conventional glass fibres reinforced composite materials by natural fibres reinforced composite materials that are more environmentally friendly. Nevertheless one challenging technological barrier to their widespread development is the optimizing of their performance to reach increasingly technical applications. To achieve this objective, one alternative is to optimize the natural fibre/matrix adhesion. This research project is therefore focused on flax fibres reinforced epoxy biocomposites and on the development of targeted and eco-friendly functionalizing treatments on flax fabrics.

The manuscript is divided into four sections.

The state of the art (Chapter 1) exposed the most important features of flax fibres, as their chemical composition, microstructure and transformation steps. Thermoset agro-composites manufacturing, key factors influencing natural fibres compatibility with polymer matrices, and chemical treatment strategies to modify fibre/matrix interfaces and the effect of these treatments on fibres and composites properties were also detailed and discussed. On one hand, several studies showed that pre-treatments such as alkaline pre-treatment can improve the mechanical interlocking between fibres and matrix. On the other hand, the surface modification of natural fibres with suitable organic molecules can improve the fibre/matrix physical-chemical interactions. As concerns epoxy based agro-composites, an alkaline pre-treatment combined with a functionalization with an aminosilane is the most commonly efficient surface treatment described in literature. Mainly discontinuous (immersion in bath) process is presented but also semi-continuous or continuous processes.

The research approach was carried out in three parts corresponding to Chapters 2, 3 and 4.

In Chapter 2, the influence of some of the successive transformation steps undergone by flax from the stem to the technical fibre (doubled sliver, roving, washed roving, (low) twisted yarns) on the flax visual aspect, their biochemical composition, their moisture content and their mechanical properties were studied. Results show limited extraction of non-cellulosic components (i.e. lipophilic extractives such as fatty acids, aldehyde, aliphatic ester and

alcohol...) in contrast with the high extraction yield of cell content and hemicellulose during the fibre washing step (from roving to washed roving steps) . A decrease in the linear density (from about 5000 to 100 Tex) and an increment in the maximal strength related to a constant linear density (0.2 - 0.3 to 200 - 450 mN/Tex) were observed from doubled sliver to yarns. This result was attributed to the increase of the friction between fibres that considerably increased after washing due to the non-cellulosic components extraction and the formation of hydrogen bonds between cellulose.

Due to the high modification of flax fibres by washing treatments (Chapter 2), a study of its influence on composites was carried out in Chapter 3.

In Chapter 3, different pre-treatments with various aqueous and organic solvents of increasing solvation capacities to extract gradually flax cell wall components were applied to unidirectional flax tow fabrics. Three levels of extraction were observed: i) a low extraction yield, carried out in ethanol and in ethanol/toluene solutions, for which lipophilic extractives were mainly extracted; ii) a medium extraction yield achieved by hot water and surfactants; and iii) a high extraction yield towards all components, especially hemicellulose, achieved using NaOH solution at 1 and 5%. Chemical extraction treatments induce the individualization of fibre bundles in elementary fibres allowing a better diffusion of the resin within the fabrics, and resulting in an improved reinforcing rate and a decrease of porosity rate. The higher individualization of the fibres, produced by the stronger treatments, decreased the transverse tensile mechanical properties, which was related to a degradation of the fibres. In contrast, the selective extraction of lipophilic extractives carried out by ethanol treatment improved greatly the maximal stress in transverse tensile, which was associated to an improvement of the interfacial adhesion. The obtained results showed the key role of non-cellulosic cell wall components on the microstructure, interfacial and mechanical behaviour of biocomposites. However, it should be noted that the difference in the reinforcing rate, matrix curing, porosity, the presence of warp yarns, ~~eteetc.~~ made difficult the analysis of the mechanical behaviour of the composites. This issue was partly solved by the use of mechanical model (Laminate Plate Theory and Mori & Tanaka model) which allowed comparing the samples at equivalent reinforcing and porosity rates and taking into account the warp yarns.

In Chapter 4, functionalization of flax fibres was carried out on a high performance unidirectional flax woven fabric with either solutions of non-bio-based molecules, i.e. organosilane (3-aminopropyltriethoxysilane or APS and 3-glycidoxypropylmethoxysilane or GPS) or solutions of bio-based molecules (gamma-aminobutyric acid or GABA and chitosan). These molecules were incorporated in ethanol and water for both organosilane (pH 5) and in acidified water for GABA (pH4) and chitosan (~pH5). Treatments were applied on fabrics using a pad machine. This method, which consists in a quick application of a solution between 2 rolls at room temperature, did not have any significant effect on fabrics dimensions, in contrast with chemical extraction treatments carried out by immersion in bath, and applied during much more time at high temperature, inducing fabric shrinkage.

The presence of functionalizing molecules onto flax fibre fabrics was confirmed using FT-IR. DSC and AFM analyses pointed out a reduction on the overall matrix cross-linking in composites compared to bulk epoxy resin. Young's modulus measured on the matrix by AFM technique allowed to observe variations in stiffness within the matrix, related to curing and cross-linking. The results showed higher modulus values around the fibres for untreated, GPS, GABA and chitosan treated flax/epoxy composites and lower values for APS treated flax/epoxy composite. For this latter, it was assumed that a siloxane network was produced around the fibres. This siloxane network was not noticeable for GPS treatment. Furthermore, a poor fibre/matrix interface was observed by AFM around untreated flax fibres. The fibre/matrix adhesion was greatly improved by the application of the different treatments, resulting in a more continuous interphase.

The improvement of the interfacial adhesion was evidenced by the mechanical properties of composites, carried out by longitudinal and transverse tensile tests. An increase of stress at break and Young's modulus was observed in transverse direction, being higher for GABA 1% treatment. A mixing law was applied on longitudinal tensile results in order to compare composites at the same reinforcing rate. For this determination, only the reinforcing rate corresponding to the weft yarns (yarns in longitudinal direction) was used. An efficiency load transfer factor (k) was calculated based on Young's modulus and stress at break experimental values. Efficiency load transfer factor related to Young's modulus was optimum (around 1) for 1% APS, GPS and GABA treatments. Efficiency load transfer factor related to stress at break

was improved for GPS 1% (around 0.6). Based on these results, it was shown that a better interfacial adhesion can be achieved with low concentrated treatments. High concentrated functionalizing treatments create a thick coating layer at the fibre/matrix interface that seems to affect the mechanical properties of the composites. Despite the improvement on the mechanical properties of flax fibre/epoxy composites by the increment of the interfacial mechanical behaviour, the flax fibre/epoxy composites (σ_L between 217 and 261 MPa and E_L between 13.2 and 19.2 GPa) analysed in this study are less performant in absolute properties than E-Glass/epoxy composites (σ_L between 380 and 1057 MPa and E_L between 21.9 and 49.9 GPa) analysed in literature. Nevertheless, the low density of flax fibre (about 1.5 g/cm³) provide to the flax fibre/epoxy composites good specific mechanical properties, making of this material, an interesting alternative to glass/epoxy composites.

Perspectives

In Chapter 3, it was shown that strong treatments (water, surfactants and NaOH treatments) produced an individualization of elementary fibres with a greater dispersion within the matrix. Although a degradation of fibres was produced by the extraction of non-cellulosic cell wall components, the individualization of fibres favours the diffusion of the epoxy resin within the flax yarns during the thermo-compression process and reduces the average bundles diameter, increasing in turns the quantity of fibre/matrix interface. Despite of this individualization, a decrease on the tensile properties was observed for too strong extraction treatments. At the same time, the efficiency of the functionalization treatments was evaluated in Chapter 4, showing a significant improvement of fibre/matrix adhesion. This efficiency depends on the type and concentration of chosen molecules, the process of application, the surface characteristics of the fibre, its chemical composition and the quantity of fibre/matrix interface. Summarizing, a washing treatment allows to (i) “cleaning” the fibre surface, (ii) maximizing the quantity of cellulose by extraction of non-cellulosic components and (iii) increasing the quantity of fibre/matrix interface. On the other hand, a functionalization treatment allows improving the adhesion between the fibre and the matrix through stronger physical chemical interactions. A combination treatments that would “clean”, individualize and functionalize elementary fibres should thus improve greatly the mechanical behaviour of composites, especially when “low cost” (e.g. tow fibres) fibres are used.

In Chapter 4, preliminary AFM investigations were carried out. These experiments allowed analysing the local composite microstructure at a high magnification. Significant differences between matrix Young's modulus around the fibre and in the bulk were measured. These variations were probably caused by different curing degrees of epoxy matrix. Some hypotheses were proposed, such as the migration of amine curing agents around the fibre or differences in thermal diffusion around the fibres and variations in molecular mobility that might have influence the resin curing at the interphase zone. These phenomena would deserve to be investigated. In this respect, several tests could be carried out, such as the study of the thermal conductivity of each component in the composite by a combination of AFM and micro-thermal analysis for the lower thermal diffusion of fibres hypothesis, or a local FT-IR or EDX analysis at different points of the flax/epoxy composite cross-section.

Abstract

Natural fibres can be considered as a relevant alternative to glass fibres in the manufacture of composite materials. Indeed, they present interesting physical characteristics, such as low density and good specific mechanical properties, which can compete with glass fibre reinforced composites. Moreover, natural fibres are obtained from renewable resources, and generally present lower environmental impacts during their production and use phases and their end of life. Unlike glass fibres, natural fibres, such as flax fibres, are complex hierarchical materials composed essentially of cellulose, hemicellulose, lignin, peptics cements and lipophilic extractives (waxes, fatty acids, etc.). This composition varies among species, collection site, plant maturity, batches, etc. Besides, the biochemical composition and structure of flax products and sub-products undergo wide variations according to the transformation steps from stems to yarns and fabrics. This influences greatly the final properties of flax fibres and their biocomposites. The first part of this study is focused on the characterization of flax fibres during their successive transformation steps. A homogenization of the chemical composition is observed at the final transformation steps, as well as an increment of the longitudinal tensile properties of flax yarns. The second part deals with the use of different washing treatments applied on flax tow fabrics and their influence on the extraction of flax cell wall components and the resulting microstructure and mechanical properties of epoxy/flax fibres reinforced biocomposites. It is shown that cell wall components play a key role in the flax yarns and elementary fibres dispersion and transverse mechanical behaviour of biocomposites. Finally, the application of different functionalization treatments onto flax fibres fabrics is investigated in order to improve the interfacial adhesion between fibres and matrix. The use of non-bio-based organosilane molecules (aminosilane, epoxysilane) and bio-based molecules (amino-acids and polysaccharides) is studied. Improved stiffness in longitudinal tension test and stiffness and tensile strength in transverse tension test are observed due to the improvement of interfacial adhesion by surface functionalization of the fibres with both bio-based and non-bio-based molecules.

Résumé

Les fibres végétales peuvent être considérées comme une alternative intéressante aux fibres de verre pour la fabrication de matériaux composites. En effet, elles présentent des caractéristiques physiques intéressantes, telles que leur faible densité et leurs bonnes propriétés mécaniques spécifiques, qui peuvent rivaliser avec les composites renforcés de fibres de verre. En outre, les fibres végétales sont obtenues à partir de ressources renouvelables, et présentent généralement moins d'impacts environnementaux lors de leurs phases de production, d'utilisation et en fin de vie. Contrairement aux fibres de verre, les fibres végétales, telles que des fibres de lin, présentent des structures hiérarchiques complexes composées essentiellement de cellulose, hémicellulose, lignine, ciments peptiques et extractibles lipophiliques (cires, acides gras, etc.). Cette composition varie selon les espèces, le lieu et les conditions de croissance, la maturité de la plante, etc. De la même façon, la composition biochimique et la structure des produits et des sous-produits issus du lin sont soumis à de grandes variations selon les étapes successives de transformation réalisées à partir des tiges de lin jusqu'aux fils et tissus. Cela influence fortement les propriétés finales des fibres de lin et de leurs biocomposites. La première partie de cette étude se concentre sur la caractérisation de fibres de lin au cours de leurs étapes successives de transformation. Une homogénéisation de la composition chimique est observée dans les étapes finales de transformation, ainsi qu'une augmentation des propriétés en traction longitudinale des mèches de fibres de lin. La deuxième partie traite de l'utilisation de différents traitements de lavage appliqués sur des tissus d'étoupes de lin et leur influence sur l'extraction des composants de la paroi cellulaire des fibres, ainsi que sur la microstructure et les propriétés mécaniques de biocomposites époxy/lin. Il est montré que les composants de la paroi cellulaire jouent un rôle clé dans la dispersion des mèches et des fibres élémentaires de lin et sur le comportement mécanique transversal de leurs biocomposites. Enfin, l'application de différents traitements de fonctionnalisation sur des tissus de fibre de lin est étudiée afin d'améliorer l'adhérence interfaciale entre les fibres et la matrice. L'utilisation de molécules de type organosilanes (aminosilane, époxysilanes) et de molécules biosourcés (acides aminés et polysaccharides) est étudiée. Une augmentation de la rigidité en traction longitudinale et de la rigidité et de la contrainte maximale en traction transverse est observée en raison de l'amélioration de l'adhésion interfaciale par la fonctionnalisation de surface des fibres avec des molécules d'origine biosourcé et non-biosourcé.